Recent developments in high-temperature proton conducting polymer electrolyte membranes

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Abstract

Progress in the area of proton conducting polymer electrolyte membranes is intimately linked with the development of polymer electrolyte membrane fuel cells, and is today largely driven by the insufficient properties of humidified Nafion® membranes at temperatures above 100 °C. Recent developments in the field include new ionomers and hybrid membranes containing inorganic nanoparticles to control morphology and enhance water retention, as well as improved systems based on the complexation of basic polymers with oxo-acids. In addition, the molecular design and synthesis of completely new all-polymeric electrolytes that rely entirely on structure diffusion of the protons holds great promise in the long perspective.

Keywords: Ionomers; Acid–base complexes; Organic–inorganic hybrids; Proton conductivity; Proton exchange membrane fuel cells

1. Introduction

Conventional proton conducting polymer electrolyte membranes (PEMs) are based on hydrated ionomers in their protonated form. These materials are typically phase separated into a percolating network of hydrophilic nanopores embedded in a hydrophobic polymer-rich phase domain. The hydrophilic nanopores contain water and the acidic moieties, and conductivity occurs via transport of dissociated protons by the dynamics of the water. The hydrophobic phase domain provides mechanical strength by stabilizing the morphology of the membrane.

Proton conducting PEMs attract considerable attention because they are key-components in polymer electrolyte membrane fuel cells (PEMFCs), which are promising environmentally friendly and efficient power sources for a wide range of different applications [1*]. During normal H₂/O₂ PEMFC operation, anodic dissociation of H₂ produces protons that are transported through the hydrated PEM to the cathode, where reduction of O₂ produces water. Potentially, this type of fuel cell gives no emissions, and the use of ozone-depleting petroleum based fuels can thus be avoided. The research activities on PEMCs have increased progressively during the last decade, and are today rather extensive as seen by the accelerating number of yearly publications (Fig. 1).

The primary demands on the hydrated PEM are high proton conductivity (at least above 0.01 S cm⁻¹), low fuel and O₂ permeability, and high chemical, thermal and mechanical stability. Conventional PEMFCs typically operate with Nafion® membranes, which offers quite good performance below 90 °C. However, to decrease the complexity and increase the efficiency and CO-tolerance of the PEMFC system, there is today a strong need for PEMs capable of sustained operation above 100 °C. Unfortunately, the proton conductivity of Nafion® suffers greatly at temperatures above 90 °C due to loss of water. Also, the barrier properties of this membrane are usually insufficient when methanol is used as fuel. These factors, in addition to the high cost of Nafion®, has triggered an extensive research for alternative PEM materials, some relying on other species than water for proton conduction [2–4*]. The present review focuses on the development of different types of high-temperature proton conducting PEMs during the last 2 years.

2. Ionomers and ionomer membranes

Ionomer-based membranes intended for high-temperature PEMFCs should preferably retain a high conduc-
tivity at low levels of humidification. There is thus a need to improve water retention at high temperatures and to improve performance at low water contents, while simultaneously giving special attention to chemical as well as morphological stability to resist excessive water swelling. The membrane morphology is important for the performance, and is linked to the nature of the ionomer and the membrane formation process in a quite complex manner. It typically depends strongly on the water content, and on the concentration and distribution of the acidic moieties [4,5,6]. For example, Kreuer has shown that hydrated membranes based on sulfonated polyetherketone have a less pronounced separation into hydrophilic/hydrophobic domains, as well as a larger distance between the acidic moieties, as compared to the Nafion® membrane [4*].

The majority of the new ionomers developed currently are based on different arylene main-chain polymers, which are characterized by excellent thermal, chemical, and mechanical properties. Some of these ionomers are shown in Fig. 2. Several research groups are working with different sulfonated polymers containing diarylsulfone units [7,8–11]. For example, Wang et al. have prepared high molecular weight polysulfones containing randomly distributed disulfonated diarylsulfone units [7*]. Analysis of the membrane morphology by atomic force microscopy revealed hydrophilic phase domains that increased in size, from 10 to 25 nm, with increasing degree of sulfonation. The membranes were stable up to 220 °C in air, and highly sulfonated ones showed conductivities of 0.17 S cm⁻¹ at 30 °C in water [7*].

Poppe et al. have produced flexible PEMs based on carboxylated and sulfonated poly(arylene-co-arylene sulfone)s [8]. As expected, the carboxylated materials showed lower water uptake and lower conductivity in comparison with the sulfonated ones. Sulfonated polysulfones have also been blended with basic polymers such as polybenzimidazole (PBI) and poly(4-vinyl pyridine) in order to improve the performance in direct methanol fuel cells [11].

Different sulfonated aromatic polyimides are also under investigation [12,13*,14,15]. These ionomers typically reach high levels of conductivity, but the hydrolytic stability is reported to be very sensitive to the chemical structure of the polyimide main-chain [13*,14]. A membrane-electrode assembly based on a sulfonated polyimide was recently evaluated in a fuel cell at 70 °C, and was found to have a performance similar to Nafion® [15].

Sulfonated PBI has been investigated by Kawahara et al. [16,17] and Asensio et al. [18]. At low water contents, PEMs of PBI grafted with sulfopropyl units showed a proton conductivity in the order of 10⁻³ S cm⁻¹ in the temperature range from 20 to 140 °C, which is superior to Nafion® under the same conditions [17]. The performance of these PEMs have also recently been investigated in fuel cells at temperatures up to 150 °C under fully humidified conditions [19].

As the operation temperature of the PEMs is increased to temperatures above 100 °C, desulfonation, i.e. loss of the sulfonic acid unit though hydrolysis, becomes an increasingly important problem. Acidic moieties having higher stability include phosphonic acid and sulfonimides. The latter is a significantly stronger acid compared to sulfonic acid, which may be especially advantageous at low water contents. Alcock et al. have prepared different poly(aryloxypophosphazene)s functionalized with phenyl phosphonic acid units with the intended use in direct methanol fuel cells [20]. Just recently, the same authors also report on the preparation of poly(aryloxypophosphazene)s having sulfonamide units [21]. Blending and radiation crosslinking have been investigated as means to reduce water swelling and methanol permeation of poly(aryloxypophosphazene) ionomers [22].

3. Organic–inorganic hybrid membranes

The incorporation of various hygroscopic, and often proton conducting, inorganic nanoparticles has shown to significantly improve the high-temperature performance of several types of PEMs [23*,24–29*,30*]. A number of research groups are developing hybrid membranes based on Nafion® to improve its high-temperature performance [23*,24–27,31]. Nafion®-silica hybrid membranes were produced by Miyake et al. via a sol–gel process [31]. Although containing more water, the con-

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Fig. 1. The number of references found in the scientific database ‘CAplus’ by using the ACS search facility ‘SciFinder® Scholar 2000’ and a combination of the words: ‘polymer’, ‘fuel’ and ‘cell’.

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Fig. 2. Examples of proton conducting polymers currently under investigation as PEM materials: (a) sulfonated poly(arylene ether sulfone) [7*]; (b) sulfophenylated polysulfone [9]; (c) sulfopropylated PBI [16,17]; (d) sulfonated poly(arylene-co-arylene sulfone) [8]; (e) sulfonated naphthalene polyimide (Ar, various aromatic moieties) [13*]; (f) poly(aryloxypophazene) having sulfonimide units [31]; (g) imidazole-terminated ethylene oxide oligomers [46*]; and (h) Nafion® marketed by the DuPont company.

...ductivity of the hybrid membranes decreased with increased silica content, and was lower than that in the unmodified membrane under all conditions investigated. Bocarsly and co-workers have prepared Nafion® PEMs containing silicon oxide [24], as well as zirconium phosphate [23*,25] particles. They found, for example, that the silicon oxide modified PEMs showed improved robustness and water retention, which resulted in high conductivities at 130 °C during at least 50 h. Staiti et al. have investigated Nafion®-silica membranes doped with phosphotungstic acid and silicotungstic acid [26]. The authors claim that the heteropolyacid-modified Nafion®-silica recast membranes showed suitable properties for operation at 145 °C in a direct methanol fuel cell. Tazi and Savadogo have prepared membranes based on Nafion®, silicotungstic acid and thiophene [27]. The modified membranes are reported to have a higher water uptake and conductivity than the unmodified membrane, resulting in improved fuel cell characteristics.

Hybrid membranes based on different arylene main-chain polymers have also been investigated [28,29*,30*,33*]. For example, nanocomposite PEMs based on phosphotungstic acid in sulfonated polysulfones have been prepared by Hickner et al. [28]. Interestingly, the presence of the nanoparticles was found to increase the proton conductivity, while at the same time decreasing the water absorption. In addition, the mechanical modulus of the material was improved after...
addition of the particles. Genova-Dimitrova et al. incorporated phosphoantimonic acid particles into sulfonated polysulfone and obtained PEMs with improved mechanical properties and conductivities close to Nafion®, while avoiding excessive water swelling at 80 °C [29*]. Bonnet et al. have studied the properties of hybrid membranes based on sulfonated polyetherketone and particles of amorphous silica, zirconium phosphate sulfophenylphosphate and zirconium phosphate as a function of temperature and humidity [30*]. In all cases the presence of the particles led to increased conductivities at 100 °C. Staiti has attached silicotungstic acid on SiO₂-support particles, and then used PBI as a binder to prepare membrane films [32]. The materials are reported to be thermally stable with a conductivity of 10⁻³ S cm⁻¹ at 160 °C and 100% relative humidity. The use of a phosphorylated PBI gave membranes with twice the conductivity at the same operating conditions [32].

A somewhat different approach has been pursued by Honma et al. who prepared different organic–inorganic hybrid materials by forming networks containing nanoparticles covalently linked by oligoether segments [33*,34]. After doping the networks with various heteropolyacids, they reported proton conductivities of 10⁻³ – 10⁻² S cm⁻¹ in the temperature range 20–140 °C under fully humidified conditions [34]. Also, the thermal stability of the oligoethers was greatly improved after formation of the hybrids. Stangar et al. have shown that a similar material based on silica functionalized by poly(propylene glycol) and doped with a heteropolyacid showed better results than Nafion® in a methanol fuel cell, mostly due to a lower methanol cross-over [35].

In conclusion, the incorporation of various nanoparticles seems to be very promising, although a great deal remains to be understood when it comes to, for example, interactions, synergy and long-term stability in these rather complex hybrid materials.

4. Membranes based on polymers and oxo-acids

Several research groups are currently developing high-temperature PEMs based on complexes of strong acids, such as H₃PO₄ and H₂SO₄, with different basic polymers, especially PBI [36–40*,41*,42,43*,44]. Typically, the mechanical properties of these PEMs are favored by low levels of acid-doping, while the conductivity is favored by high doping levels and increasing water concentrations. Various polymers beside PBI have been evaluated for use in these types of membranes [36–39]. Bozkurt and Meyer have for example investigated poly(4-vinylimidazole)-H₃PO₄ complexes and found by thermogravimetry that they were stable up to 150 °C [36]. When increasing the concentration of H₃PO₄, they found that the materials became softer and that the conductivity at ambient temperature increased to reach approximately 10⁻⁴ S cm⁻¹ at 2 mol H₃PO₄ per mol imidazole unit. Lassègues et al. found that complexes of an amorphous polyamide with H₃PO₄ showed high conductivities, but had poor mechanical properties and poor chemical stability above 90 °C [37].

Pu et al. have used dielectric spectroscopy to investigate the proton conduction mechanism in poly(4-vinylimidazole) [38] and PBI [40*] doped with H₃PO₄ and H₂SO₄. The results showed that the proton transport in the PBI-based materials mainly is controlled by proton hopping and diffusion, rather than by segmental motions of the polymer chains. For the poly(4-vinylimidazole)-based materials in the glassy state, the proton transport was controlled by a hopping mechanism, while the segmental motions and diffusion also contributed above the glass transition temperature.

The concept of the PBI–H₃PO₄ system has been further exploited. For example, Qingfeng et al. found that the conductivity of PBI–H₃PO₄ complexes was insensitive to humidity, but strongly dependent on the acid content, reaching values of 0.13 S cm⁻¹ at 160 °C and high acid-doping levels [41*]. It was also shown that the water drag due to proton transport was almost zero in these PEMs. Asensio et al. have synthesized and compared the performance of different sulfonated and unsulfonated PBIs and their complexes with H₃PO₄ [18]. They found that the complexes were stable up to 400 °C, and that sulfonation of a PBI promoted the conductivity of the complex in comparison to when the unsulfonated polymer was used. Furthermore, Hasiotis et al. have prepared blends of sulfonated polysulfones and PBI which were doped with H₃PO₄ [42,43*]. These PEMs showed improved mechanical properties and conductivities above 10⁻⁲ S cm⁻¹ at 160 °C and 80% relative humidity, which was higher than for acid-doped PBI membranes under the same conditions. Initial work has also indicated the suitability of the blend membranes in fuel cells [44]. A membrane-electrode assembly based on PBI–H₃PO₄ complexes has recently been evaluated in a H₂/O₂ fuel cell [44]. Finally, the Celanese company has announced the introduction of a commercial membrane-electrode assembly based on the same system.

5. All-polymeric electrolytes

Kreuer et al. have outlined a very interesting approach to obtain proton conducting polymeric systems based on nitrogen-containing heterocycles, such as imidazole, benzimidazole and pyrazole [45*]. These heterocycles form hydrogen bonded networks similar to that found in water, and also their transport properties are similar to that of water with proton transfer occurring via structure diffusion. An important advantage of the heterocycles over water is that they can be covalently incorporated into polymer structures to obtain all-poly-
meric proton conductors, thus avoiding any volatile low molecular weight species. It is, however, important that the incorporation is accomplished in such a way that the heterocyclic groups retain a high mobility. Recently, Schuster et al. showed that imidazole-terminated ethylene oxide oligomers can reach conductivities of up to $10^{-5}$ S cm$^{-1}$ at 120 °C [46]. The conductivity was further enhanced after acid-doping. In another study, Yoon et al. prepared a polyurethane having imidazole units in the main-chain which reached conductivities of $10^{-4}$ S cm$^{-1}$ at 140 °C [47]. Notably, these levels of conductivity were obtained in the complete absence of water.

6. Theoretical studies

Several theoretical studies have recently been carried out to increase the knowledge concerning the mechanism of proton transport in ionomer membranes [48–54]. Studies that take into account molecular structure and membrane morphology may play a vital role in the development of new ionomers and membranes.

Eikerling et al. were able to predict experimental values of PEM conductivities by using a model based on a heterogeneous membrane structure, and addressing relevant experimental parameters such as the concentration of acidic moieties and the level of hydration [48]. In another study, the same authors carried out computations to evaluate the proton dissociation of various acidic moieties at different levels of hydration [49]. They found that the sulfonimide moieties have higher degrees of proton dissociation at low water contents as compared to triflic acid, CF$_3$SO$_2$H, which has a higher acidic moiety at different levels of hydration [49].

In these systems, the use of suitable nanoparticles may prove fruitful. For nearly all PEM systems there is a further need for carefully designed polymers to control structure and morphology in order to manipulate interactions and processes taking place on the molecular scale.

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References and recommended reading

- of special interest
- of outstanding interest


Review describing the evolution of PEMFC technology and outlining some future challenges to advance the technology.


Provides an insight to some fundamental differences between sulfonated polyetherketone and Nafion® when it comes to water uptake, morphology, and transport properties.


7. Conclusions

It seems reasonable that operational temperatures up to approximately 130 °C may be reached in PEMFCs by using, for example, well-designed hydrated organic–inorganic hybrid PEMs. However, in order to attain operational temperatures above 150 °C, focus has most probably to be on different modes of proton conduction using durable non-volatile components. In this context, PBI–HPO$_4$ complexes have already been evaluated with good results, even if the critical long-term stability remains to be proven. The perspective of all-polymeric electrolytes based on imidazoles is appealing and initial results are encouraging. A future challenge is to develop useful PEMs based on this concept, combining high conductivity, and high thermal, chemical and mechanical stability. Also in these systems, the use of suitable nanoparticles may prove fruitful. For nearly all PEM systems there is a further need for carefully designed polymers to control structure and morphology in order to manipulate interactions and processes taking place on the molecular scale.
Different methods to achieve PEMs with high-temperature performance are evaluated, including the preparation of organic–inorganic hybrid and non-aqueous materials.


A study on sulfonated polysulfone where conductivities close to Nafion, as well as improvements in swelling and mechanical properties were measured after including phosphoantimonic acid particles.


Study on hybrid membranes of sulfonated polyethyetherketone and a variety of different inorganic proton conductors.


Presents an interesting hybrid membrane concept based on nanoparticles linked by various oligoethers.


