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On the development of proton conducting polymer membranes for hydrogen and methanol fuel cells

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Abstract

The transport properties and the swelling behaviour of NAFION and different sulfonated polyetherketones are explained in terms of distinct differences on the microstructures and in the pK_a of the acidic functional groups. The less pronounced hydrophobic/hydrophilic separation of sulfonated polyetherketones compared to NAFION corresponds to narrower, less connected hydrophilic channels and to larger separations between less acidic sulfonic acid functional groups. At high water contents, this is shown to significantly reduce electroosmotic drag and water permeation whilst maintaining high proton conductivity. Blending of sulfonated polyetherketones with other polyaryls even further reduces the solvent permeation (a factor of 20 compared to NAFION), increases the membrane flexibility in the dry state and leads to an improved swelling behaviour. Therefore, polymers based on sulfonated polyetherketones are not only interesting low-cost alternative membrane material for hydrogen fuel cell applications, they may also help to reduce the problems associated with high water drag and high methanol cross-over in direct liquid methanol fuel cells (DMFC). The relatively high conductivities observed for oligomers containing imidazole as functional groups may be exploited in fully polymeric proton conducting systems with no volatile proton solvent operating at temperatures significantly beyond 100°C, where methanol vapour may be used as a fuel in DMFCs. © 2001 Elsevier Science B.V. All rights reserved.

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1. Introduction

The concept of polymer electrolyte membrane fuel cells (PEM-FC) has been well established since early 1960s, and PEM-FCs are successfully commercialised for niche applications, such as electrical power sources in space crafts and submarines. During the last decade, however, the use of PEM-FCs as power sources in mass products, such as the electrical vehicles and portable electrical devices, was also

brought into focus. This puts new demands on the materials being used, and is in particular true for the separator membrane material, which, traditionally, is a hydrated perfluorosulfonic polymer such as NAFION.

Although such membranes show superior performance in fuel cells operating at moderate temperature (<90°C) and high relative humidity with pure hydrogen as a fuel, their inherently high cost of production makes their use in cost critical applications, such as fuel cells for electrical vehicles, unlikely. In addition the properties of such polymer membranes are insufficient if higher temperatures and/or fuels different from pure hydrogen are used. Currently, there is an increasing interest in using hydrogen-rich gases

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produced by reforming methanol or even gasoline. Such gases contain traces of different gases in particular CO, which reduces the activity of platinum or platinum-alloys (e.g. [1]), which are generally used as anode catalysts. The CO tolerance, however, increases with increasing temperature, and therefore, fuel cell operation at somewhat higher temperature is desirable. Also the direct electrochemical oxidation of methanol is significantly promoted with increasing temperature. For direct liquid methanol fuel cells (DMFC), however, water and methanol cross-over significantly increases with temperature, which reduces the fuel efficiency and requires an expensive water management systems (e.g. [2]).

In short, limited operation temperature due to the humidification requirements, water and methanol cross-over and cost are severe disadvantages of plain perfluorosulfonic polymers.

These limitations have already stimulated a variety of approaches in the development of alternative polymeric proton exchange membranes (for a recent review see [3]). Most of them are sulfonated polymers, but also sulfamides have been used as thermally more stable acid functional groups [4]. In any case, proton conductivity relies on proton solvation by water at high water activities, and the limitations of their use in fuel cells are generally similar to those of NAFION.

Modification of such membranes by the inclusion of small inorganic particles such as silica [5–7] or zirconiumphosphates sulfophenylphosphonates [7] leads to some improvement of the performance of such membranes especially in pressurised fuel cells operating at temperatures up to 140°C [5]. Also the morphological stabilisation of acidic polymers by either acid/base blending or covalent cross-linking [8,9] appears to reduce swelling and water and methanol cross-over. But reduced conductivity and brittleness in the dry state emerge as new problems.

Distinctly different approaches are based on the complexation of basic polymers, such as polybenzimidazole, with oxo-acids (e.g. [10,11]) especially for phosphoric acid, high acid to polymer ratios lead to conductivities close to that of the pure acid. As in the case of pure phosphoric acid [12], proton conductivity of such adducts is predominantly carried by structure diffusion, i.e. proton transfer between phosphate species and phosphate reorientation. Phosphoric acid is successively immobilised with decreasing

acid/polymer ratio, while proton conductivity still remains relatively high [13]. Due to the low transport coefficients of other species in the highly viscous phosphoric matrix and the low solubility of methanol at high temperatures, methanol cross-over is drastically reduced compared to hydrated acidic polymers [14].

In this paper, two approaches towards membrane materials operating at higher temperatures will be presented. The first is based on the modification of the microstructure of sulfonated polyaryls by blending with other polymers. It will be demonstrated that water cross-over can drastically be reduced while maintaining high proton conductivity, which is of significant importance for applications in direct liquid methanol fuel cells. In the second approach, the use of heterocycles as proton solvating species will be examined. This may lead the way to fully polymeric proton conductors, which may allow further extension of the operation temperature in low humidity environments.

Apart from already published results (see references), some recent, as yet unpublished, results are included in this general discussion. Experimental and methodological details will be published elsewhere.

2. Hydrated polymers based on sulfonated polyetherketones

The choice of polyaryls, in particular polyetherketones instead of perfluorinated polymer backbones, was mainly based on cost and stability considerations [15]. Although sulfonated polyaryls have been demonstrated to suffer from hydroxy radical initiated degradation [16] we found sulfonated polyetherketones to be durable under fuel cell conditions over several thousand hours. Polyetherketones (PEEKK and PEEK) functionalised by electrophilic sulfonation with sulfuric acid (similar to the procedure described in [17]) were supplied by Hoechst–Aventis. The hydration behaviour and the transport of protonic charge carriers and water have been examined and compared to the corresponding properties of NAFION. The distinct differences are qualitatively explained by differences in the microstructures and the acidity of the sulfonic acid functional groups [15,18,19]. The variation of these features by chemical modification, blending or cross-linking may provide space for the

adaptation of the polymer properties to particular fuel cell applications.

Perfluorosulfonic polymers naturally combine, in one macromolecule, the extremely high hydrophobicity of the perfluorinated backbone with the extremely high hydrophilicity of the sulfonic acid functional groups. Especially in the presence of water, this gives rise to some hydrophobic/hydrophilic nano-separation. The sulfonic acid functional groups aggregate to form a hydrophilic domain. When this is hydrated, protonic charge carriers form within inner space charge layers by dissociation of the acidic functional groups, and proton conductance assisted by water dynamics occurs. While the well connected hydrophilic domain is responsible for the transport of protons and water, the hydrophobic domain provides the polymer with the morphological stability and prevents the polymer from dissolving in water.

The situation in sulfonated polyetherketones was found to be distinctly different with respect to both transport properties and morphological stability. As a result of the smaller hydrophilic/hydrophobic difference (the backbone is less hydrophobic, and the

sulfonic acid functional group is less acidic and therefore, also less polar) and the smaller flexibility of the polymer backbone, the separation into a hydrophilic and a hydrophobic domain is less pronounced.

This can directly be inferred from the results of small angle X-ray scattering (SAXS) experiments. For a hydrated sulfonated polyetherketone compared to NAFION the ionomer peak is broadened and shifted towards higher scattering angles and the scattering intensity at high scattering angles (Porod-regime) is higher (Fig. 1). This indicates a smaller characteristic separation length with a wider distribution and a larger internal interface between the hydrophobic and hydrophilic domain for the hydrated sulfonated polyetherketone. The SAXS data and water self-diffusion coefficients obtained by pulsed-field-gradient (PFG)-NMR have been used to consistently parameterise a simple model for the microstructure, which is based on a cubic hydrophilic channel system in a hydrophobic matrix. Data for channel diameter, channel separation, degree of branching and number of dead-end channels have been obtained for both type of polymers [19]. As schematically illustrated in Fig. 2, the

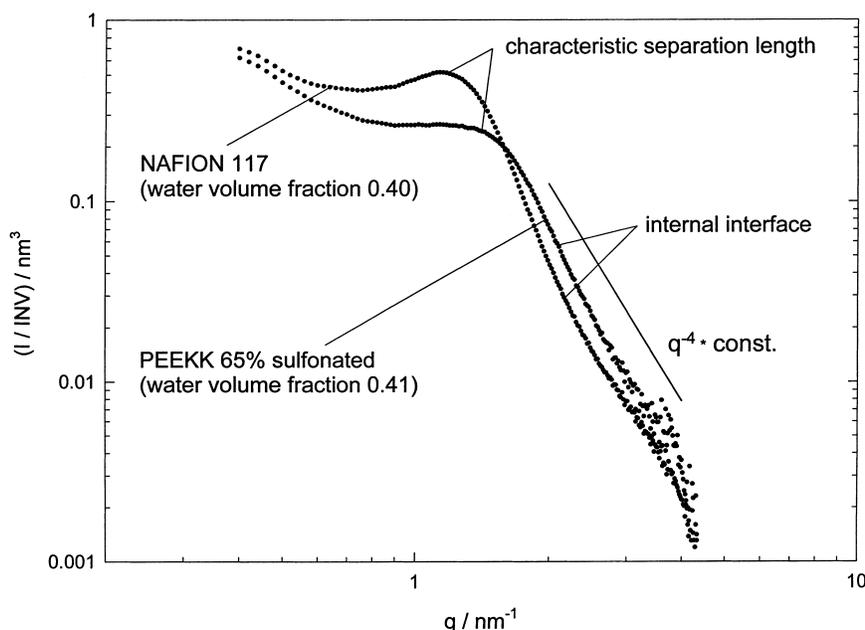


Fig. 1. Small angle X-ray scattering spectra of hydrated NAFION and a hydrated sulfonated polyetherketone. The characteristic hydrophobic/hydrophilic separation lengths are obtained from the position of the ionomere peaks while the internal hydrophobic/hydrophilic interfaces are obtained from the intensities in the Porod-regimes [19].

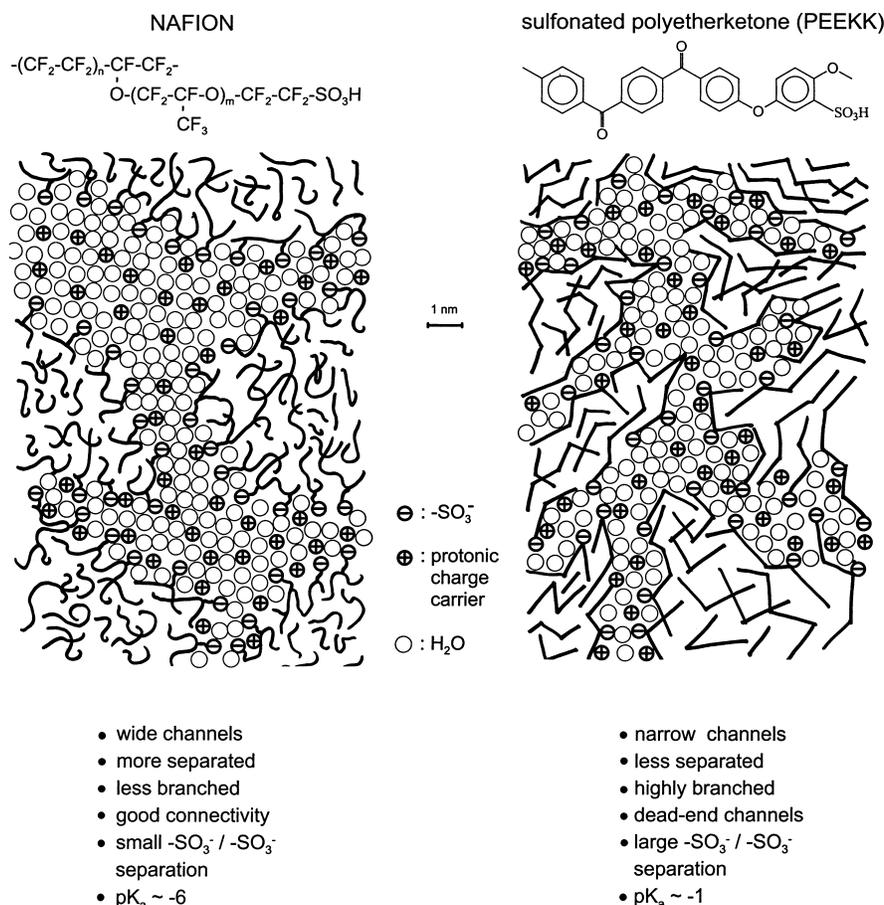


Fig. 2. Schematic representation of the microstructures of NAFION and a sulfonated polyetherketone (derived from SAXS experiments [19]) illustrating the less pronounced hydrophobic/hydrophilic separation of the latter compared to the first.

water filled channels in sulfonated PEEKK are narrower compared to those in NAFION. They are less separated and more branched with more dead-end “pockets”. These features correspond to the larger hydrophilic/hydrophobic interface and, therefore, also to a larger average separation of neighbouring sulfonic acid functional groups. The stronger confinement of the water in the narrow channels of the aromatic polymers leads to a significantly lower dielectric constant of the water of hydration (about 20 compared to almost 64 in fully hydrated NAFION [20,21] (Fig. 3)).

For high water volume fractions the percolation in the hydrophilic domain is similar in both microstructures, and since the water/polymer interaction is small in this regime, also the water self-diffusion coefficients

(D_{H_2O}) are comparable (Fig. 4). With decreasing water volume fraction, however, the water diffusion coefficient decreases more rapidly in sulfonated PEEKK compared to NAFION. The mobility of protonic charge carriers (D_σ), as obtained from conductivity data via the Nernst–Einstein relationship assuming full dissociation of the sulfonic acid functional groups, shows a similar behaviour since this is roughly related to the water diffusion coefficient (Fig. 4). At very high water contents, however, D_σ is somewhat higher than D_{H_2O} indicating some intermolecular proton transfer being involved in the mobility of protonic charge carriers as in the case of dilute aqueous solutions of acids (structure diffusion [22–24]). At very low water contents, the opposite is true. As a result of the decreasing

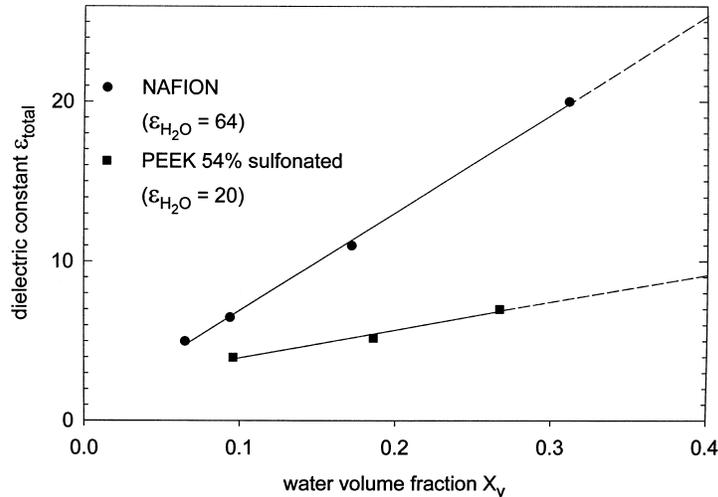


Fig. 3. Dielectric constant (ϵ_{total}) for hydrated NAFION and a sulfonated polyetherketone obtained at 5 GHz as a function of the degree of hydration [20,21]. The dielectric constant of the water of hydration ($\epsilon_{\text{H}_2\text{O}}$) has been obtained by extrapolating the data to a water volume fraction of unity (pure water).

degree of dissociation of the acidic functional group and the decreasing dielectric screening of the anionic counter charge, the excess protons tend to be more localised in the vicinity of the sulfonic acid functional groups, which leads to a stronger decrease of D_σ com-

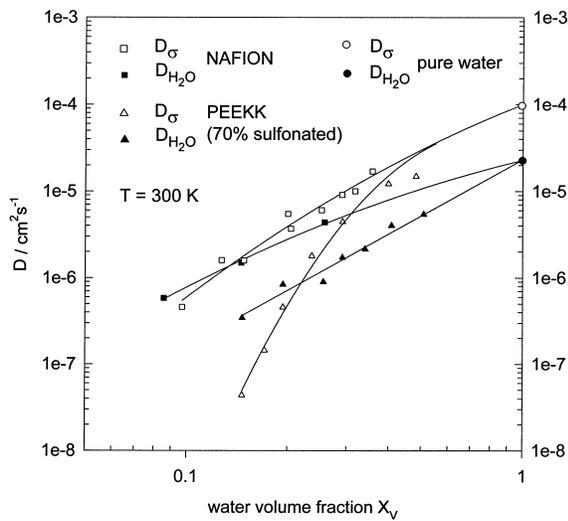


Fig. 4. Water self-diffusion coefficient ($D_{\text{H}_2\text{O}}$) and proton mobility (D_σ) as a function of the water volume fraction in NAFION and a sulfonated polyetherketone (data taken from [15]).

pared to $D_{\text{H}_2\text{O}}$ with decreasing water volume fraction. While this effect is negligible for NAFION, it is quite pronounced in sulfonated PEEKK as a consequence of the higher $\text{p}K_a$ of the acidic functional group (approximately -1 compared to -6 for the superacid NAFION as calculated by the program “ $\text{p}K_a$ database 4.0” [25]) and the lower dielectric constant of the water of hydration (see also Fig. 3), which allows only for a weak dielectric screening of the negative charge of the sulfonic acid anion. Percolation and proton localisation effects explain why the proton conductivity in sulfonated aromatic polymers decrease much more severely with decreasing hydration levels than in NAFION.

While the mobility of protonic charge carriers, the self-diffusion and even the chemical diffusion of water are random walk processes on a molecular scale with no or only small drift velocity superimposed, the electroosmotic drag and the water permeation correspond to the collective flow of water through the membrane, either as a result of a proton flux or a total pressure gradient. As opposed to the first, the latter transport coefficients depend in a direct way on the size of the channels (Hagen–Poiseuille-type problem [19]). An important consequence of the narrow channels in sulfonated polyetherketones is that the electroosmotic drag (Fig. 5) as well as the permeation coefficient

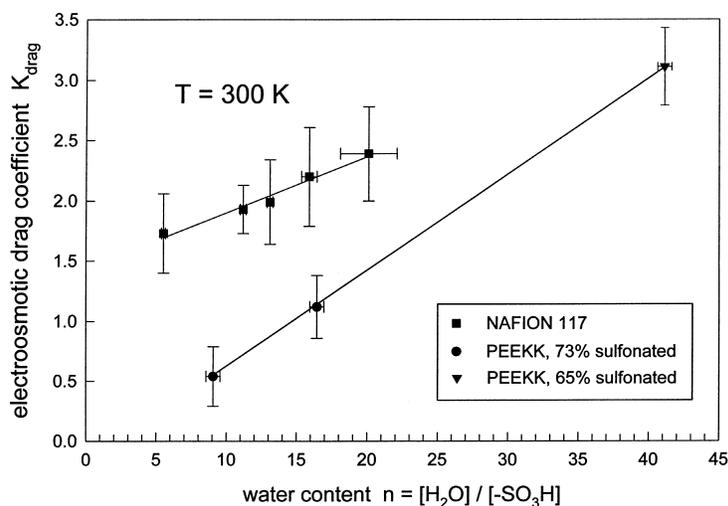


Fig. 5. Electroosmotic drag coefficient obtained by electrophoretic-NMR as a function of the water content $n = [\text{H}_2\text{O}]/[-\text{SO}_3\text{H}]$ [26].

(Table 1) are distinctly lower than in well separated perfluorosulfonic polymers for a given water content [19,26].

In the dry state, such membranes are quite brittle, while they become soft in the presence of water. Fig. 6 shows the swelling behaviour of sulfonated polyetherketones (PEEKK) with different degrees of sulfonation compared to that of NAFION. For a sulfonation level of about 70% per repeat unit (1.40 meq./g), which corresponds to a similar concentration of acid functional groups as in NAFION, the onset of exaggerated swelling is about 50°C below that of NAFION. For degrees of sulfonation higher than 80% (1.78 meq./g), PEEKK even becomes water soluble.

As membrane materials for fuel cells, plain sulfonated polyetherketones apparently have some advantages and disadvantages compared to perfluorosulfonic polymers. The low drag coefficients facilitate

the water management under operating conditions [27–29], and the low solvent (water and methanol) cross-over, which has contributions from electroosmotic drag and permeation, is of advantage especially in direct methanol fuel cells (e.g. [2]). On the other hand, the stronger decrease of the conductivity upon dehydration allows only operation close to the dew point of water. While this is not a severe disadvantage in many cases, the brittleness of pure sulfonated polyetherketones makes their handling difficult and may cause mechanical membrane failure during operation. Also the lower maximum operation temperature of about 80°C, compared to about 140°C for NAFION (see Fig. 6) is a severe limitation for fuel cell applications.

Based on the above analyses, however, the following chemical and microstructural modifications of sulfonated polyetherketones should lead to a combination

Table 1
Water permeation coefficients ($P_{\text{H}_2\text{O}}$) for different membrane materials immersed in water ($T = 300 \text{ K}$, $\Delta p = 20 \text{ hPa}$).

| Membrane material | Titrated ion exchange capacity/(meq./g) | Water content n / ($[\text{H}_2\text{O}]/[-\text{SO}_3\text{H}]$) | $P_{\text{H}_2\text{O}}/(\text{mol cm}^{-1} \text{ s}^{-1} 10^5 \text{ Pa}^{-1})$ |
|-------------------------------------|---|--|---|
| NAFION 117 | 0.91 | 16 | 1.52×10^{-9} |
| PEEKK (65% sulfonated) | 1.43 | 19 | 8.9×10^{-10} |
| PEEK (54% sulfonated) + 10 w/o PES | 1.39 | 11 | 7.42×10^{-11} |
| PEEK (100% sulfonated) + 21 w/o PBI | 1.40 | 7 | 2.19×10^{-11} |

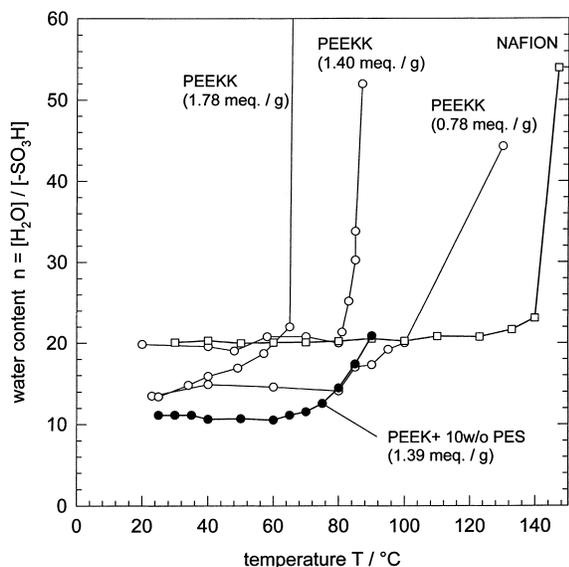


Fig. 6. Swelling in water for NAFION, plain sulfonated polyetherketones (PEEKK) with different degrees of sulfonation and a blend of a sulfonated PEEK and PES (ion exchange capacities are given in brackets).

of some advantages of both type of polymers.

1. In order to reduce the drastic decrease of the proton conductivity with decreasing water content, the sulfonic acid functions should be more acidic (superacid) and their concentration in the hydrophilic domain should be high, i.e. their average separation should be low.
2. A well-connected system of very narrow channels should allow for low solvent permeation and electroosmotic drag coefficient along with high mobility of the protonic charge carriers.
3. Since narrow channels imply the absence of any significant hydrophilic/hydrophobic separation, the morphological stability must be achieved by other means, e.g. by blending and/or cross-linking [18].

Blends of sulfonated polyetherketones with other aromatic polymers already provides some of these features.

One approach is based on the entanglement of a sulfonated PEEKK and an unsulfonated polyethersulfone (PES). Blends of the two polymers show higher flexibility in the dry state and an improved morphological stability as indicated by less swelling in water (e.g. a

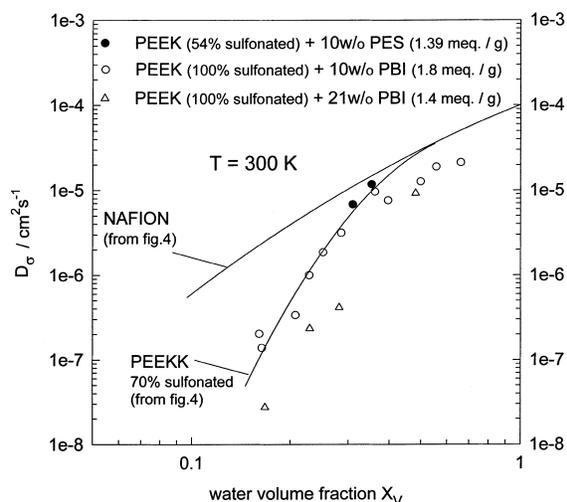


Fig. 7. Proton mobility in hydrated blends of sulfonated PEEK with PES and PBI, respectively. The proton mobilities in NAFION and plain sulfonated polyetherketone is shown for comparison.

blend of 54% sulfonated PEEK with 10% PES takes up only 20 $\text{H}_2\text{O}/\text{-SO}_3\text{H}$ in water at 90°C (Fig. 6)). For high water volume fractions, the proton mobility (D_σ) is virtually identical to that of the plain sulfonated polyetherketone (Fig. 7). Since the material shows very low swelling at low temperatures, pretreatment in water (e.g. at 90°C) is required to achieve water volume fractions, which allow the very high proton conductivities required especially for hydrogen fuel cell applications. For DMFC applications, however, the reduced swelling and the absence of any significant hydrophobic/hydrophilic separation, as indicated by the virtual disappearance of the ionomer peak in the SAXS spectrum, are essential advantages, since these features are expected to reduce the electroosmotic drag as well as the methanol permeation (see above). A significant reduction of water permeation has already been verified experimentally (Table 1) while measurements of drag coefficients by E-NMR are underway.

Another approach, as suggested by Kerres et al. [8,30], relies on the acid/base interaction between a sulfonated polyetherketone and another basic polymer, preferentially polybenzimidazole (PBI), which is well known to be durable under fuel cell conditions as constituent of PBI-phosphoric acid adducts [11,14]. In these blends, only part of the acidic functional groups are neutralised by the basic amine groups of PBI.

The proton (charge) transfer between the two types of polymers leads to the formation of an inner salt, i.e. cross-linking by means of coulomb interaction, which also reduces swelling in water. For a blend of a fully sulfonated PEEK with 10 w/o PBI (corresponding to an equivalent weight of a 60% sulfonated PEEKK) about 39 H₂O/-SO₃H are absorbed at 80°C. Surprisingly, there is no further swelling at higher temperatures (up to 120°C). This high but constant water level gives rise to the high proton conductivity of this blend. The proton mobility is in fact similar to plain sulfonated PEEKK (70% sulfonation) for high water contents (Fig. 7). It should, however, be mentioned that acid/base cross-linking is not strong enough to prevent the highly sulfonated constituents of such blends to be slowly leached out in water. Of course, this can be prevented by reducing the degree of sulfonation of the acid component (sulfonated polyetherketone), but the price to be paid is a somewhat lower conductivity (Fig. 7). In this respect, blends with PES, discussed above, behave more advantageously. For an initial ion exchange capacity of 1.39 meq./g the ion exchange capacity slowly decreases in water only for temperatures higher 90°C.

3. Polymers with immobilised heterocycles as proton solvents

Since the very high proton conductivity of hydrated polymers relies on the presence of liquid water as thermodynamically distinct phase in the hydrophilic domain [15,18], the maximum operation temperature is approximately given by the boiling point of water, i.e. 100°C at $p = 10^5$ Pa. It has been shown, however, that substitution of water by heterocycles, such as imidazole, pyrazole or benzimidazole leads to proton conductivities between 150 and 250°C which are comparable to the conductivities of hydrated polymers [31,32]. Indeed, such heterocycles form similar hydrogen bond networks to water, and the transport properties in the liquid state are similar to water for a given temperature relative to the melting point (e.g. for a mixture of benzimidazole with 10 m/o H₃PO₄ a conductivity of 5×10^{-2} S cm⁻¹ is observed at 200°C [32]). While such adducts are of high interest for applications in closed electrochemical cells, such as supercapacitors and electrochromic devices, the volatility of the heterocycles prevents them from being used in open electrochemical systems, such as

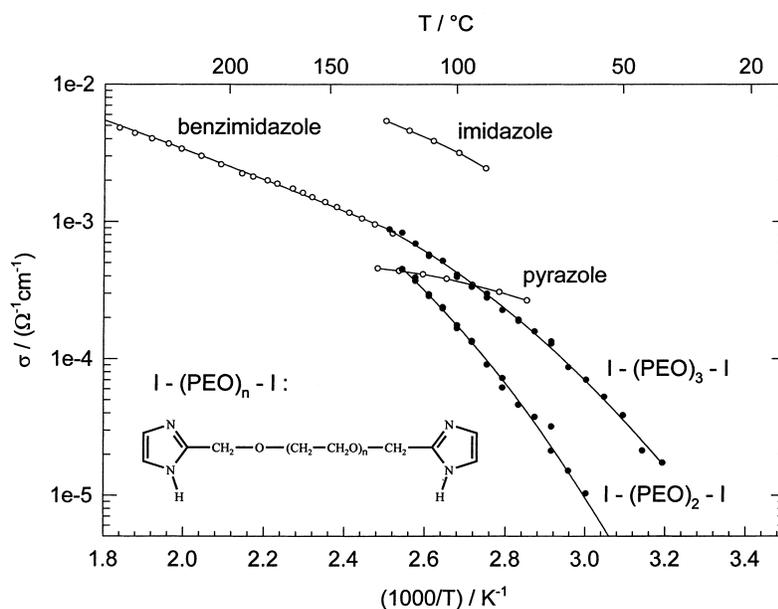


Fig. 8. Proton conductivity of pure monomeric heterocycles and oligomers terminated by imidazole [32,34].

fuel cells. In contrast to using water as the proton solvent, which is usually supplied to the membrane by humidifying the anode and cathode gases and is produced by the electrochemical reaction itself at the cathode, the use of heterocycles as the proton solvent requires the immobilisation of the solvent in the polymer membrane in such a way that high mobility of the protonic charge carriers is still guaranteed. While proton mobility in hydrated polymers has large contributions from the diffusion of hydrated protons [15,18], proton mobility in an environment of immobilised heterocycles must completely rely on structure diffusion (Grotthuss-type mechanism [24]) comprising proton transfer between heterocycles and solvent reorganisation. This is generally a very complex process requiring the thermally activated accessibility of quite different configurations, such as very short and elongated hydrogen bonds [33]. As a typical many-particle feature, such a situation is preferred in systems with high concentration of solvent molecules with minimised restrictions for the local degrees of freedom (compared to the pure liquid solvent).

As a first attempt, we have therefore, prepared oligomers consisting of a short polyethylenoxide segment terminated by imidazole groups [34]. Such oligomers are highly viscous oils which locally aggregate in such a way, that strong hydrogen bonds are formed between terminating groups of different oligomers. Like monomeric heterocycles [31,32], these oligomers show significant self-dissociation, i.e. formation of protonic charge carriers in the absence of an explicit acid, and a proton conductivity, which is only slightly lower than for the monomers (Fig. 8).

On the basis of these encouraging results, the effects of polymerisation of such oligomers, their grafting to inert polymeric networks and the effects of acid doping are currently under investigation.

4. Summary and conclusions

The clue to the understanding the different mechanical and transport properties of hydrated perfluorosulfonic polymers (here NAFION) and low-cost sulfonated polyaryls (here sulfonated polyether-

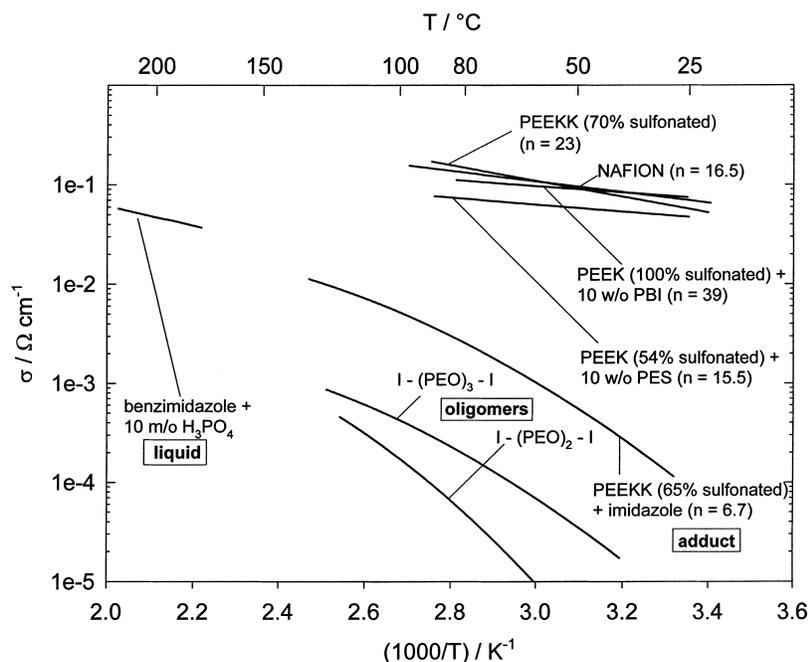


Fig. 9. Proton conductivity of different fully hydrated acidic polymers [15,18] (for ion exchange capacities see Table 1), and a liquid, an adduct, and an oligomer containing heterocycles as proton solvent [31,32,34].

ketones) appears to be differences in the pK_a of the sulfonic acid functional groups and of the microstructures. The less pronounced hydrophobic/hydrophilic separation of sulfonated polyetherketones compared to NAFION corresponds to narrower, less connected hydrophilic channels and to larger separations between the less acidic sulfonic acid functional groups. On one side, this leads to a disadvantageous swelling behaviour and a stronger decrease of water and proton transport coefficients with decreasing water content; on the other hand side, however, the hydrodynamic flow of water, i.e. electroosmotic drag and water permeation, is reduced compared to NAFION, which is an essential advantage, especially for DMFC applications.

Blending of sulfonated polyetherketones with inert polymers (here PES) or basic polymers (here PBI) significantly improves the swelling behaviour without reducing the high proton conductivity at high water contents (Fig. 9), blending with PES even yields flexibility in the dry state. Blending also further reduces the hydrophilic/hydrophobic separation and therefore, also hydrodynamic solvent transport (water and probably also methanol permeation). Therefore, polymers based on sulfonated polyetherketones are not only interesting low-cost alternative membrane materials for hydrogen PEM fuel cell applications, they may also help to reduce the problems associated with high water and methanol cross-over in DMFCs using aqueous solutions of methanol as a fuel.

A completely different approach for obtaining high proton conductivity at temperatures significantly higher than 100°C is based on heterocycles as proton solvent. Their transport properties are surprisingly close to these of water for a given temperature relative to the respective melting point (about 90°C for imidazole). High proton conductivities are easily achieved for liquid systems and adducts of acidic polymers and monomeric heterocycles (e.g. imidazole intercalated into a sulfonated polyetherketone) (Fig. 9).

While these conductivities still have large contributions from the mobility of solvated protons, e.g. imidazolium (vehicle mechanism [35]), the relatively high conductivity of pure oligomers such as I-(PEO)_n-I (see Fig. 9) indicates also the presence of structure diffusion which may be exploited in fully polymeric proton conducting systems with no volatile proton solvent operating at temperatures significantly

beyond 100°C, where methanol vapour may be used as a fuel in DMFCs.

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