## Abstract

Development of proton exchange membrane fuel cell (PEMFC) to mitigate environmental pollution and to meet energy demand is one of the foremost growing research topics. PEMFCs have several advantages that includes lower functioning temperature and one of the highest power densities in comparison to other fuel cells. DuPont's Nafion<sup>®</sup> is the state-of-the-art proton exchange membrane (PEM) owing to its superior performance as well as high oxidative stability. Nevertheless, Nafion<sup>®</sup> costs very expensive due to perfluorinated structure as well as depletion in performance was observed at elevated temperature due to high fuel (H<sub>2</sub>, methanol) permeability. These deterioration in performance inspired to investigate for alternative PEMs with semifluorinated backbones and exhibiting enhanced physicochemical properties that includes thermal, chemical stability, mechanical properties alongside high proton conductivity.

Consequently, main objective of our present research was focused on to introduce different free radical scavenging moieties like 2,6-sterically hindered pyridine, 2,5sterically hindered thiophene as well as fluoro (-F) and trifluoromethyl (-CF<sub>3</sub>) in polymer main chains and to study the physicochemical impacts on PEM properties. Functionalities like -CF<sub>3</sub> and -F was proven to impart polymers enhanced thermal stability, mechanical properties in addition to oxidative stability. Fluorinated moieties like tetrafluorophenyl were also introduced in polymer backbones as building block. Presence of fluorinated moieties in polymer chains also resulted in exclusive phase segregated morphology which is essential for maintaining hydrated proton transport pathways throughout the membranes for higher PEMFC performance. Presence of flexible aryl ether groups and pendant groups like trifluoromethyl groups break apart close packing of polymer chains and increase solubility and mechanical properties. Effects of 2,6-hindered pyridine as a constituent part of hydrophobic segment and as a part of both hydrophobic and hydrophilic segments, whereas thiophene as part of hydrophobic segment were studied and protection of polymer chains through selective scavenging of free radicals were observed. We studied radical scavenging pertinency of ortho-substituted pyridine/thiophene moieties and their impact on other physicochemical properties through preparing several sets of PEMs. In conclusion, physicochemical properties of PEMs were thoroughly examined and comparatively studied with change in specific structural features to know how tuning in molecular design effects variation in proton conductivity, oxidative stability, mechanical property, thermal stability and other PEM properties.

**Keywords**: Sulfonated polytriazole, sterically hindered pyridine, 2,5-substituted thiophene, radical scavenging property, proton conductivity.