

_Short Side Chain Ionomers
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Around the 1980s, Dow Chemical developed a new PFSA characterized by a short-side-chain (SSC) carrying the ionic functionality. Though the superior properties (higher crystallinity, higher glass transition temperature) of the SSC ionomer compared with existing (LSC) Nafion® and their possible implications for fuel cell (FC) application were soon recognized obtaining significant improvements in FC performance, Dow never brought this PFSA ionomer to commercial scale.

More recently Solvay introduced a simpler chemical route to the synthesis of the SSC monomer sulfonic precursor which allowed restarting development of SSC PFSA polymer, membranes and dispersions now commercially available under the tradename Aquivion®. Another PFSA ionomer recently developed by 3M has a side chain with length intermediate between Aquivion® and Nafion® and correspondingly intermediate properties.

PFSA ionomers are normally described as having micro-segregated structures, with an hydrophobic fluorinated portion well separated from the ionic domains constituted by the clustered ion-exchange groups. The mechanical consistency of ionomeric membranes is directly proportional to the level of crystallinity of the polymer present outside the ionic cluster structures, thus resulting quite evident the advantage of the SSC structure that shows higher crystallinity at a given equivalent weight (= given density of sulphonic groups) when compared to the LSC structures.

The SSC structures are frequently described to have lower gas crossover compared to the LSC ones, this could indicate a smaller ionic cluster dimension or a better packaging of the polymeric chains. This property is extremely appreciated in applications/operating conditions where gas crossover is perceived as a serious limitation, like for example water electrolysis when operated at high pressure or automotive condition where open circuit voltage operation are quite frequent.

On the other way around, the shorter length of the side chain may enable to the synthesis of extremely reduced EW ionomers (in the range of 600 g/eq) while keeping some residual crystallinity. In the LSC structure residual crystallinity is kept until EW decrease down to ~800 g/eq, that is to state the practical impossibility to have LSC membrane structures with lower EW (amorphous ionomers shows huge water swelling and inconsistent mechanical properties). Combining the very high ionic conductivity and the water affinity given by the low EW with the relatively limited water swelling given by the presence of residual crystallinity, the SSC structure enables to produce ionomers and membranes in the range of 600-800 g/eq with optimal properties. This is one of the reasons why low EW ionomers are of extreme importance when compared to the conductivity targets set forth by car manufacturers, especially when reactant humidification is very low (or absent), low EW PFSA are the state of the art material to keep high conductivity.

The second reason why SSC ionomers are appreciated by car manufacturer is the high glass transition temperature of this structure; even if different literature shows quite a range of values there is consensus that SSC structure enhances the FC operating temperature of around 40°C when compared with LSC one, well exceeding the long term target value of 120°C for the

automotive application (120°C means higher tolerance to pollutants for precious metal catalyst and smaller size of the car's radiator = lower system cost).

Another important characteristic of fuel cell membranes is their chemical stability in the highly aggressive environment of the fuel cell or electrolysis cell. Though Nafion® PFSA ionomers were originally selected due to their high chemical inertness, as demonstrated by lifetimes in excess of 57 000 hours, in recent years it became evident that the degradation mechanism of PFSA strongly depends from the operative conditions. Curtin mechanism (attach of the chain end groups via ·OH radicals) had been accepted, demonstrated equally active in SSC and LSC ionomers and being prevented by a process of chemical stabilization (=conversion of unstable end groups in more stable one at the level of ionomer precursor) of the polymer. On the other hand different studies (some of them focusing on the thermally or UV-assisted degradation) recognized the existence of weak ionomer parts, subject to degradation in correspondence of the side chain, evidencing a clear advantage in the stability of short, linear side chain structures (due to the absence of tertiary carbon in the side chain, present in Nafion like structures).

Short side chain PFSA ionomers are considered unique candidates for the promotion of fuel cell, especially for automotive application where the combination of high chemical inertness, high conductivity especially in dry environment and good mechanical consistency in high temperature operation find the best available compromise.