## Abstract

The research in developing new polymers for proton exchange membrane fuel cells (PEMFCs) is one of the most emerging research fields in the area of alternate energy sources in current days. This has gained immense acceptance in both mobile and stationary applications. A proton exchange membrane (PEM) is considered as an ionselective transport channel which selectively transfers protons from anode to cathode and itself acts as a barrier between the fuel gas and oxidant in high performance proton exchange membrane fuel cells (PEMFCs). Compared to other energy converting devices, PEMFCs are clean and eco-friendly as no toxic by product is generated during cell operation and also provide higher energy efficiency. At present, the commercially available state-of-the-art materials Nafion<sup>®</sup> and Flemion<sup>®</sup> are extensively used as PEM materials due to their excellent physical and chemical stability combined with high proton conductivity values. However, there are a few limitations of Nafion<sup>®</sup> like, high cost, high fuel crossover, low operation temperature ( $\leq 80 \circ C$ ) etc. which limit their utility for practical applications. In addition, these polymers lose membrane performance at high temperature and low humidity. All these factors stimulate and motivate researchers in developing alternative proton conducting polymer membranes with low cost and better overall performance.

In this context, semifluorinated sulfonated polytriazoles were chosen to be potential candidates for PEM primarily due to the ease of synthesis and higher thermalchemical stability. Different series of novel semifluorinated sulfonated co-polytriazoles were prepared and their various physical, chemical and PEM properties were systematically investigated. The principal objective of our present research was to introduce the flexible ether (-O-) linkages and bulky pendent trifluoromethyl  $(-CF_3)$ groups into the polytriazole copolymer backbone for the improvement of structural architecture and desired PEM properties. Hence, some of the semifluorinated monomers were chosen to achieve this. The C-F bond in the structure of the polymer imparts high thermal stability, good oxidative and hydrolytic stability, high tensile strength, and more significantly, distinct phase separated morphology which is essential for better water management and ion transport pathway with high proton conductivity. In addition, the bulky -CF<sub>3</sub> groups disrupt the inter-chain packing density and due to this reason the fractional free volume (FFV) of the polymers become enhanced which in turn increases the solubility and processability of the polymers. On the other hand, it was also planned to control the PEM properties of the polymers by varying the functionality and molecular weight of the preferred monomer units, thereby, controlling the overall ion exchange capacity of the polymers. Finally, we have correlated the various PEM properties with chemical structure, composition of the co-polytriazoles, the effect of sulfonation content, fluorine content and molecular design.

**Keywords:** Semifluorinated sulfonated co-polytriazoles, Thermal and mechanical properties, Water Uptake, Oxidative stability, Proton conductivity with phase separated morphology.