

Review

## Novel Blend Membranes Based on Acid-Base Interactions for Fuel Cells

Zicheng Zuo, Yongzhu Fu and Arumugam Manthiram \*

Electrochemical Energy Laboratory & Materials Science and Engineering Program, The University of Texas at Austin, Austin, TX 78712, USA; E-Mails: zuozic@hotmail.com (Z.Z.); yfu@utexas.edu (Y.F.)

\* Author to whom correspondence should be addressed; E-Mail: manth@austin.utexas.edu; Tel.: +1-512-471-1791; Fax: +1-512-471-7681.

Received: 20 August 2012; in revised form: 25 September 2012 / Accepted: 26 September 2012 / Published: 11 October 2012

---

**Abstract:** Fuel cells hold great promise for wide applications in portable, residential, and large-scale power supplies. For low temperature fuel cells, such as the proton exchange membrane fuel cells (PEMFCs) and direct methanol fuel cells (DMFCs), proton-exchange membranes (PEMs) are a key component determining the fuel cells performance. PEMs with high proton conductivity under anhydrous conditions can allow PEMFCs to be operated above 100 °C, enabling use of hydrogen fuels with high-CO contents and improving the electrocatalytic activity. PEMs with high proton conductivity and low methanol crossover are critical for lowering catalyst loadings at the cathode and improving the performance and long-term stability of DMFCs. This review provides a summary of a number of novel acid-base blend membranes consisting of an acidic polymer and a basic compound containing N-heterocycle groups, which are promising for PEMFCs and DMFCs.

**Keywords:** proton exchange membrane fuel cell; direct methanol fuel cell; proton conductivity; acid-base interaction; blend membrane

---

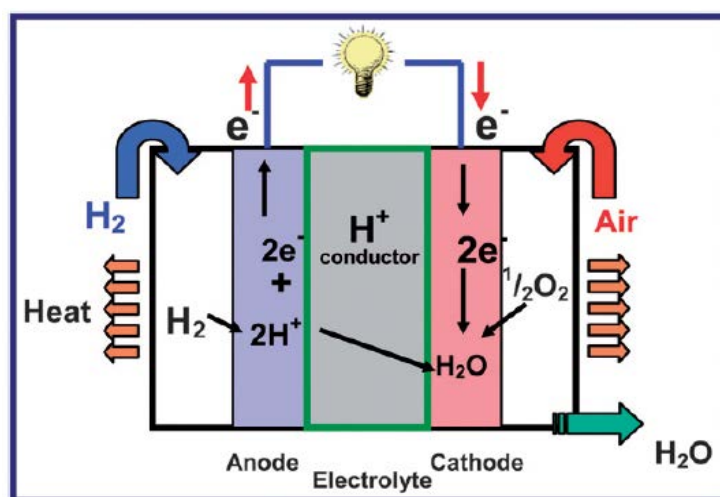
### 1. Introduction

Environmental concerns caused by the use of fossil fuels and the increasing demand for energy have accelerated the research in alternative energy technologies for several decades. Fuel cells, an

electrochemical energy conversion device converting chemical energy in fuels directly into electricity without combustion, offer inimitable superiorities in management, energy density, fuel sources and environmental friendliness. They are appealing for commercial, residential, and military applications and are one of the most promising pathways to provide clean energy and address the increasing energy demand [1–3]. Among the various types of fuel cells, proton exchange membrane fuel cells (PEMFCs) [4] and direct methanol fuel cells (DMFCs) [5] are both considered as the most promising devices for power generating and have attracted intensive attention in the past decades.

Figure 1 illustrates the operating principles of a PEMFC that uses hydrogen as a fuel and oxygen as an oxidant.  $H_2$  gas is oxidized at the anode producing  $H^+$  ions, which are transported to the cathode through a proton-conducting membrane (PEM), while the electrons flowing through the external circuit to the cathode.  $O_2$  gas combines with the  $H^+$  ions and electrons to produce water at the cathode. PEMFCs have many advantages as power supplies such as high efficiency, low emission, and quick shift in power demand. Compared to other fuel cells, PEMFCs generate more power for a given weight of fuel and are considered as one of the most promising fuel cells for transportation and stationary applications [1]. In DMFCs, methanol is oxidized at the anode producing  $H^+$  ions, electrons, and  $CO_2$  gas. The protons transported through the membrane then combines with the oxygen and electrons at the cathode to produce water. DMFCs are an attractive power supply for portable electronics due to the use of renewable and low-cost liquid methanol as a fuel. Compared to PEMFCs, DMFCs are relatively safe in operation and have simplified system configurations.

**Figure 1.** Operating principles of a proton exchange membrane fuel cell (PEMFC).



One of the major disadvantages of PEMFCs is that high-purity hydrogen fuel with very low ppm level of carbon monoxide (CO) is required as CO can poison the platinum catalyst used in fuel cells when the operating temperature is below  $100\text{ }^\circ\text{C}$  [6]. There are many advantages to operate PEMFCs above  $100\text{ }^\circ\text{C}$ , such as high electrocatalytic activity with high tolerance to CO poisoning and simple water and thermal management subsystems. However, high temperature (e.g.,  $100\text{--}150\text{ }^\circ\text{C}$ ) PEMs are far from developed although some advancement has been achieved [3]. In DMFCs, the methanol fuel can crossover through the membrane along with  $H^+$  ions and water from the anode to the cathode, which is one of the formidable challenges facing the commercialization of DMFCs [7]. Methanol

crossover not only reduces the fuel utilization, but also decreases the lifetime of catalysts. Therefore, for both PEMFCs and DMFCs, the PEM is a key component, which needs to have the following properties: (i) high proton conductivity under the operating conditions; (ii) high chemical and mechanical stability; (iii) low permeability of fuels; and (iv) low cost [6]. Currently, the commercially available perfluorinated Nafion<sup>®</sup> membranes are predominantly used in both PEMFCs and DMFCs as the PEM owing to their high proton conductivity and excellent chemical stability. However, the high cost, low operating temperature, and high methanol crossover associated with Nafion membranes have created tremendous interest in the design and development of new membranes that can operate at high temperature under low relative humidity (RH) conditions or have low methanol crossover.

A variety of alternative PEMs have been developed in the last decades for high temperature PEMFCs and DMFCs [8]: such as chemically and physically cross-linked membranes [9–13], organic-inorganic hybrid materials [14–17], and acid-base blend membranes [18–22]. As one of the most promising candidates, acid-base blend membranes consisting of an acidic polymer and a basic compound containing *N*-heterocycle groups have attracted much attention and there are many acid-base blend membranes fabricated during the past decade. In this review, we will particularly focus on the structure and performance of acid-base blend membranes for PEMFCs at high temperatures and for DMFCs. Other alternative PEMs have been systematically reviewed by Hickner *et al.* [2], Zhang *et al.* [3], and Bose *et al.* [8].

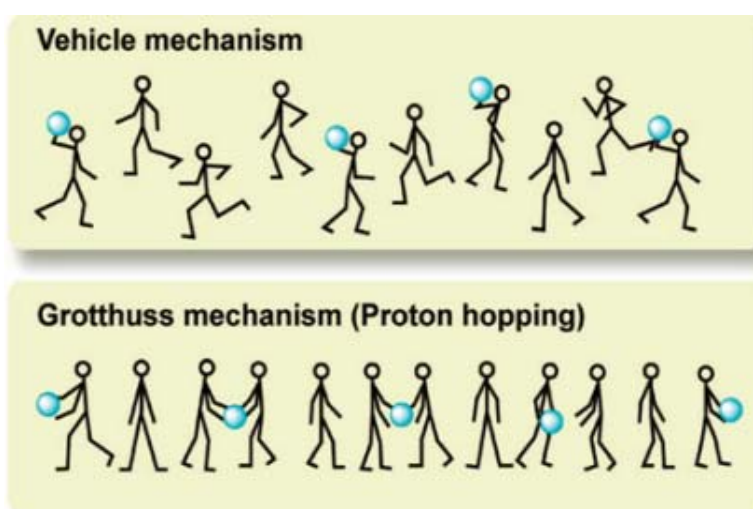
## 2. Proton-Conducting Mechanisms

There are two plausible proton-conducting mechanisms in PEMs: vehicle-type and Grotthuss-type mechanisms shown in Figure 2 [23,24]. In the vehicle-type mechanism, protons migrate through the medium along with a “vehicle” or proton solvent such as  $\text{H}_3\text{O}^+$ ,  $\text{H}_5\text{O}_2^+$ , and  $\text{H}_9\text{O}_4^+$  [25]. The overall proton conductivity is strongly dependent on the vehicle diffusion rate. In the Grotthuss-type mechanism, protons are transferred from one site to another through the formation and breaking of hydrogen bonds (proton hopping), so a vehicle or proton solvent is not needed. However the reorganization of the proton environment, involving reorientation of individual species or even more extended ensembles, is necessary for the formation of an uninterrupted path for proton migration. The proton conductivity is directly affected by the proton transfer rate ( $\Gamma_{\text{trans}}$ ) and reorganization rate ( $\Gamma_{\text{reo}}$ ) of its environment in this mechanism. Normally, both of these mechanisms are not independent in PEMs and often could make cooperative contributions to proton conductivity. Basically, in all the sulfonic acid attached PEMs, the vehicle-type mechanism is predominant in presence of water while the Grotthuss-type mechanism also contributes in the form of proton transfer via water molecules (*i.e.*, hydrogen bond forming and breaking). In the *N*-heterocycle (e.g., imidazole) containing membranes at low temperatures, the vehicle-type mechanism is still dominant while the contribution of Grotthuss-type mechanism is greatly increased.

For high temperature PEMFCs above 100 °C, it is difficult to retain water in the membranes. High-temperature proton solvents like imidazole can be used to assist proton transfer, transforming vehicle-mechanism dominated PEMs to Grotthuss-mechanism dominated ones. For DMFCs, highly selective PEMs with high proton conductivity, but minimal transport of methanol are needed, which can be realized by reducing the vehicle-type mechanism while increasing the Grotthuss-type

mechanism. Accordingly, blend membranes based on acid-base interactions have been developed in recent years, which will be the focus of this review. While the acid components in the blend membranes provide protons, the base components support proton transfer by a hopping mechanism. The mostly available acidic polymers include Nafion and sulfonated aromatic polymers like sulfonated poly(ether ether ketone) (SPEEK) and sulfonated polysulfone (SPSf). The basic components could be *N*-containing small organic molecules like imidazole and triazole or polymers with *N*-containing groups. In the sections below, the acid-base blend membranes for both high-temperature PEMFCs and DMFCs are reviewed and discussed.

**Figure 2.** Scheme of proton transfer mechanisms (vehicle and Grotthuss mechanisms). (Reprinted with permission from [26]. Copyright 2008 The American Chemical Society).



### 3. Acid-Base Membranes for High Temperature PEMFCs

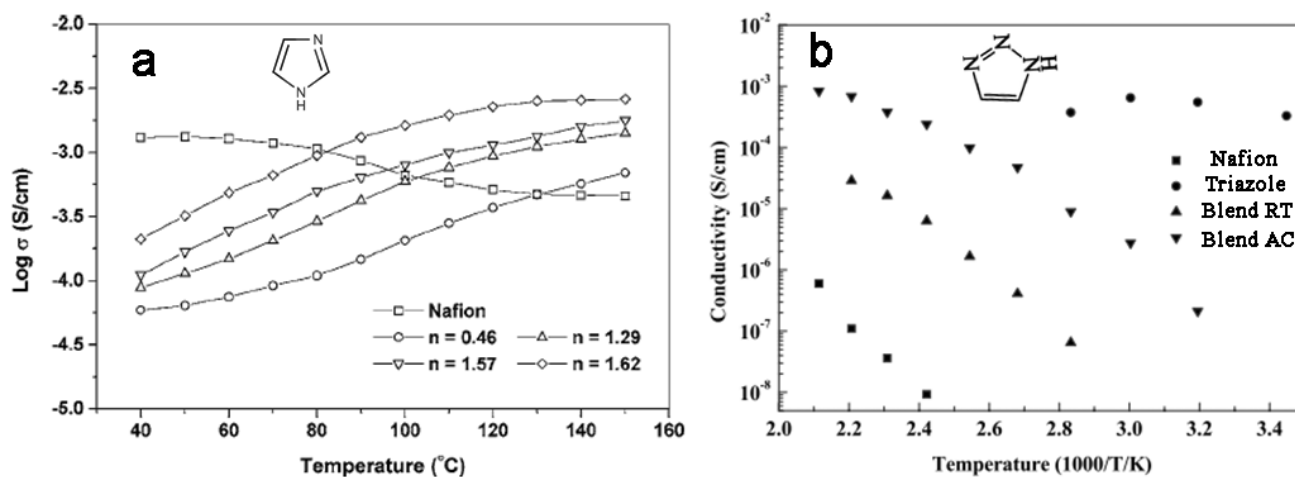
Acid-base membranes containing acidic polymers and basic additives, which can be functionalized inorganic, organic and polymers, have been largely developed for high-temperature PEMFCs [27–30]. This approach has been widely used in the modifications of the state-of-the-art Nafion, SPEEK, SPSf, and sulfonated polystyrene as well as novel synthesized copolymers. In this section, the recent progress in acid-base membranes based on these polymers for PEMFCs and the potential of these membranes are discussed.

#### 3.1. Nafion-Based Acid-Base Membranes

*N*-heterocycles like imidazole as proton solvents have been found to show good proton conduction behavior at elevated temperatures based on the Grotthuss-type mechanism [27,31]. Replacement of water by *N*-heterocycles in Nafion membrane can significantly improve the proton conductivity of these membranes under anhydrous conditions [32–34]. For example, our group studied Nafion-imidazole and Nafion-imidazole- $\text{H}_3\text{PO}_4$  composite membranes for high temperature PEMFCs. It was found that both of these composite membranes exhibit higher proton conductivity than the plain Nafion membrane under anhydrous conditions at  $T > 100\text{ }^\circ\text{C}$ , as shown in Figure 3a [33]. One issue with free imidazole molecules used in PEMFCs is its poisoning effect on Pt catalyst [32]. By adding

$\text{H}_3\text{PO}_4$  that can form an imidazolium salt, the poisoning effect of imidazole on Pt catalysts was significantly suppressed. For example, the Nafion-imidazole- $\text{H}_3\text{PO}_4$  composite membrane exhibits much better fuel cell performance than the membrane without  $\text{H}_3\text{PO}_4$  at low temperatures. The fuel cell performance was further improved by replacing the Pt catalyst with a Pd-Co-Mo catalyst, which is more tolerant to imidazole. The Nafion-imidazole- $\text{H}_3\text{PO}_4$  membranes with the Pd-Co-Mo catalyst show better performance than Nafion membrane with the Pt or Pd-Co-Mo catalyst in PEMFCs at 100 °C. Imidazole was also used in many other composite membranes, which show great potential in PEMFCs [35–37], especially for the low humidity condition at high temperature.

**Figure 3.** The proton conductivities of (a) Nafion-imidazole and (b) Nafion-triazole composite membranes as a function of temperature for high temperature PEMFCs. (Reprinted with permission from [41]. Copyright 2008 The Electrochemical Society).



Triazole and its derivatives, which contain one more nitrogen than imidazole [34,38–41], have also been found to show the potential to replace water in high temperature PEMFCs, as shown in Figure 3b. Ghassemi *et al.* [34,38] did extensive work on triazole-containing composite membranes and showed that the triazole derivatives are viable proton transport facilitators. For example, 4,5-Dicyano-1H-[1,2,3]-triazole [38], which is a crystalline compound, might have different proton conduction mechanism compared to the rotationally coupled intermolecular proton transfer. It shows good electrochemical stability in the potential window for fuel cell applications, and its adsorption on Pt catalysts has no drastic poisoning effect.

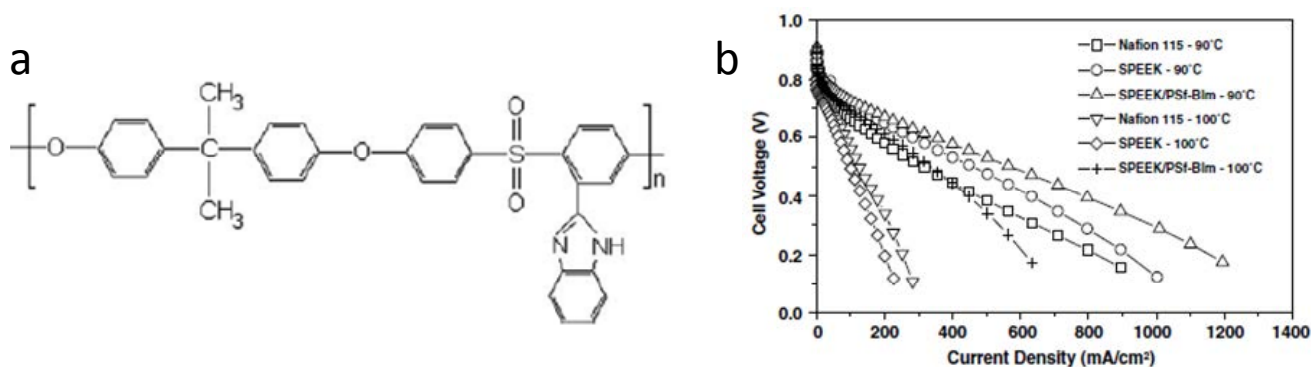
These small *N*-heterocycle molecules are effective in maintaining high proton conductivity at high temperature under anhydrous conditions, but they are not stable in the membranes due to their solubility in water. *N*-heterocycle attached polymers are preferred basic components in acid-base blend membranes.

### 3.2. SPEEK-Based Acid-Base Membranes

Because of the high-cost of Nafion membranes and the poor performance under high temperature, much research is being focused on the development of alternative membranes that show promising properties in high-temperature PEMFCs. SPEEK is a low-cost material with controllable proton

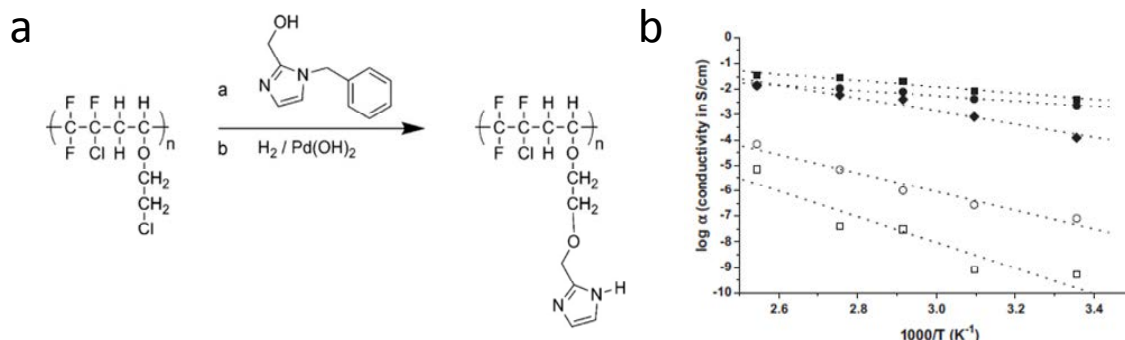
conductivity, good mechanical properties, and excellent chemical stability. For fabricating high-performance membranes under low-humidity conditions, Kreuer *et al.* [35] introduced imidazole and pyrazole as proton solvents in SPEEK and found that higher proton conductivity could be obtained at elevated temperatures compared to plain SPEEK. Our group developed a novel polysulfone containing pendant benzimidazole groups (PSf-BIm) as shown in Figure 4a and investigated them as an additive in SPEEK membranes. The blend membrane exhibited better performance in PEMFCs at 90 and 100 °C than the plain SPEEK and Nafion membranes, as shown in Figure 4b. The pendant benzimidazole groups may insert into the hydrophilic domains via the acid-base interaction in the SPEEK membranes and promote proton transfer via Grotthuss-type mechanism, reducing the dependence on water. The investigation indicates that this basic polymer provides a promising pathway for developing new alternative membranes that can be used at higher temperatures with low relative humidity [42].

**Figure 4.** (a) Polysulfone bearing benzimidazole side group; (b) fuel cell performance of SPEEK/PSf-BIm blend membranes in comparison with plain SPEEK and Nafion. (Reprinted with permission from [42]. Copyright 2006 Elsevier).



It is well known that the performance of Nafion greatly depends on the perfluorinated structure [43]. To utilize the advantages of fluorinated structure, a novel base copolymer containing a chlorotrifluorinated backbone and pendant imidazole groups has been developed by David *et al.* [44], and it could be used as one component for fabricating acid-base blend membranes for PEMFCs. The pendant imidazole group was first protected by a benzyl group before polymerization as shown in Figure 5a and then was deprotected after polymerization to form the pendant imidazole groups that can participate in the proton transfer process via the Grotthuss-type mechanism. Subsequently, the acid-base blend membranes of the resultant copolymer and SPEEK were prepared by varying the  $-NH/-SO_3H$  ratio between 1 and 100. The water uptake experiment indicated that this kind of membranes with imidazole content  $\geq 1 \text{ mmol g}^{-1}$  shows remarkably low water uptake ( $<25\%$ ). The conductivities were measured at different temperatures (25–120 °C) and relative humidity (25%–100%) as shown in Figure 5b, and it was found that the dependence of conductivity on relative humidity became significantly decreased as the imidazole content increased at 120 °C.

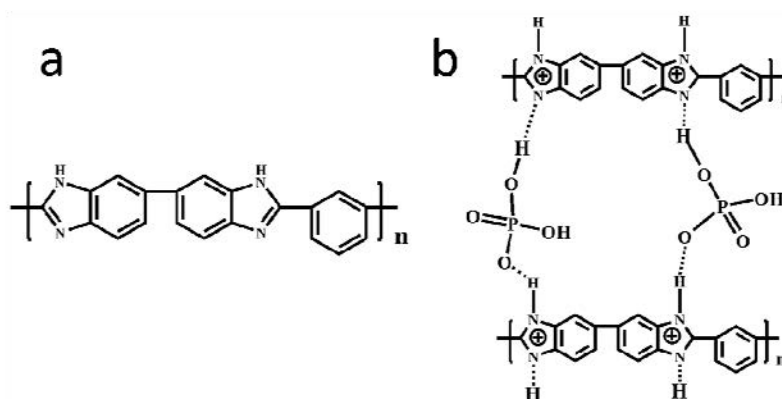
**Figure 5.** (a) Preparation of fluorinated copolymer bearing pendant imidazole groups and (b) logarithm of proton conductivity vs. reciprocal temperature for the blend membranes consisting of SPEEK and the copolymer-containing pendant imidazole groups. (Reprinted with permission from [44]. Copyright 2011 Elsevier).



### 3.3. Polybenzimidazole-Based Acid-Base Membranes

Polybenzimidazole (PBI) doped with acids like  $\text{H}_3\text{PO}_4$ , shown in Figure 6, is a robust high-temperature membrane, which has attracted increasing interest for applications in PEMFCs [45]. Based on the acid-base interaction between the acids and the benzimidazole groups in PBI, good proton conductivity at high temperature has been obtained.

**Figure 6.** (a) Chemical structure of polybenzimidazole (PBI) and (b) possible proton transfer mechanism of PBI- $\text{H}_3\text{PO}_4$  blend membrane.



Savinell and coworkers [46] first recognized the high conductivity associated with the phosphoric acid-doped PBI. In He's group, a series of poly (aryl sulfone benzimidazole) and its copolymers were designed and synthesized. Combination of the stiff para-phenylene and flexible aryl sulfone linkages in the backbone produced high molecular weight copolymers with good solubility. When doped with phosphoric acid at an acid doping level of 11 mol  $\text{H}_3\text{PO}_4$  per average molar repeat unit, the membrane exhibited high tensile strength, and a power density of  $346 \text{ mW/cm}^2$  was found in PEMFCs at  $180 \text{ }^\circ\text{C}$  under ambient pressure [47]. Jones's group [16] prepared a series of novel highly sulfonated polybenzimidazoles (sPBI) with high molecular weight by direct polycondensation. The degree of sulfonation of the final polymers was modulated by varying the proportion of sulfonated to nonsulfonated monomers used in the synthesis. Therefore, copolymers with ion exchange capacity

(IEC) in the range of 0.87–4.68 mequiv g<sup>-1</sup> were synthesized. The dynamic thermogravimetric analysis in air showed no weight loss below 350 °C, indicating their good thermal stability for high-temperature PEMFCs. Further characterization indicated that the bisphenyl bridge has great influence on the water uptake and through-plane proton conductivity of the resulting sPBI membranes, with the hexafluoroisopropylidene links providing membranes with high conductivity as well as good film-forming characteristics. Some other novel PBI-based acid-base membranes have also been prepared by chemically grafting benzylic sulfonic [48] and alkylsulfonic acid [49] moieties onto the PBI backbone. A comprehensive work on PBI membranes for high temperature PEMFCs has been reviewed by Li *et al.* [45].

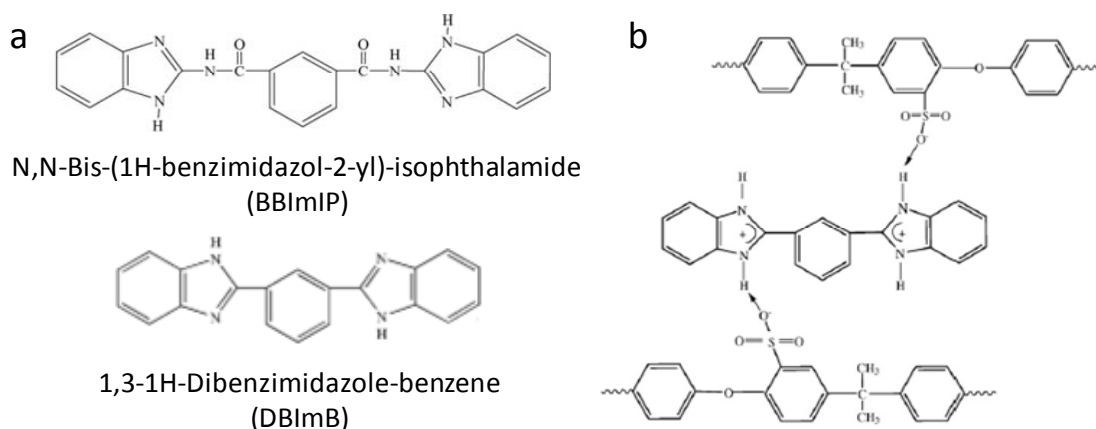
#### 4. Acid-Base Membranes for DMFCs

DMFCs are an attractive power supply for portable electronics due to the high theoretical energy density, easy storage and handling of methanol fuel. However, the high methanol permeability through the extensively-studied Nafion membrane remains to be a serious obstacle to their widespread application. The high methanol crossover from the anode to the cathode through the membrane not only wastes fuel and decreases the power density, but also reduces the DMFC lifetime [50]. In this section, various membranes based on acid-base interactions, which suppress methanol crossover while offering acceptable proton conductivity and power density, are discussed.

##### 4.1. Nitrogen-Containing Small Basic Molecules

Low-cost SPEEK and SPSf membranes with suitable degree of sulfonation exhibit low methanol crossover in DMFCs due to their narrow ion pathways [51,52]. Two small basic molecules containing: *N,N*-Bis-(1H-benzimidazol-2-yl)-isophthalamide (BBImIP) [53] and 1,3-1H-Dibenzimidazole-benzene (DBImB) [54] (Figure 7a) have been investigated by our group as additives in SPEEK and SPSf. The benzimidazole groups in the small basic molecules locating into the hydrophilic channels of the sulfonated polymers could assist proton transport via Grotthuss-type mechanism shown in Figure 7b, while blocking the passage of methanol molecules.

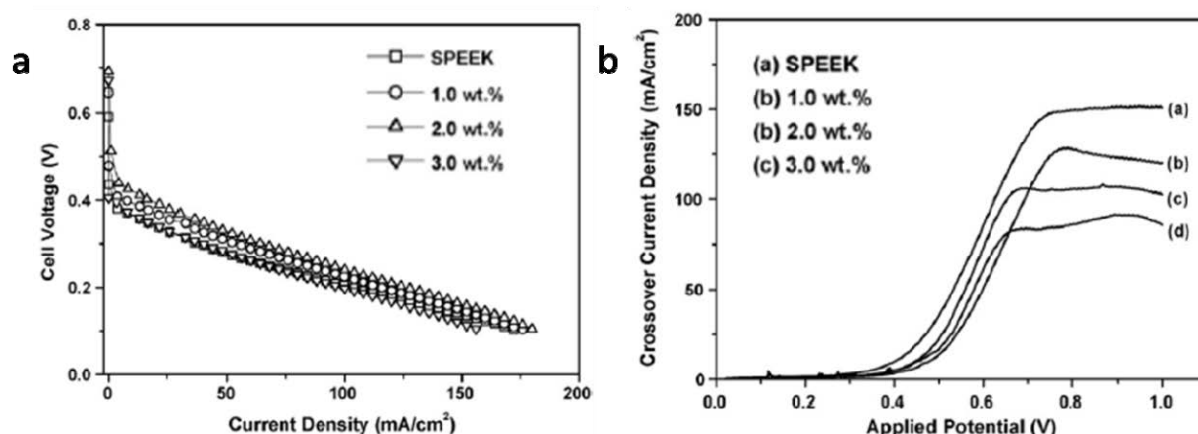
**Figure 7.** (a) Structure of BBImIP and DBImB and (b) illustration of the assistance of benzimidazole in the Grotthuss-type proton conduction mechanism in the blend membranes. (Reprinted with permission from [54]. Copyright 2008 Elsevier).





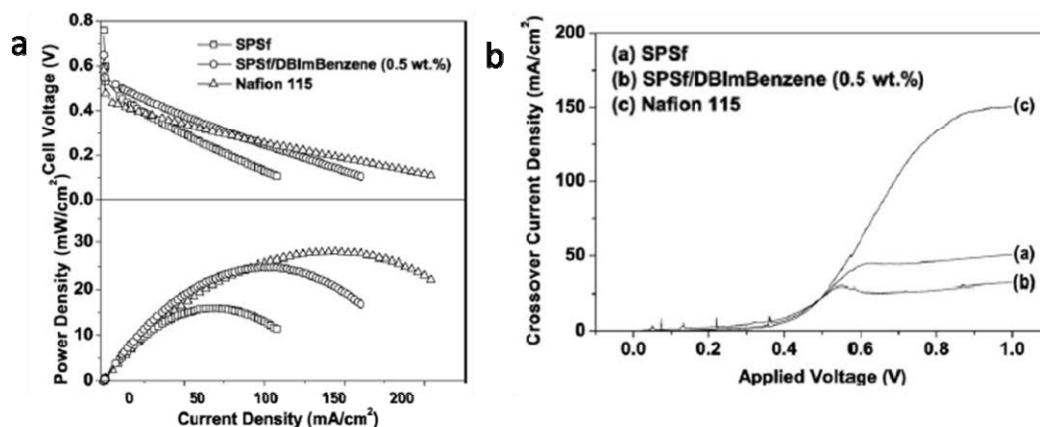
BBIImIP containing two 2-amino-benzimidazole groups has served as a basic additive in both SPSf and SPEEK membranes. The blend membranes containing different BBIImIP contents have been characterized by ion-exchange capacity and proton conductivity measurements as well as single cell and methanol crossover measurements in DMFCs at 65 °C. It has been found that the presence of BBIImIP in the SPSf/BBIImIP blend membranes depress proton conductivity and cell performance compared to plain SPSf. However, all the SPSf/BBIImIP blend membranes show higher open-circuit voltages (OCVs) than the plain SPSf membrane, which could be related to the reduced methanol crossover and a reduced cathode catalyst poisoning. [55] Contrarily, by increasing the BBIImIP content up to 3 wt %, the SPEEK/BBIImIP blend membranes show cell performance at 65 °C comparable to or better than that of plain SPEEK membrane as well as reduced methanol crossover, as shown in Figure 8.

**Figure 8.** (a) Comparison of the polarization curves of the plain SPEEK and SPEEK/BBIImIP blend membranes in direct methanol fuel cells (DMFCs); and (b) comparison of the variations of the methanol crossover current density for the plain SPEEK and SPEEK/BBIImIP blend membranes in DMFCs. The wt % values refer to the BBIImIP content. Methanol concentration: 1 M and cell temperature: 65 °C. (Reprinted with permission from [53]. Copyright 2008 Elsevier).



DBImB which contains two benzimidazole groups has also been investigated as an additive (up to 2.0 wt %) in SPSf membranes to promote proton conduction via acid–base interactions. The SPSf/DBImB blend membranes with various DBImB contents have been characterized by proton conductivity measurements and electrochemical polarization and methanol crossover measurements in DMFCs. The blend membranes with a DBImB content of 0.5 and 1.0 wt % show higher proton conductivities at 65 °C ( $3.4$  and  $2.9 \times 10^{-4}$  S/cm, respectively) than plain SPSf ( $2.4 \times 10^{-4}$  S/cm) even though the blend membranes have lower IECs (0.81 and 0.75 mequiv/g, respectively) than plain SPSf (0.86 mequiv/g). The blend membrane with DBImB content of 0.5 wt % exhibit much better electrochemical performance than the plain SPSf and Nafion 115 membranes, and lower methanol crossover, as shown in Figure 9. These results indicate that moderate amount of acid-base interactions between DBImB and SPSf could increase the proton conductivity and prominently lower methanol crossover, which is advantageous for DMFCs.

**Figure 9.** (a) Comparison of the polarization curves of the SPSf/DBImB blend membranes with those of plain SPSf and Nafion 115 membranes in DMFCs (b) comparison of the variations of the methanol crossover current density for the plain SPSf, Nafion 115, and SPSf/DBImB blend membranes in DMFCs. Methanol concentration: 1 M, temperature: 80 °C. (Reprinted with permission from [54]. Copyright 2008 Elsevier).

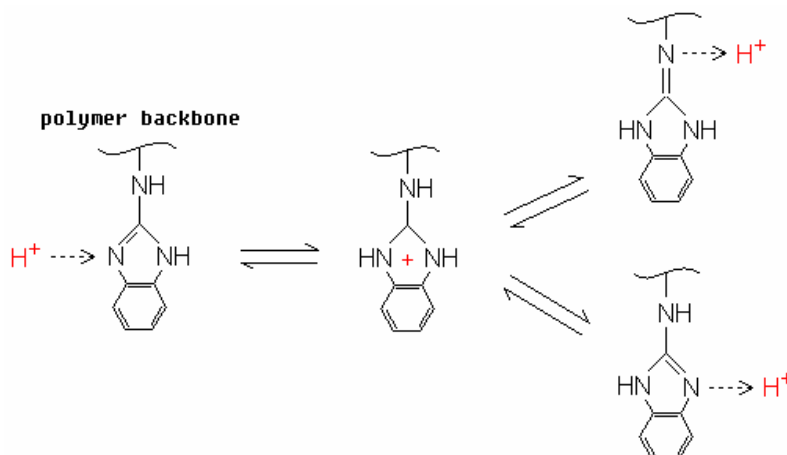


#### 4.2. Nitrogen-Containing Polymers

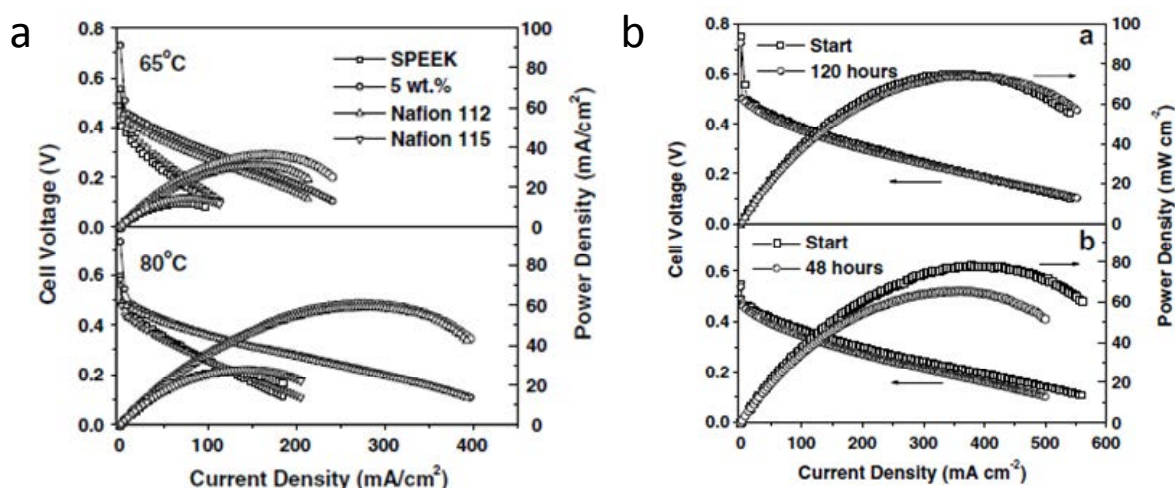
The positive effects of acid-base interactions in membranes have attracted much attention in modifying the SPEEK membranes by introducing basic materials. Besides for the introduction of small molecules outlined above, a series of SPEEK/basic polymer blended membranes have been developed with better stability and promising properties than those with small molecules [21,22]. For example, a novel polysulfone-2-amide-benzimidazole (abbreviated as PSf-ABIm) containing pendant 2-amino-benzimidazole has been developed as a basic polymer and used with SPEEK as a blend membrane by our group [56]. 2-Amino-benzimidazole contains three nitrogen atoms, which could greatly promote proton conduction in the presence of a sulfonic acid polymer. The three nitrogen atoms of the 2-amino-benzimidazole unit could act equally as proton donors or acceptors as shown in Figure 10, increasing the probability of proton transfer compared to one nitrogen atom of the pyridine- and two nitrogen atoms of the imidazole- or benzimidazole-doped systems.

The SPEEK/PSf-ABIm blend membrane exhibits much better performance than Nafion 115 and comparable performance to Nafion 112 at both 65 and 80 °C, but with a remarkably superior long-term performance than Nafion 112 due to significantly reduced methanol crossover in DMFC, as shown in Figure 11. These blend membranes have also been used to fabricate MEAs for operation at high methanol concentrations [57]. The performance of DMFCs fabricated with this blend membrane has been compared with the MEAs of plain SPEEK and Nafion 115. The SPEEK ionomer has been found to provide improved compatibility as well as a lower interfacial resistance compared to Nafion ionomers in the SPEEK/PSf-ABIm blend membranes. Moreover, the MEAs fabricated with the blend membranes and SPEEK ionomer in the electrodes exhibit better performance in DMFCs compared to that with Nafion membrane and Nafion ionomer because of the lower methanol crossover. Further investigations have indicated that the MEAs of the blend membranes exhibit less performance dependence on methanol concentration (1–10 M) compared to the Nafion membranes, and they are promising for the DMFCs to operate at high methanol-feed concentrations.

**Figure 10.** Possible proton transfer in the SPEEK/PSf-ABIm blend membranes. (Reprinted with permission from [56]. Copyright 2007 Elsevier). Where PSf-ABIm is polysulfone-2-amide-benzimidazole.



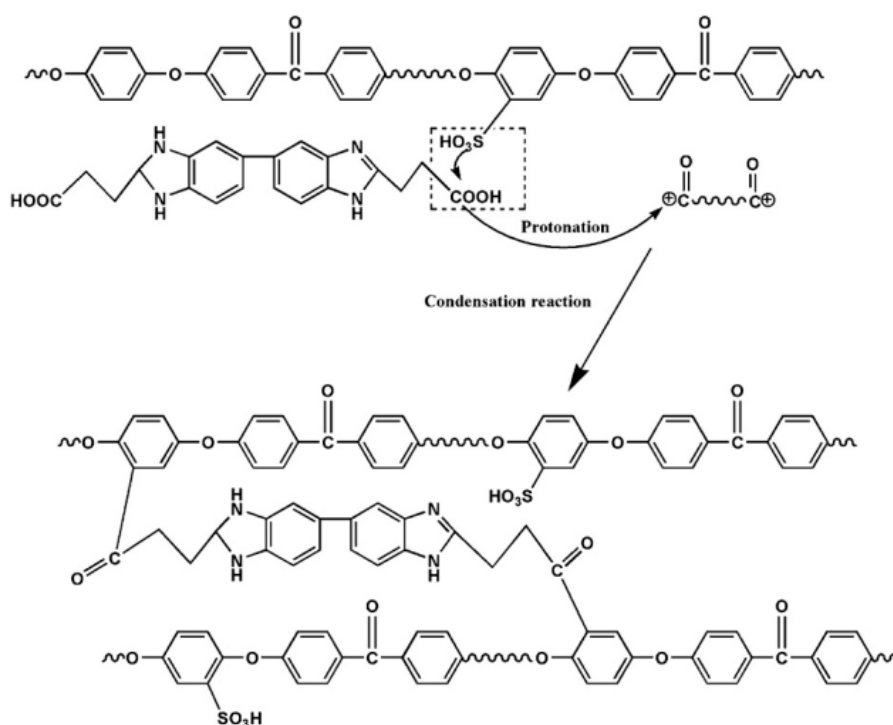
**Figure 11.** (a) Comparison of the polarization curves of the SPEEK/PSf-ABIm (5 wt % of PSf-ABIm) blend membrane with those of SPEEK, Nafion 112, and Nafion 115 membranes in DMFC at 65 and 80 °C with a methanol concentration of 1 M; (b) Long-term performance tests carried out with the (a) SPEEK/PSf-ABIm (3 wt %) blend membrane and (b) Nafion 112 membrane at 80 °C in DMFC with a methanol concentration of 2 M. (Reprinted with permission from [56]. Copyright 2007 Elsevier).



Besides the physical crosslinking between the *N*-containing groups and the sulfonic acid groups in acid-base blend membranes, hydrogen bonding was also envisioned in the preparation of acid-base PEMs. In Ye *et al.*'s research [58], noncovalent cross-linked membranes were prepared with the formation of biocomplementary hydrogen bonding between uracil-terminated telechelic sulfonated polyimides (SPI-U) and an adenine-based crosslinking agent (SMA-A). The modified blend membranes showed increased proton conductivity at high temperature and low relative humidity, lower methanol permeability, and higher oxidative stability. Thus, it provided an applicable strategy to design novel physically cross-linked PEMs with high performance for fuel cells.

Chemically cross-linked approach is one of the most effective methods to further improve the stability of acid-base blend membranes. Many cross-linked methods have been applied in preparing cross-linked SPEEK membranes, which have shown many exciting results compared to the commercial Nafion membranes in DMFCs [9]. The novel benzimidazole trimer (alkyl-BI), which is synthesized using 3,3'-diaminobenzidine and succinic acid as monomers, has served as a small molecular cross-linker for preparing cross-linked SPEEK membranes by a thermal condensation reaction, as shown in Figure 12 [59]. The introduction of alkyl-BI not only cross-links with the sulfonic acid group on the SPEEK, but also brings the basic groups, which are necessary for forming acid-base interactions in the membranes. A series of cross-linked membranes (c-SPEEK-Xs) have been prepared and systematically studied for water uptake and swelling ratio, thermal and chemical stability, mechanical properties, proton conductivity, and methanol permeability as a function of different loading ratios of the alkyl-BI trimer. The results indicate that all the properties of the cross-linked membranes are significantly improved over the plain SPEEK membranes. Further investigations with transmission electron microscopy (TEM) indicated that the structure of the cross-linker evidently influence the hydrophilic/hydrophobic two-phase separation morphologies, which have dramatic effects on the proton conductivity and methanol permeability.

**Figure 12.** Cross-linked SPEEK membrane by benzimidazole trimer.

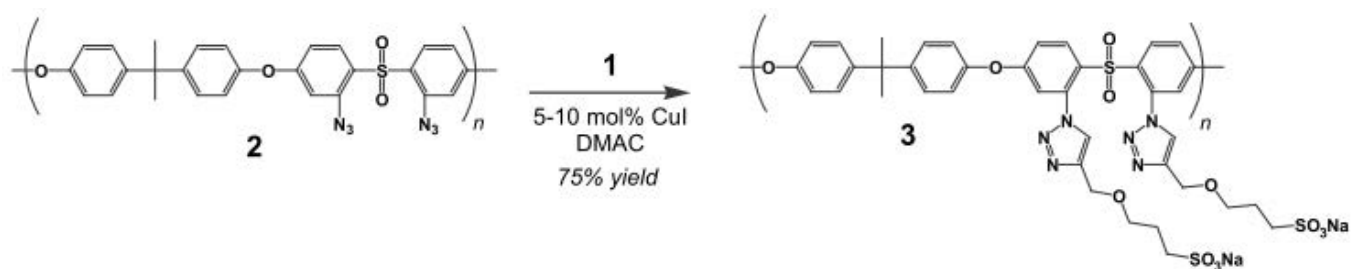


Besides the SPEEK-based membranes, some attention has been focused on the sulfonation of other commercially available polyaromatic materials as well. The sulfonated poly(sulfone)s based PEMs have been well studied because of the low-cost, easy-modification, and good stability [60,61]. The poly(sulfone)s carrying the sulfonic groups and basic units have been designed and synthesized according to the copper-catalyzed 1,3-dipolar “click” cycloaddition reaction, as shown in Figure 13 [62]. By “click” chemistry, both the acid and basic groups have been attached to the

poly(sulfone) main chains simultaneously, and the acid-base interaction in the membranes has been well controlled. The residual azide groups on the poly(sulfone) has also served as the active spots and cross-linked with 1,7-octadiyne to form cross-linked membranes. Membranes with various degrees of sulfonation and cross-linking have been prepared and the performances of the MEAs have been compared with those of Nafion 117. The maximum power output based on one kind of cross-linked membranes reached about  $130 \text{ mW/cm}^2$  at  $65 \text{ }^\circ\text{C}$ , which was nearly the same with that obtained with Nafion 117 membrane.

In addition, click reaction [63] and polycondensation reaction [64] have been adopted to prepare acid-base copolymers with triazole groups in the backbone. The as-prepared membranes from the click reaction have a random distribution of ion channels and show comparable conductivity and lower methanol permeability than Nafion 117 at ambient temperatures and  $80 \text{ }^\circ\text{C}$  under low relative humidity. The membranes based on copolymers from the polycondensation reaction exhibit increased proton conductivity up to  $2 \times 10^{-3} \text{ S cm}^{-1}$  at  $120 \text{ }^\circ\text{C}$  under 5% relative humidity when it was doped with 85 wt % phosphoric acid.

**Figure 13.** Acid-base copolymer synthesized by the “click” cycloaddition reaction.



## 5. Conclusions

Both PEMFCs and DMFCs are promising for portable, stationary, and transportation applications. However, the proton conductivity and fuel crossover properties of PEM membranes greatly influence the performances of PEMFCs and DMFCs, impeding their widespread commercialization prospects. Although Nafion membrane exhibits many advantages such as good stability and high proton conductivity, its high-cost and high fuel permeability are still great challenges to be conquered. In addition, the proton conductivity of Nafion membranes is intensely dependent on the water content in it, which prevents its applications at high temperatures ( $>100 \text{ }^\circ\text{C}$ ). These challenges have created enormous interest in the development of alternative membranes, and the blend membranes consisting of an acidic polymer and a basic compound have become especially appealing in this regard. Through acid-base interactions, the blend membranes not only show good mechanical and thermal stabilities due to the ionic cross-linking, but also exhibit enhanced the proton conductivity at high temperatures and suppressed the fuel crossover, particularly suppressed methanol crossover. Accordingly, several acid-base blend membranes have been explored in recent years for PEMFCs and DMFCs. The properties and performances of the acid-base blend membranes could be optimized by controlling the contents of the basic polymers. Overall, the acid-base blend membranes offer great potential and further exploration with novel synthesis and processing approaches could enhance the commercialization prospects of high-temperature PEMFCs and DMFCs.

## Acknowledgments

This work was supported by the Office of Naval Research MURI grant No. N00014-07-1-0758 and Welch Foundation grant F-1254.

## References

1. Borup, R.; Meyers, J.; Pivovar, B.; Kim, Y.S.; Mukundan, R.; Garland, N.; Myers, D.; Wilson, M.; Garzon, F.; Wood, D.; Zelenay, P.; More, K.; Stroh, K.; Zawodzinski, T.; Boncella, J.; McGrath, J.E.; Inaba, M.; Miyatake, K.; Hori, M.; Ota, K.; Ogumi, Z.; Miyata, S.; Nishikata, A.; Siroma, Z.; Uchimoto, Y.; Yasuda, K.; Kimijima, K.; Iwashita, N. Scientific aspects of polymer electrolyte fuel cell durability and degradation. *Chem. Rev.* **2007**, *107*, 3904–3951.
2. Hickner, M.A.; Ghassemi, H.; Kim, Y.S.; Einsla, B.R.; McGrath, J.E. Alternative polymer systems for proton exchange membranes (PEMs). *Chem. Rev.* **2004**, *104*, 4587–4612.
3. Zhang, H.; Shen, P.K. Recent development of polymer electrolyte membranes for fuel cells. *Chem. Rev.* **2012**, *112*, 2780–2832.
4. Shao, Y.; Yin, G.; Wang, Z.; Gao, Y. Proton exchange membrane fuel cell from low temperature to high temperature: Material challenges. *J. Power Sources* **2007**, *167*, 235–242.
5. Kim, Y.S.; Kim, D.S.; Guiver, M.D.; Pivovar, B.S. Interpretation of direct methanol fuel cell electrolyte properties using non-traditional length-scale parameters. *J. Membr. Sci.* **2011**, *374*, 49–58.
6. Zaidi, S.M.J. Research Trends in Polymer Electrolyte Membranes for PEMFC. In *Polymer Membranes for Fuel Cells*; Zaidi, S.M.J., Matsuura, T., Eds.; Springer Publishing Co.: New York, NY, USA, 2006; pp. 7–25.
7. Ahmed, M.; Dincer, I. A review on methanol crossover in direct methanol fuel cells: Challenges and achievements. *Int. J. Energy Res.* **2011**, *35*, 1213–1228.
8. Bose, S.; Kuila, T.; Nguyen, T.X.H.; Kim, N.H.; Lau, K.-T.; Lee, J.H. Polymer membranes for high temperature proton exchange membrane fuel cell: Recent advances and challenges. *Prog. Polym. Sci.* **2011**, *36*, 813–843.
9. Zhu, Y.; Zieren, S.; Manthiram, A. Novel crosslinked membranes based on sulfonated poly(ether ether ketone) for direct methanol fuel cells. *Chem. Commun.* **2011**, *47*, 7410–7412.
10. Hande, V.R.; Rao, S.; Rath, S.K.; Thakur, A.; Patri, M. Crosslinking of sulphonated poly (ether ether ketone) using aromatic bis(hydroxymethyl) compound. *J. Membr. Sci.* **2008**, *322*, 67–73.
11. Ishikawa, J.-I.; Fujiyama, S.; Inoue, K.; Omi, T.; Tamai, S. Highly sulfonated poly(aryl ether ketone) block copolymers having a cross-linking structure. *J. Membr. Sci.* **2007**, *298*, 48–55.
12. Lee, K.-S.; Jeong, M.-H.; Lee, J.-P.; Lee, J.-S. End-group cross-linked poly(arylene ether) for proton exchange membranes. *Macromolecules* **2009**, *42*, 584–590.
13. Ye, Y.-S.; Chen, W.-Y.; Huang, Y.-J.; Cheng, M.-Y.; Yen, Y.-C.; Cheng, C.-C.; Chang, F.-C. Preparation and characterization of high-durability zwitterionic crosslinked proton exchange membranes. *J. Membr. Sci.* **2010**, *362*, 29–37.
14. Kayser, M.J.; Reinholdt, M.X.; Kaliaguine, S. Amine grafted silica/SPEEK nanocomposites as proton exchange membranes. *J. Phys. Chem. B* **2010**, *114*, 8387–8395.

15. Zarrin, H.; Higgins, D.; Jun, Y.; Chen, Z.; Fowler, M. Functionalized graphene oxide nanocomposite membrane for low humidity and high temperature proton exchange membrane fuel cells. *J. Phy. Chem. C* **2011**, *115*, 20774–20781.
16. Yang, C.-C.; Lue, S.J.; Shih, J.-Y. A novel organic/inorganic polymer membrane based on poly(vinyl alcohol)/poly(2-acrylamido-2-methyl-1-propanesulfonic acid/3-glycidyloxypropyl trimethoxysilane polymer electrolyte membrane for direct methanol fuel cells. *J. Power Sources* **2011**, *196*, 4458–4467.
17. Kim, Y.; Choi, Y.; Kim, H.K.; Lee, J.S. New sulfonic acid moiety grafted on montmorillonite as filler of organic-inorganic composite membrane for non-humidified proton-exchange membrane fuel cells. *J. Power Sources* **2010**, *195*, 4653–4659.
18. Oh, S.Y.; Yoshida, T.; Kawamura, G.; Muto, H.; Sakai, M.; Matsuda, A. Inorganic-organic composite electrolytes consisting of polybenzimidazole and Cs-substituted heteropoly acids and their application for medium temperature fuel cells. *J. Mater. Chem.* **2010**, *20*, 6359–6366.
19. Lin, H.L.; Hu, C.R.; Lai, S.W.; Yu, T.L. Polybenzimidazole and butylsulfonate grafted polybenzimidazole blends for proton exchange membrane fuel cells. *J. Membr. Sci.* **2012**, *389*, 399–406.
20. Acar, O.; Sen, U.; Bozkurt, A.; Ata, A. Proton conducting membranes based on Poly(2,5-benzimidazole) (ABPBI)-Poly(vinylphosphonic acid) blends for fuel cells. *Int. J. Hydrog. Energy* **2009**, *34*, 2724–2730.
21. Li, W.; Fu, Y.Z.; Manthiram, A.; Guiver, M.D. Blend membranes consisting of sulfonated poly(ether ether ketone) and polysulfone bearing 4-nitrobenzimidazole for direct methanol fuel cells. *J. Electrochem. Soc.* **2009**, *156*, B258–B263.
22. Li, W.; Manthiram, A.; Guiver, M.D. Blend membranes consisting of sulfonated poly(ether ether ketone) and 1h-perimidine tethered polysulfone for direct methanol fuel cells. *Electrochem. Solid State Lett.* **2009**, *12*, B180–B184.
23. Goodenough, J.B. *Proton Conductors: Solids, Membranes and Gels-Materials and Devices*; Colomban, P., Ed.; Cambridge University Press: Cambridge, UK, 1992.
24. Kreuer, K.D. On the complexity of proton conduction phenomena. *Solid State Ionics* **2000**, *136–137*, 149–160.
25. Peckham, T.J.; Holdcroft, S. Structure-morphology-property relationships of non-perfluorinated proton-conducting membranes. *Adv. Mater.* **2010**, *22*, 4667–4690.
26. Ueki, T.; Watanabe, M. Macromolecules in ionic liquids: Progress, challenges, and opportunities. *Macromolecules* **2008**, *41*, 3739–3749.
27. Yamada, M.; Honma, I. Anhydrous proton conducting polymer electrolytes based on poly(vinylphosphonic acid)-heterocycle composite material. *Polymer* **2005**, *46*, 2986–2992.
28. Li, Q.; He, R.; Jensen, J.O.; Bjerrum, N.J. Approaches and recent development of polymer electrolyte membranes for fuel cells operating above 100 °C. *Chem. Mater.* **2003**, *15*, 4896–4915.
29. Li, Y.; Li, Z.L.; Lu, X.F.; Zhang, C.C.; Wang, Z.J.; Kong, L.R.; Wang, C.; Liu, X.C. Composite membranes based on sulfonated poly(aryl ether ketone)s containing the hexafluoroisopropylidene diphenyl moiety and poly(amic acid) for proton exchange membrane fuel cell application. *Int. J. Hydrog. Energy* **2011**, *36*, 14622–14631.

30. Verma, A.; Scott, K. Development of high-temperature PEMFC based on heteropolyacids and polybenzimidazole. *J. Solid State Electrochem.* **2010**, *14*, 213–219.
31. Fontanella, J.J.; Wintersgill, M.C.; Wainright, J.S.; Savinell, R.F.; Litt, M. High pressure electrical conductivity studies of acid doped polybenzimidazole. *Electrochim. Acta* **1998**, *43*, 1289–1294.
32. Yang, C.; Costamagna, P.; Srinivasan, S.; Benziger, J.; Bocarsly, A.B. Approaches and technical challenges to high temperature operation of proton exchange membrane fuel cells. *J. Power Sources* **2001**, *103*, 1–9.
33. Fu, Y.-Z.; Manthiram, A. Nafion-imidazole-H<sub>3</sub>PO<sub>4</sub> composite membranes for proton exchange membrane fuel cells. *J. Electrochem. Soc.* **2007**, *154*, B8–B12.
34. Subbaraman, R.; Ghassemi, H.; Zawodzinski, T. Triazole and triazole derivatives as proton transport facilitators in polymer electrolyte membrane fuel cells. *Solid State Ionics* **2009**, *180*, 1143–1150.
35. Kreuer, K.D.; Fuchs, A.; Ise, M.; Spaeth, M.; Maier, J. Imidazole and pyrazole-based proton conducting polymers and liquids. *Electrochim. Acta* **1998**, *43*, 1281–1288.
36. Herz, H.G.; Kreuer, K.D.; Maier, J.; Scharfenberger, G.; Schuster, M.F.H.; Meyer, W.H. New fully polymeric proton solvents with high proton mobility. *Electrochim. Acta* **2003**, *48*, 2165–2171.
37. Schuster, M.F.H.; Meyer, W.H.; Schuster, M.; Kreuer, K.D. Toward a new type of anhydrous organic proton conductor based on immobilized imidazole. *Chem. Mater.* **2004**, *16*, 329–337.
38. Subbaraman, R.; Ghassemi, H.; Zawodzinski, T.A. 4,5-dicyano-1H-[1,2,3]-triazole as a proton transport facilitator for polymer electrolyte membrane fuel cells. *J. Am. Chem. Soc.* **2007**, *129*, 2238–2239.
39. Kim, J.D.; Mori, T.; Hayashi, S.; Honma, I. Anhydrous proton-conducting properties of Nafion-1,2,4-triazole and Nafion-benzimidazole membranes for polymer electrolyte fuel cells. *J. Electrochem. Soc.* **2007**, *154*, A290–A294.
40. Sen, U.; Bozkurt, A.; Ata, A. Nafion/poly(1-vinyl-1,2,4-triazole) blends as proton conducting membranes for polymer electrolyte membrane fuel cells. *J. Power Sources* **2010**, *195*, 7720–7726.
41. Kim, J.-D.; Oba, Y.; Ohnuma, M.; Jun, M.-S.; Tanaka, Y.; Mori, T.; Choi, Y.-W.; Yoon, Y.-G. Physico-chemical properties of highly flexible temperature tolerant anhydrous Nafion-1,2,3-triazole blend membranes. *J. Electrochem. Soc.* **2010**, *157*, B1872–B1877.
42. Fu, Y.; Manthiram, A.; Guiver, M.D. Blend membranes based on sulfonated poly(ether ether ketone) and polysulfone bearing benzimidazole side groups for proton exchange membrane fuel cells. *Electrochem. Commun.* **2006**, *8*, 1386–1390.
43. Ameduri, B. From vinylidene fluoride (VDF) to the applications of VDF-containing polymers and copolymers: Recent developments and future trends. *Chem. Rev.* **2009**, *109*, 6632–6686.
44. Frutsaert, G.; David, G.; Ameduri, B.; Jones, D.J.; Rozière, J.; Glipa, X. Synthesis and characterisation of novel fluorinated polymers bearing pendant imidazole groups and blend membranes: New materials for PEMFC operating at low relative humidity. *J. Membr. Sci.* **2011**, *367*, 127–133.
45. Li, Q.; Jensen, J.O.; Savinell, R.F.; Bjerrum, N.J. High temperature proton exchange membranes based on polybenzimidazoles for fuel cells. *Prog. Polym. Sci.* **2009**, *34*, 449–477.



46. Wainright, J.S.; Wang, J.-T.; Savinell, R.F.; Litt, M.; Moaddel, H.; Rogers, C. Acid-doped polybenzimidazole, a new polymer electrolyte. *Proc. Electrochem. Soc.* **1994**, *94*, 255–264.
47. Yang, J.; Li, Q.; Cleemann, L.N.; Xu, C.; Jensen, J.O.; Pan, C.; Bjerrum, N.J.; He, R. Synthesis and properties of poly(aryl sulfone benzimidazole) and its copolymers for high temperature membrane electrolytes of fuel cells. *J. Mater. Chem.* **2012**, *22*, 11185–11195.
48. Glipa, X.; El Haddad, M.; Jones, D.J.; Rozière, J. Synthesis and characterisation of sulfonated polybenzimidazole: A highly conducting proton exchange polymer. *Solid State Ionics* **1997**, *97*, 323–331.
49. Kawahara, M.; Rikukawa, M.; Sanui, K.; Ogata, N. Synthesis and proton conductivity of sulfopropylated poly(benzimidazole) films. *Solid State Ionics* **2000**, *136–137*, 1193–1196.
50. Beattie, P.D.; Orfino, F.P.; Basura, V.I.; Zychowska, K.; Ding, J.; Chuy, C.; Schmeisser, J.; Holdcroft, S. Ionic conductivity of proton exchange membranes. *J. Electroanal. Chem.* **2001**, *503*, 45–56.
51. Fu, Y.Z.; Manthiram, A. Synthesis and characterization of sulfonated polysulfone membranes for direct methanol fuel cells. *J. Power Sources* **2006**, *157*, 222–225.
52. Yang, B.; Manthiram, A. Sulfonated poly(ether ether ketone) membranes for direct methanol fuel cells. *Electrochem. Solid State Lett.* **2003**, *6*, A229–A231.
53. Li, W.; Bellay, A.; Fu, Y.Z.; Manthiram, A. *N,N'*-Bis-(1H-benzimidazol-2-yl)-isophthalamide as an additive in sulfonated polymer membranes for direct methanol fuel cells. *J. Power Sources* **2008**, *180*, 719–723.
54. Fu, Y.; Li, W.; Manthiram, A. Sulfonated polysulfone with 1,3-1H-dibenzimidazole-benzene additive as a membrane for direct methanol fuel cells. *J. Membr. Sci.* **2008**, *310*, 262–267.
55. Ren, X.; Springer, T.E.; Gottesfeld, S. Water and methanol uptakes in nafion membranes and membrane effects on direct methanol cell performance. *J. Electrochem. Soc.* **2000**, *147*, 92–98.
56. Fu, Y.; Manthiram, A.; Guiver, M.D. Acid-base blend membranes based on 2-amino-benzimidazole and sulfonated poly(ether ether ketone) for direct methanol fuel cells. *Electrochem. Commun.* **2007**, *9*, 905–910.
57. Lee, J.K.; Li, W.; Manthiram, A.; Guiver, M.D. Blend membranes based on acid-base interactions for operation at high methanol concentrations. *J. Electrochem. Soc.* **2009**, *156*, B46–B50.
58. Ye, Y.S.; Huang, Y.J.; Cheng, C.C.; Chang, F.C. A new supramolecular sulfonated polyimide for use in proton exchange membranes for fuel cells. *Chem. Commun.* **2010**, *46*, 7554–7556.
59. Han, M.; Zhang, G.; Li, M.; Wang, S.; Zhang, Y.; Li, H.; Lew, C.M.; Na, H. Considerations of the morphology in the design of proton exchange membranes: Cross-linked sulfonated poly(ether ether ketone)s using a new carboxyl-terminated benzimidazole as the cross-linker for PEMFCs. *Int. J. Hydrog. Energy* **2011**, *36*, 2197–2206.
60. Zhu, Y.; Manthiram, A. Synthesis and characterization of polysulfone-containing sulfonated side chains for direct methanol fuel cells. *J. Power Sources* **2011**, *196*, 7481–7487.
61. Li, W.; Manthiram, A. Sulfonated poly(arylene ether sulfone) as a methanol-barrier layer in multilayer membranes for direct methanol fuel cells. *J. Power Sources* **2010**, *195*, 962–968.
62. Norris, B.C.; Li, W.; Lee, E.; Manthiram, A.; Bielawski, C.W. “Click”-functionalization of poly(sulfone)s and a study of their utilities as proton conductive membranes in direct methanol fuel cells. *Polymer* **2010**, *51*, 5352–5358.

63. Huang, Y.J.; Ye, Y.S.; Yen, Y.C.; Tsai, L.D.; Hwang, B.J.; Chang, F.C. Synthesis and characterization of new sulfonated polytriazole proton exchange membrane by click reaction for direct methanol fuel cells (DMFCs). *Int. J. Hydrog. Energy* **2011**, *36*, 15333–15343.
64. Boaventura, M.; Ponce, M.L.; Brandão, L.; Mendes, A.; Nunes, S.P. Proton conductive membranes based on doped sulfonated polytriazole. *Int. J. Hydrogen Energy* **2010**, *35*, 12054–12064.

© 2012 by the authors; licensee MDPI, Basel, Switzerland. This article is an open access article distributed under the terms and conditions of the Creative Commons Attribution license (<http://creativecommons.org/licenses/by/3.0/>).

Copyright of Polymers (20734360) is the property of MDPI Publishing and its content may not be copied or emailed to multiple sites or posted to a listserv without the copyright holder's express written permission. However, users may print, download, or email articles for individual use.