Chapter 18

Design rules for the improvement of the performance of hydrocarbon-based membranes for proton exchange membrane fuel cells (PEMFC)

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1 REQUIREMENTS

All fuel cells require an electrolyte that is capable of selectively transporting an ionic species, but at the same time has no electronic conductivity and effectively separates the anode and cathode space in order to prevent direct reaction between fuel and oxidant. In the proton exchange membrane fuel cell (PEMFC) and the direct methanol fuel cell (DMFC), this electrolyte is a thin polymeric membrane made from a polyelectrolyte that contains acidic groups as a source of charge carriers to ensure sufficient proton conductivity.

The exact set of requirements for such proton-conducting membranes depends largely on the application the fuel cell is being designed for and the fuel to be used. Fuels are typically hydrogen for PEMFC and methanol for DMFC. This article focuses on PEMFC for automotive applications with hydrogen and air as fuel and oxidant.

Assuming that a fuel cell vehicle will have to deliver performance, range, cost-effectiveness, and comfort comparable to state-of-the-art vehicles with internal combustion engines (ICE), the most important factors for the fuel cell system are probably power, power density, durability, robustness, maintenance requirements, and cost, plus considerations concerning fuel storage capacity and the refueling process. The desire for low cost (including low maintenance cost) and high power density result in the demand for a most simple system, with as few components as possible (see System design for vehicle applications: GM/Opel, Volume 4). This has been interpreted to mean the ability of the system to run under a wide variety of ambient conditions, especially outside air temperature and humidity, without the need for extra systems to provide constant conditions. For automotive systems it can be concluded that this requires a fuel cell, and hence a membrane, that can operate more or less independent of the humidity of the outside air. Calculator calculations have shown that if the radiator of a fuel cell powered car is the same size as that of an ICE-driven car of comparable power (see System design for vehicle applications: GM/Opel, Volume 4), the fuel cell will have to operate for short time periods at a temperature of 120°C.

About 10 years ago, it was believed that Nafion® and similar poly(perfluorosulfonic acid) (PFSA) membranes are the best basis for commercial fuel cells, because they provide sufficient durability and performance. The main problems were seen in the price of the PFSA membranes, and, for automotive applications, in their inability to operate at temperatures around 120°C and low relative humidity. On the other hand, a projection of potential prices for PFSA membranes at increasing demand from car manufacturers by General Motors[1] indicated that the cost target is likely to be achieved, assuming mass production of fuel cell powered cars, despite the presently high prices of Nafion® and similar membranes.
At present, the performance of the membrane at low humidity appears to be the most critical factor and deserves the most attention in future membrane development. In order to simplify the fuel cell system, a membrane with a proton conductivity of no less than 0.1 $\text{S cm}^{-1}$ at relative humidities (RH) between 25 and 50% in the temperature range of 60–80°C is required (see System design for vehicle applications: GM/Opel, Volume 4). In addition, the expected drive cycle leads to occasional operation at higher temperatures up to 120°C, still at 25–50% relative humidity, but only for a maximum of 1% of the total operating time (see System design for vehicle applications: GM/Opel, Volume 4). The proton conductivity must be maintained under these conditions.

Another important issue in membrane development is durability. It has been found that operation at higher temperatures is less of a problem for many membranes than operation at low humidity (see Highly durable PFSA membranes: Factors influencing ionomer degradation, Volume 5). While long continuous operation of PEMFC with PFSA membranes such as Nafion® has been shown several years ago, this was usually done under constant operating conditions. Life time up to 50,000 h have been shown under ideal conditions, namely nearly constant current density operation, and under full humidification.[3] However, in a car the fuel cell is not going to operate under constant conditions for extended periods of time. Start-up and shut-down will be frequent, and power consumption will vary considerably during a drive cycle: for example, if a vehicle is waiting at a traffic light, only the power for the electronic systems may be required, while a few seconds later the full power will be drawn during acceleration. Hence, the quantity of heat and water produced by the fuel cell changes quickly leading to fluctuations of the relative humidity to which the membrane is exposed. Operation at low humidity appears to be the most demanding situation for a membrane with respect to chemical degradation. In addition, operation at low current density also leads to faster degradation of the proton-conducting membrane than that at high current density.[4]

Besides the problems that may occur when a fuel cell is running at low power, the other requirements for a fuel cell and its components for automotive applications differ significantly from those for other applications. In order to achieve a sufficient level of power and power density that is likely to be necessary for a vehicle that is accepted by the average customer, it was found that the membrane should be much thinner than the ca 175 $\mu\text{m}$ of Nafion 117®, which is still often cited as a reference in scientific publications. Switching to membranes with thicknesses in the range of 25 $\mu\text{m}$ and below revealed an unexpected instability of the polymer. It undergoes thinning (which is much more of a problem for thin membranes) and finally failure through chemical degradation, releasing fluoride, occurs.[5–10] The hydrofluoric acid released by fluorinated membranes not only limits the life time of the membrane but also causes corrosion problems in all metal components that are in contact with the water and exhaust gas produced in the fuel cell.[13] Recently, it was found that this chemical degradation can be prevented by the addition of a stabilizer[12] that reacts with any free radicals formed and hence disrupts the degradation reaction (see Highly durable PFSA membranes, Volume 5).

While the issue of chemical degradation and fluoride release can thus be solved, another critical issue is the behavior of the fuel cell and the membrane during operation without humidification of fuel and oxidant, and especially under conditions with fast cycling from wet to dry. Such conditions may occur when a vehicle is operated under dry ambient conditions with varying load levels: at low load, only low amounts of water are formed, and the membrane may dry out; at high load, the amounts of water formed will be sufficient to fully humidify the membrane. Thus, under these load-cycling conditions, the hygrothermal membrane contraction and expansion induced by the changes in membrane water content can result in significant mechanical stresses and, ultimately, in membrane rupture (see Mechanical durability characterization and modeling of ionomic membranes, Volume 5). In addition, hygrothermal membrane expansion inside a fuel cell stack may lead to increased local compressive forces (normal to the membrane), which can result in membrane damage via puncturing by the gas diffusion medium (see Conductivity, permeability, and ohmic shorting of ionomic membranes, Volume 5), which is typically a stiff, fibrous material (see Diffusion media materials and characterization, Volume 3). However, it is not clear to date how much swelling or dimensional change, respectively, is tolerable from the standpoint of durability or damaging of other components.

Still the most difficult problem appears to be the loss of performance of the fuel cell with decreasing humidity of hydrogen and air. This is related to the loss of proton conductivity on drying. It is observed for all membranes whose proton transport mechanism is based on the presence of water. For instance, Nafion® loses 90% of its proton conductivity at 80°C when the relative humidity of its environment decreases from 80 to 20%: the conductivity drops from 100 $\text{mS cm}^{-1}$ at 80% RH to below 10 $\text{mS cm}^{-1}$ at 20% RH. Hydrocarbon membranes typically show an even steeper drop of conductivity with decreasing humidity (see Hydrocarbon membranes, Volume 3). Figure 1 shows a comparison.

Assuming the necessity of at least some water within the membrane for proton transport, and an operation temperature below 100°C, which does allow the presence of water, it is reasonable to assume that the membranes with the best property profile will be those that “use” the water present most efficiently for proton transport. Such membranes will lose less proton conductivity than others on
decreasing relative humidity. They will also need less water for the same proton conductivity, allowing for less swelling in the presence of liquid water, and hence less problems with mechanical durability.

The following chapters present a series of guidelines for the improvement of the performance of proton-conducting membranes, especially hydrocarbon-based ones.

2 GUIDELINES

2.1 Guideline 1: microphase-separated block copolymers are preferred over random copolymers

Hydrogen/air fuel cells produce water, which will be present in the liquid state at temperatures below 100°C, if the fuel cell is operated at high load. Thus, the membrane will be in contact with liquid water under certain conditions. High water uptake and a large degree of swelling of the membrane are detrimental to the lifetime of the fuel cell, as described above (see Mechanical durability characterization and modeling of ionomeric membranes, Volume 5). Solubility of the membrane material in water at operating temperatures (up to 95°C) would of course be catastrophic. On the other hand, as long as the proton transport is based on the presence of water within the membrane and the charge carriers (protons or rather hydronium ions) in the membrane are created by hydrolytic dissociation of acidic groups, high proton conductivity requires a sufficient water content of the membrane (see First principles modeling of sulfonic acid based ionomer membranes, Volume 3). Increasing the number of acidic groups (ion exchange capacity (IEC)) increases the proton conductivity not only under fully hydrated conditions but also under dry conditions, because the membrane takes up and retains more water. At very high IEC values, the membrane materials become water soluble (see Perfluorinated membranes, Volume 3). Obviously, there is a conflict between the desire for high proton conductivity, which can be achieved by a high IEC of the membrane, and the need for low water uptake and swelling, which is necessary for durability.

Besides this, a high content of acidic (typically sulfonic acid) groups in a polymer tends to make it brittle in the dry state. It is obvious that brittleness in the dry state is a severe problem for a membrane that is supposed to go through many swelling–deswelling cycles, because it is likely to form cracks due to the cyclical stress associated with this.

Block copolymers in contrast to random copolymers (see Figure 2a) present an ideal way to work around these conflicts. The requirements of a high degree of sulfonation for high proton conductivity on one side and a low degree of sulfonation for good mechanical properties and low water uptake on the other side can be separated: highly sulfonated and unsulfonated segments can be combined in the block copolymer. Microphase separation, which is typical for block copolymers, creates a situation in which there are hydrophilic domains formed by aggregation of highly sulfonated chain segments and hydrophobic domains formed by aggregation of the nonsulfonated segments. The hydrophilic domains can serve as transport pathways for the protons, while the hydrophobic domains take care of the mechanical properties. Thus, the proton transport can occur through domains with a very high local concentration of acidic groups, a concentration that would make random copolymers water soluble. In block copolymers, the formation of the hydrophobic domains prevents water solubility. Therefore, much higher local acid concentrations (IEC values) can be utilized than that in conventional polymers. Figure 2 shows the general concept.

Figure 3(b) shows a comparison of the proton conductivities and their dependence on relative humidity for membranes from block copolymers and random copolymers of similar overall composition.

It is clear that the block copolymer membranes exhibit higher proton conductivity at comparable global IEC. Other publications have confirmed these findings.[18–22] At the same time, global water uptake is lower for our block copolymer membranes. The triblock Gen1 exhibited a water uptake of 50 wt% after the membrane was boiled for 2 h in water, whereas the weight of the random
Figure 2. Concept of block copolymers for fuel cell membranes. (a) Schematic drawings of random and block copolymers; the black sections depict the acid sites. (b) Different thermodynamic equilibrium morphologies, which are discussed for diblock polymers for the strong phase segregation regime; note that the equilibrium morphology amongst other things depends on the composition of the diblock. [Reproduced from Ref. [16]. © American Chemical Society, 1995.] (c) Block copolymers can in principle phase segregate into larger domains of the respective blocks; however, the obtainable morphology depends on the preparation conditions (this is discussed in more detail in guideline 2); a transition from a disordered to a lamellar morphology is shown. (d) Two morphologies for the same triblock copolymer polymaterials Gen 1 (see structure in Figure 3a) are shown being different in the order of orientation.

copolymer increased by more than 100 wt% under the same circumstances.

One can assume that most of the water will accumulate in the hydrophilic sulfonated domains rather than the hydrophobic nonsulfonated ones. Thus, the acidic hydrophilic domains, created by association of the acid-functionalized segments of the block copolymers, present proton transport “channels” in a hydrophobic matrix. This situation can be compared with the morphology of Nafion® and similar PFSA membranes, although the “channels” formed in block copolymer membranes are larger (of the order of 10–100 nm) than those discussed for Nafion® on a molecular level.[23]

Conclusions

- Block copolymer membranes can exhibit higher proton conductivity than random copolymer membranes of comparable IEC.
- Block copolymer membranes can exhibit lower water uptake.

2.2 Guideline 2: morphology control is essential

From the considerations described above, it is immediately clear that a bicontinuous morphology (see Figure 2b) can
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Figure 3. Comparison of block and random copolymers. (a) Chemical structures. Polymaterials' Gen 1 triblock (the IEC was determined by titration: 1.3 meq g\(^{-1}\); the molecular mass of the hydrophobic endblocks was approximately 20k and that of the sulfonated middleblock was approximately 27k) and a comparable random copolymer (determined IEC = 1.4 meq g\(^{-1}\)) and Hirano and coworkers' multiblock BPS-1 (IEC = 1.78 meq g\(^{-1}\); the composition of the multiblock was estimated by the synthesis data provided by the authors: the molecular mass of both the hydrophobic and sulfonated hydrophilic blocks was approximately 27k) and the comparable random copolymer RPS-1 (IEC = 1.73 meq g\(^{-1}\)); (b) in-plane conductivities dependent on the relative humidity of Polymaterials' membranes (\(T = 80^\circ\)C) and Hirano and coworkers’ membranes (this data was taken from Ref. [17]).
be expected to provide the best proton conductivity, since the transport channels in such a structure are not blocked by “dead ends”, i.e. hydrophobic matrix. An alternative is a relatively disordered morphology without long-range order and with many contacts between the hydrophilic domains (compare to left picture in Figure 2d).

Evidence for this is given by Kim and coworkers.[24] Membranes were cast from polystyrene-block-poly(ethylene-ran-butylene)-block-polystyrene (SEBS) triblock copolymers, which were selectively sulfonated only in the polystyrene segments. Depending on the casting solvents, a very well developed lamellar morphology, or a much more disordered morphology without long-range order could be achieved. The proton conductivity of the membrane with the disordered morphology is about 1 order of magnitude higher than that of the membrane with the highly ordered morphology, although both were cast from the exact same material. More evidence is given by Elabd et al.[22] They compare membranes from sulfonated polystyrene and sulfonated polystyrene-block-poly(isobutylene)-block-polystyrene (SIBS) triblock copolymers. There was no morphology observed for the sulfonated polystyrene membranes, and they had relatively low proton conductivities. On the other hand, clear microphase separation was observed in the block copolymer membranes, and these had much higher proton conductivities, even higher than Nafion® at high IEC values.

A similar observation can be made for triblock copolymers based on PAEKs, which were synthesized in our laboratories. As can be seen in Figure 4, membranes cast from the exact same polymer, but different solvents and/or treated differently exhibit different morphologies. As one could expect there is a strong correlation between the morphology and the proton conductivity. The lowest conductivity is observed for the morphology with isolated spherical hydrophilic domains. An ordered lamellar structure leads to an increase in conductivity by a factor of about 4.5, while a more disordered morphology increases the conductivity by a factor of about 6.5, owing to the larger number of interconnects between the hydrophilic domains in the disordered morphology.

**Conclusion**

- Disordered morphologies (or bicontinuous morphologies) with interconnecting ionic pathways are preferred over long-range-ordered morphologies.

### 2.3 Guideline 3: side chain sulfonation is preferable over main chain sulfonation

Nafion® consists of a perfluorocarbon backbone, to which fluorocarbon side chains are attached. These side chains carry a sulfonic acid group at their ends. It has been argued frequently in the literature that Nafion® owes its good proton conductivity at relatively low water uptake to its morphology.[25–27] This morphology is based on Nafion®’s molecular structure: the strongly polar sulfonic acid groups are immiscible with the nonpolar fluorocarbon backbone and tend to aggregate. This is clearly facilitated by their rather flexible attachment via side chains: the acidic groups can move rather independently of the polymer main chain or backbone. An illustration of a possible microstructure of Nafion® can be found in *Hydrocarbon membranes*, Volume 3.

Most hydrocarbon membranes, especially the fully aromatic ones, possess sulfonic acid groups (or acid groups in general), which are directly attached to the phenyl rings of the polymer backbone. These acidic groups cannot aggregate as freely as those of Nafion®, because for

![Figure 4. Morphologies and in-plane conductivities of sulfonated poly(arylene ether ketone) triblock copolymers (polymaterials Gen 1, see structure in Figure 3a). Transmission electron micrographs (TEM) and the corresponding in-plane conductivities are shown, which were obtained at 80°C and 51%RH for the same polymer using different membrane preparation conditions (in order to gain control over the drying process, the membranes were prepared by pouring the polymer solutions into Petri dishes. These were then covered with a lid in such a way that the solvent could evaporate through a small gap between the Petri dish and the lid and put in an oven at a specific temperature. This method leads to a very slow drying process). The spherical morphology (a) was obtained by using a solvent mixture of 40 vol% of dimethyl sulphoxide (DMSO) and 60 vol% of N,N-dimethylformamide (NMP) and a drying temperature of 120°C. Long-range order of lamellae (b) was obtained by using a solvent mixture of 80 vol% of DMSO and 20 vol% of NMP and a drying temperature of 120°C. The more disordered morphology of lamellae with a short-range order (c) was obtained by using a solvent mixture of 90 vol% of DMSO and 10 vol% of water and a drying temperature of 100°C.](image-url)
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A group attached in this way, a segment of the polymer backbone needs to move, and not just an independent side chain. Thus, aggregation can occur only under conditions where the whole polymer backbone is mobile enough. Also, there will always be a trade-off between the relaxed coil shape of the polymer backbone and a strained shape of the backbone, which is required to allow aggregation of the acidic groups. There is no doubt that this impedes aggregation of the acidic groups, and hence the formation of “proton transport channels” as discussed for Nafion®.

Clearly, attaching the acidic groups to the backbone via side chains can be expected to be beneficial. However, the chemical stability of the structures involved (hydrolytic stability, stability against oxidation, and reduction) should be taken into consideration in the interest of longevity of the membranes. A good example for the effect of the side chain on conductivity can be found in a paper by Rikukawa and Sanui.[28]

The conductivities of membranes from two polymers, which are built from very similar building blocks, are compared: a sulfonated PEEK and a sulfonated polypara-phenylene derivative (S-PPBP). They are almost isomers of each other, but for the additional ether bridge in the S-PEEK. In the S-PEEK, the sulfonic acid groups are attached to phenyl rings in the backbone, while in the S-PPBP, the sulfonic acid groups are attached to the phenoxybenzoyl side chain. As clearly seen in Figure 5(b), the side chain sulfonated polymer membranes exhibit a significantly higher proton conductivity throughout the whole range of humidity.

Further evidence for our hypothesis is given by Yin and coworkers.[29] They compare a polyimide that is sulfonated in the backbone with a polyimide that holds the sulfonic acids in side chains. Figure 6 clearly shows that the side chain sulfonated polyimide has a much higher conductivity for a given water uptake than the main chain sulfonated polyimide. This difference in conductivity becomes more pronounced the lower the water uptake. Only for a water uptake larger than 100 wt%, the conductivity curves of both materials coincide.

Another example of the effect of side chain sulfonation versus main chain sulfonation in hydrocarbon membranes can be seen from Figure 7. Here, microphase-separated PAEK block copolymers are compared, which were synthesized in our laboratories. They differ in the type of hydrophilic block: in one type, sulfonic acid groups are introduced into phenyl rings within the polymer backbone in conventional ways; in the other type, the sulfonic acid groups are part of an aromatic side chain (Figure 7a).

It is clear from Figure 7(b) that the main chain sulfonated polymers do exhibit significantly higher conductivities in the range of relative humidity studied here.

In addition, swelling can be reduced at comparable IEC values, when sulfonic acid groups are attached via side chains rather than directly to the main chain. The water uptake for our side chain multiblock copolymer at 80 °C in liquid water was 80 wt%, whereas the main chain copolymer already absorbed 160 wt% at 60 °C. The rationale behind this observation seems clear: decoupling the acidic groups from the motions of the main chain by attaching them to a side chain or spacer will allow the acidic groups to aggregate, dissociate, hydrate, etc., without or at least with less interference with the random coil shape of the main chain. The situation in water vapor is less clear. Whereas the side chain sulfonated polyimide...
Figure 6. Side chain versus main chain sulfonated polyimide membranes. (a) Structure of main chain sulfonated polyimide (left picture, the membrane had an IEC of 2.72 meq g$^{-1}$) and side chain sulfonated polyimide (right picture, the membrane had an IEC of 2.89 meq g$^{-1}$); (b) in-plane conductivity versus water uptake at 50 °C; and (c) water uptake versus relative humidity at 50 °C. The data shown in the plot are taken from Ref. [29].

(Figure 6c) seems to confirm our observations in liquid water at least for relative humidities below 90%RH, the sulfonated PPBP in comparison to the sulfonated PEEK exhibit the opposite trend (Figure 5c). However, the latter two materials although being structural isomers might not be directly comparable.

Conclusions

- Attachment of sulfonic acid groups via side chains can increase the proton conductivity, especially at lower relative humidity.
- Side chain sulfonation can also reduce water swelling at the same IEC values as compared to main chain sulfonation.

2.4 Guideline 4: in poly(arylene ether) polymers, thioether sulfone backbones exhibit higher proton conductivity than ether ketone backbones for sulfonated fuel cell membranes

It has been frequently reported that sulfonated poly(arylene thioether sulfone) membranes exhibit very high proton...
Figure 7. Comparison of main chain and side chain functionalized poly(arylene ether ketone) multiblock copolymers. (a) Chemical structures; both the main chain and the side chain sulfonated multiblock consisted of hydrophobic blocks with a molecular mass of approximately 5000 g mol\(^{-1}\); the molecular mass of the hydrophilic blocks of the main chain sulfonated multiblock was approximately 10000 g mol\(^{-1}\) whereas that of the side chain sulfonated multiblock was 12000 g mol\(^{-1}\); and (b) humidity-dependent in-plane proton conductivity of block copolymer membranes at 80°C. The degree of sulfonation was comparable for both membranes: side chain sulfonated multiblock copolymer, IEC = 1.6 meq g\(^{-1}\); main chain sulfonated multiblock copolymer, IEC = 1.7 meq g\(^{-1}\).

For example at 65°C and 85% RH these random copolymers achieve – depending on the exact degree of sulfonation – a conductivity of up to 420 mS cm\(^{-1}\).\(^{[33]}\) This is about three to four times the value Nafion\(^{®}\) reaches at the same conditions.

In comparison to other hydrocarbon membranes, e.g., like sulfonated PAEKs, poly(arylene thioether sulfone) not only have a higher conductivity at a comparable IEC level but also demonstrate a significantly lower dependence of the proton conductivity on relative humidity. This can be clearly seen in Figure 8.

The origin for this observation is not as clear at present. One hypothesis for an explanation is related to the formation of hydrogen bonds. Thioethers are less likely
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Figure 8. Comparison of the in-plane proton conductivity of multiblocks consisting of sulfonated poly(arylene thioether sulfone) (PATS) and poly(arylene ether ketone) PAEK hydrophobic blocks, respectively; (a) structure of the PATS multiblocks; molecular mass of the hydrophobic blocks was approximately 2000 g mol\(^{-1}\) and that of the hydrophilic sulfonated PATS blocks was approximately 3000 g mol\(^{-1}\) for the 2.1 meq g\(^{-1}\) membrane and 2000 g mol\(^{-1}\) for the 1.7 meq g\(^{-1}\) membrane; the structure of the main chain sulfonated PAEK multiblock can be seen in Figure 7(a) upper picture; and (b) conductivity versus relative humidity at 80\(^{\circ}\)C, the IEC of both membranes were determined by titration and are given in milliequivalent per gram.

As to the possible effect of ketone groups in comparison to sulfone groups, there is the possibility that at low humidity the keto group can be protonated, while this may not happen as easily with the sulfone group. It is known that PAEKs can be dissolved in sulfuric acid,\(^{[34]}\) which is attributed to partial protonation of the carbonyl groups. The sulfone group is more electron withdrawing, and hence may be less easy to protonate. Alternatively, it has been argued that the larger electron withdrawing effect of the sulfone group should increase the acidity of the sulfonic acid groups, if they are attached to those phenyl rings of the repeating unit that are bound directly to the sulfone linkage. However, this effect is not very large, since the sulfone and sulfonic acid groups are in meta-orientation toward each other, which causes the weakest interactions, and the sulfonic acid groups are ortho to an electron-rich ether linkage, which should weaken the effect further.

Whatever the reasons are, the sulfonated poly(arylene thioether sulfone)s do show remarkably good proton transport efficiency. This can be seen in a plot of proton conductivity versus the volume fraction of water of the membrane (Figure 9).

The plot in Figure 9 shows that different membranes need different amounts of water present to achieve the same proton conductivity. This can be interpreted as efficiency: some membranes make better use of the water present for the transport of the protons. Poly(perfluorosulfonic acid) membranes such as Nafion\(^{8}\) show the best efficiency. Only the sulfonate poly(arylene thioether sulfone) membranes come close. In addition, it can be seen that block copolymers have higher efficiency than random copolymers, and also that side chain sulfonation result in higher efficiency than main chain sulfonation.

It appears that the hydrophobicity of the polymer backbone does indeed have an effect on the proton conductivity. It is reasonable to speculate that this is connected to the
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Polymer materials triblocks with

Gen 2:

Hydrophobic endblocks

Hydrophilic middleblocks

Gen 3:

PATS-50

Figure 9. Water efficiency of various membranes. (a) Chemical structures of polymer materials Gen 2 (IEC = 1.1 meq g\(^{-1}\)) and Gen 3 (IEC = 1.0 meq g\(^{-1}\)) triblocks (composition of Gen 2 and Gen 3: hydrophobic endblocks: 20k; hydrophilic middleblock: 20k), the structure of Gen 1, IEC = 1.3 meq g\(^{-1}\) is illustrated in Figure 3(a), and the sulfonated random poly(arylene thioether sulfone) copolymer PATS-50 that was synthesized according to\(^{33}\) (IEC = 1.8 meq g\(^{-1}\)); (b) in-plane conductivities versus the volume fraction of water at 80°C, for comparison the curve of Nafion® 112 (IEC = 0.9 meq g\(^{-1}\)) was also plotted.
degree of interaction between the polymer chains and the water molecules, and possibly also the H$_2$O$^+$. The less the interaction is, the less likely are the water molecules to be near the polymer chains, and the more readily they are available near the sulfonic acid groups for dissociation, and in the end for proton transport.

Conclusions

- The more hydrophobic the polymer backbone, the more "efficient" the use of water and acid groups for proton transport.
- The less interaction between the polymer backbone and water (and possibly also H$_2$O$^+$), the higher the proton conductivity at given IEC.

2.5 Guideline 5: in block copolymers, choose the most hydrophobic hydrophobic block

This relates especially to block copolymers that are prepared by polycondensation procedures. This typically leads to broad molecular weight distributions, following the Schulz–Flory distribution rather than the Poisson distribution. As a result, there will be block copolymers that contain very short hydrophilic segments linked to long hydrophobic segments. Even though microphase separation takes place, these very short segments are probably not going to be able to leave the hydrophobic phase completely owing to restricted motion, which originates from their chemical link to the hydrophobic chain segments. As a consequence, there will always be a few hydrophilic segments, and hence acidic groups present in the hydrophobic domains.[35] These acid groups will bind some water, which is likely to add to the overall swelling of the membrane, but is not available for proton transport or acid dissociation in the hydrophilic phase. This will reduce the proton conductivity and the "water efficiency" of the membrane.

Our hypothesis therefore is that block copolymer membranes should be most efficient when their hydrophobic segments are as hydrophobic as possible and when the microphase separation is as complete as possible, only then the highest fraction of the absorbed water will be available in the hydrophilic domains for the dissociation of the acids and the actual proton transport.

Figure 10 shows a comparison of the conductivities of multiblock copolymer membranes with identical hydrophilic blocks but with different hydrophobic segments. If the assumption is appropriate that the hydrophobicity increases with increasing fluorine content then the illustrated trends seem to validate our hypothesis. First, the multiblocks with fluorinated hydrophobic blocks show a higher conductivity over almost the whole range of humidity. Especially at low humidities, where only small amounts of water are present, the conductivity increases significantly with increasing fluorine content of the hydrophobic blocks. It can be assumed that this trend was even more pronounced had the conductivity of the multiblock MB-150 been measured at 80°C. Second, it can be concluded from Figure 10 that the dependence of the proton conductivity becomes less pronounced with higher fluorine content or hydrophobicity of the hydrophobic blocks, respectively.

Conclusions

- Despite microphase separation and the assumption that proton transport occurs through hydrophilic channels, the hydrophobicity of the hydrophobic domains has an effect on the proton conductivity.
- Choose the most hydrophobic block.

2.6 Guideline 6: block copolymer morphology control can be used to make more mechanically robust membranes

It is critical that fuel cell membranes are mechanically and chemically durable over the range of conditions experienced during fuel cell operation. Fuel cells cannot operate effectively if even small amounts of gas are able to permeate the membrane through microscopic pinholes. Ultimately, fuel cells fail because such pinholes develop and propagate within the polymer membranes.

During operation, PEM fuel cells are subjected to temperatures ranging from subzero to 100°C as well as a variety of humidification levels including exposure to liquid water. As proton exchange membranes absorb water, they undergo significant volumetric swelling. Nafion® NR-111 (25 µm solution-cast) adsorbs 50 wt% of water at 100°C, and undergoes 10 and 15% linear expansion at 23 and 100°C, respectively.[38] Upon dehydration, membranes can shrink to smaller than their original size. For example, Nafion® shrinks by about 7 and 11% from its initial area upon dehydration after being soaked in water at 80 and 100°C, respectively.[39–41] These membranes will experience tensile, compressive, and shear stresses as their dimensions change in a constrained fuel cell architecture with fluctuations in temperature and humidity level. The membranes also experience other stresses during fuel cell operation. For example, the membranes are compressed between sheets of carbon-based diffusion media at pressures up to 3.5 MPa. As in other engineering materials, mechanical fatigue can reduce the membrane strength over time, leading to mechanical membrane degradation and reduced fuel cell durability. Further complicating matters, the glass transition temperature of PFSA acid membranes such as Nafion® occurs within fuel cell operating temperature range, 60−100°C.[38, 41, 42] Thus, the polymer experiences structural as well as dimensional changes during fuel cell
operation. Furthermore, PFSA membranes are susceptible to chemical attack by peroxide radicals, which subsequently impacts the mechanical integrity of the membrane.

There has been significant research recently on alternatives to PFSA membranes but most of this work has focused on membrane performance, particularly conductivity at high temperatures and low relative humidity. However, little attention has been given to the durability of these materials. A variety of randomly sulfonated hydrocarbon and partially fluorinated hydrocarbon membranes have been tested for mechanical durability. None of the hydrocarbon or partially fluorinated hydrocarbon polymer membranes lasted for more than 400 RH cycles (0–150% RH at 80 °C) before developing a crossover leak.

It is desirable to develop membrane materials that have higher glass transition temperatures than PFSA and that are stable to attack by radical species generated during fuel cell operation. Here we investigate the impact of block copolymer morphology on the mechanical durability of sulfonated poly(arylene ether) block copolymers. We also compare the relative impact of mechanical and chemical degradation on PFSA and sulfonated poly(arylene ether) block copolymer membranes.
An in situ test has been developed to study the mechanical durability of fuel cell membranes by cycling the humidity of the membrane in the absence of electric potential or reactive gases. Previously reported results show that the stresses imposed solely by cycling between wet and dry operating conditions can create membrane failure leading to gas crossover.\cite{42-44} In this study we subject membranes to cyclic stresses by intermittently flowing wet and dry inert gases over the membrane in a nonoperating fuel cell.\cite{86}

Polymaterials Gen 1 triblock copolymer (Figure 3a) membranes with two different morphologies shown in Figure 2(d) were tested for RH cycling durability. The progression of crossover leak as a function of the number of humidity cycles is shown in Figure 11. Failure in these tests is defined as 10 sccm crossover. The random copolymer membrane PATS-50 (see Figure 9a) failed very quickly, whereas the phase-segregated membranes with lamellar morphologies lasted longer. The membrane with highly oriented lamellae failed after 500 RH cycles and the membrane with a low degree of lamellar orientation ran for nearly 3000 RH cycles before crossover failure. Thus, the same morphological control that leads to higher proton conductivity (as described above) also leads to improved mechanical membrane durability.

While PFSA membranes are chemically stable, they are known to degrade in the fuel cell environment via peroxy-radical attack (see Catalyst coated composite membranes, Volume 3), and are strongly enhanced in the presence of trace iron contamination (see Mechanisms of membrane degradation, Volume 3). The mechanism is quite complicated, depending on ionomer structure, iron level, catalyst components, electrode design, relative humidity, temperature, and other factors. Fortunately, several research groups are focused on understanding this mechanism, and good progress is being made.\cite{45}

To evaluate the impact of chemical degradation on membrane mechanical failure, we have run our in situ 50 cm\(^2\) RH cycling test with reactive gases (H\(_2\) and air) and at a constant current density of 0.1 A cm\(^{-2}\). The results for a 25-\(\mu\)m Nafion\textsuperscript{®} 1100EW membrane (DuPont\textsuperscript{®} NR-211) and Polymaterials Gen 1 triblock (Figure 3a) with a low degree of lamellar orientation are shown in Table 1.

The NR-111 PFSA membrane ran for 4500 cycles in the inert RH cycling test, but when subject to RH cycling at 0.1 A cm\(^{-2}\), the NRE-211 developed a crossover failure after only 800 cycles. Thus, chemical degradation induced by fuel cell operation causes a 5× acceleration of membrane failure under humidity cycling conditions. This 5× acceleration of fuel cell operation of membrane failure under humidity cycling conditions has been reported for other nonstabilized PFSA membranes.\cite{43} The sulfonated poly(arylene ether) block copolymer membrane, however, failed the inert RH cycling test after 2900 RH cycles, but ran for 3800 RH cycles at 0.1 A cm\(^{-2}\). The sulfonated poly(arylene ether) membrane actually undergoes an increase in lifetime when exposed to an electric potential and fuel cell reactants, suggesting that chemical degradation does not play a significant role in membrane failure of these materials. A similar observation was recently published by Sethuraman and coworkers for the poly(arylene ether sulfone) random copolymer BPSH-35.\cite{46} The increase in lifetime under fuel cell operation can be attributed to the fact that the small amount of water generated at the cathode at 0.1 A cm\(^{-2}\) is sufficient to prevent the membrane from completely drying out at the 0%RH feed conditions, and thus resulting in a less severe RH cycles that for the inert RH cycling test. The hydrocarbon membrane actually outlives the nonchemically stabilized NR-111 PFSA membrane.

Postmortem analysis of the membrane after 3800 RH cycles at 0.1 A cm\(^{-2}\) shows that failure is due to mechanical stress (crack formation, see Figure 12) rather than due to chemical degradation. As can be seen in Figure 13, the infrared (IR) analysis of the block copolymer membrane

<table>
<thead>
<tr>
<th>MEA</th>
<th>Cycles to failure w/o load</th>
<th>Cycles to failure @ 0.1 A cm(^{-2})</th>
</tr>
</thead>
<tbody>
<tr>
<td>DuPont\textsuperscript{®} Nafion\textsuperscript{®} (NRE-211)</td>
<td>4500</td>
<td>800</td>
</tr>
<tr>
<td>Polymaterials Gen 1 triblock</td>
<td>2900</td>
<td>3800</td>
</tr>
</tbody>
</table>
Design rules for the development of hydrocarbon-based membranes for PEMFC

Figure 12. Failure of a hydrocarbon sulfonated poly(arylene ether) block copolymer membrane by mechanical crack formation after 3800 RH cycles at 0.1 A cm$^{-2}$.

Figure 13. IR spectra of the membrane from Figures 11 and 12 before and after accelerated aging. There is no significant change of the IR spectrum, especially not of the band at 1022 cm$^{-1}$, which can be assigned to the symmetric stretching of sulfonate group.[47]

before and after the test indicates no chemical degradation. In the same situation, unstabilized Nafion® fails by chemical degradation, as evidenced by a loss of thickness.

Conclusion

- Phase-separated block copolymers exhibit enhanced mechanical durability.
- Chemical degradation does not appear to be a problem of hydrocarbon membranes.

3 SUMMARY

Applying these guidelines, it has been possible to design a sulfonated hydrocarbon membrane that can meet the performance of PFSA membranes not only at full humidification but also down to 50%RH (Figure 8). At the same time, hydrocarbon membranes are more durable than unstabilized Nafion® in an accelerated aging test. Most significantly, in contrast to the expectations, hydrocarbon membranes do not fail due to chemical degradation. However, it still does have a disadvantage at humidities below 50%. Also, it fails faster than stabilized Nafion®. Nevertheless, we have no doubt that the guidelines described above can serve as a basis for further development of more durable and better performing membranes in the future.

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