## Abstract

Proton exchange membranes (PEMs) are of great interest due to their application as solid electrolyte in fuel cells, because fuel cells are currently considered as one of the promising clean energy technologies for present and future energy challenges. In this regard, Dupont's Nafion<sup>®</sup> are the most commonly used materials because of their excellent oxidative and chemical stability along with high proton conductivity. However, deterioration in the conductivity and the mechanical strength at high temperature over 80 °C, and high preparation cost of Nafion<sup>®</sup> urge the necessity to develop alternative proton conducting polymers. As a common phenomenon in most hydrocarbon based PEMs, they exhibit poor phase separated morphology and electrochemical stability and bear a tradeoff between proton conductivity, and mechanical and dimensional stability. In this context, semifluorinated polymers are conceived as a middle approach to balance the advantages and disadvantages of hydrocarbon-based polymers and perfluoro-polymers.

In this research, three different series of semifluorinated sulfonated co-poly(ether sulfone)s (co-SPESs) were prepared using a trifluoromethyl (-CF<sub>3</sub>) substituted comonomer. As initial, the structure of -CF<sub>3</sub> substituted comonomer is optimised for high thermal stability and high mechanical strength through preparation of several new fluorinated polymers. Three different diphenol moieties e.g. (imido bishydroxy(IB), 4,4'isopropylidene diphenol (BPA) and 4,4'-hexafluoroisopropylidene diphenol (6FBPA) were used to systematically to vary the fluorine content and polarity of the co-SPESs. The trifluoro methyl groups are effective in improving the oxidation stability and the tensile properties of the copolymer membranes. They showed good solubility due to the synergetic effects of the pendant trifluoro methyl groups in the backbones, which disrupted the regularity of the molecular chains and hindered the dense chain stacking. Also, trifluoro methyl groups increased the hydrophobicity, and helped in lower water uptake and lower swelling and phase separated morphology. Increasing fluorine content resulted in improved ratio of conductivity to water uptake indicating better management of water in the facilitation of proton conductivity, whereas polar group incorporation helps in exclusion of water with moderate conductivity due to specific definite interaction among the various polymer moieties. An attempt is made to correlate the various PEM properties with chemical structure of co-SPES through the effect of sulfonation content, fluorine content, and cardo polar group.

*Keywords:* Fluorinated co-poly(arylene ether sulfone)s, Thermal properties, Mechanical properties, Oxidative stability, Proton conductivity