

Acid Functionalized Poly(arylene ether)s for Proton-conducting Membranes*Chong Kyu Shin^{a,b}, Gerhard Maier^a, Günther G. Scherer^c*

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Fuel Cells are clean and efficient electrochemical devices that convert the chemical energy stored in a fuel with oxygen from air directly into usable electricity without using a conventional combustion process. Because of the great importance of proton conducting membranes in fuel cells for certain applications as mobile power generators, significant research efforts have been devoted to these membranes during the last 30 years. Among the proton conducting membranes, perfluorinated ionomers introduced by DuPont under the registered trademark Nafion[®] in 1966 have been the most generally accessible and widely used membranes due to their excellent properties in terms of thermal stability, chemical resistance, electro-chemical stability, etc. Concerning the morphology of the perfluorinated ionomers, it is widely accepted that ionic clusters in the form of spherical domains are formed in the water swollen Nafion[®] membrane separated from the hydrophobic matrix, interconnected by short narrow channels.

However, the relative high cost of these Nafion[®] membranes (about US\$ 780/m²) is an incentive to develop an alternative membrane based on hydrocarbons in order to produce materials being less expensive. Only a very limited number of polymer backbone types have a chance to withstand the extremely demanding conditions a fuel

cell membrane is exposed to. Aromatic polyethers are among the first choice for this application. Thus, poly(ether ketone)s and poly(ether sulfone)s were selected in the present work as polymer backbone structures and sulfonic acid groups were chosen as proton donating groups because of their relatively high acidity and the ease of introduction of these groups into monomers and polymers. The sulfonic acid groups were primarily introduced into the monomers, and then the sulfonated monomers were polymerized by adaptation of established procedures rather than directly into the polymer, which offered improved control of the position, number, and distribution of the sulfuric acid groups along the polymer backbone. However, thermal cross-linking of these sulfonated polymers resulted in extremely brittle membranes. Thus, this approach was no longer pursued but a novel route for synthesizing block copolymer ionomers was designed.

Block copolymer ionomers fully based on hydrocarbons were synthesized successfully by a two-stage process: first the hydrophobic block was prepared with the desired length, then the monomers for the hydrophilic block were added at the desired stoichiometry to adjust the length. Thus, each block copolymer ionomer consists of an alternating sequence of several hydrophobic and hydrophilic blocks. Also, desired block copolymer ionomers having different IEC were prepared successfully by varying the stoichiometry of the monomers. This approach provided not only a novel route for preparing polymer electrolytes comprising an alternating sequence of hydrophobic non-sulfonated and hydrophilic sulfonated blocks without any further sulfonation procedures of any precursor polymers and without any further crosslinking procedures of the corresponding sulfonated polymers, but also improved control over chemical structures

leading to good overall performance in terms of morphology, proton conductivity, mechanical properties, insolubility at an elevated temperature of water, etc.

The phase separation is critical for the concept of the block copolymer membranes, which was probed by scanning electron microscopy (SEM). Hydrophilic spheres, hydrophilic cylinders, lamellae phases, hydrophobic cylinders, and hydrophobic spheres are expected depending on the relative block volume fraction. Block copolymer membrane containing a volume fraction of approximately 33 % of the hydrophilic segments resulted in spherical domains rather than cylindrical ones. In an ideal system of diblock copolymers, this should result in cylindrical domains. However, in the multiblock copolymer system studied here and under the drying conditions used, phase separation may not reach equilibrium due to restricted moiety of the polymer chains. Because of the high reactivity of the sulfonyl groups, the temperatures during membrane casting and drying must be kept for below the glass transition temperatures. The multiblock structure of the chains limits mobility strongly, as long as one of the phases is below T_g . Thus, the morphology is highly "frozen" in a rather early stage of solidification during solvent removal after casting, and it is not in thermodynamic equilibrium.

The specific resistivity of these membranes was simultaneously dependant on the ion exchange capacity, the volume fraction of hydrophilic blocks, and the degree of sulfonation in the hydrophilic blocks. Specific resistivity decreased with increasing of the IECs and with increasing of the volume fraction of hydrophilic blocks in the same series. Membranes containing one sulfonic acid group per one phenyl ring in each

repeating unit of hydrophilic blocks showed lower specific resistivity than the same composition as membrane containing 1/2 sulfonic acid group per one phenyl ring, and membranes containing 1/3 sulfonic acid group per one phenyl ring in each repeating unit of hydrophilic blocks. This is due to the higher degree of sulfonation in the hydrophilic blocks resulting in higher conductivity.

The DMTA measurements of these membranes clearly showed the high T_g 's and good dimensional stability. The T_g 's taken as maximum or end point in the $\tan \delta$ curves in these measurements were in the range of 178-210 ($^{\circ}\text{C}$), depending on the exact structure of the repeating unit. The stress-strain measurements of these membranes exhibited high tensile and yield stress (up to 80 MPa and 88 MPa, respectively) with an elongation at break up to 290 %. These block copolymer membranes are insoluble in organic solvents as well as in DI water in their acid form.

Preliminary fuel cell tests showed good stability as well as the acceptable performance of the membrane during the operation compared to Nafion[®] membranes. Thus, membranes manufactured from these block copolymer ionomers are promising candidates for the application in PEMFCs.