Abstract

Proton exchange membrane fuel cells (PEMFCs) have emerged as the most promising and in-demand renewable and sustainable energy sources amid an energy crisis and environmental issues. The most vital part of a PEMFC is the proton exchange membrane (PEM), which selectively allows protons to pass through while preventing crossover of fuel gases between the electrodes. Dupont perfluorosulfonic acid (PFSA)-based Nafion® membrane is considered the state-of-the-art PEM material owing to its excellent mechanical properties, high proton conductivity, and superior oxidative stability values. Despite this exceptional set of properties, it has a few shortcomings, such as high fuel gas permeability, a limited operating temperature (> 80 °C), high cost, and a negative environmental impact during fuel cell testing, which demand the design and development of alternative PEM materials for PEMFC applications. In this regard, a wide range of hydrocarbon- and fluorocarbon-based sulfonated PEM materials has attracted significant attention owing to their superior PEM properties.

Recently, sulfonate polytriazoles (SPTs) synthesized via the “Click” reaction have attracted special attention as an alternative PEM material owing to their simple synthetic process, high yields, functional diversity, and high mechanical stability. Although a few sets of fluorinated and fluorine-free SPTs have been studied as PEM materials, the primary concerns are their low oxidative stability, excessive water uptake, and inadequate proton conductivity. Consequently, radical scavenging phosphine oxide (P=O)- and pyridinyl-based SPTs anchored with sulfone (-SO_2-), thioether (-S-), and trifluoromethyl (-CF_3) groups are synthesized and fabricated for PEMFC applications. The presence of polar P=O, pyridine, and sulfone moieties, along with hydrophobic -CF_3 and -S- moieties, improved the solubility and dimensional stability of the SPTs through ionic and dipolar interactions. The fluorine-free phosphaphenanthrene- and thioether-based SPTs appended with the P=O moiety exhibited high dimensional and oxidative stability, owing to their radical-scavenging properties. The fluorinated P=O- and pyridinyl-based SPTs showed excellent oxidative stability and interconnected phase morphology. The phosphonic acid (-$PO(OH)_2$)- and pyridinyl-based SPTs demonstrated robust PEM properties and extremely high proton conductivity owing to the synergistic effect of the phosphonic and sulfonic acid groups.

Keywords: Click polymerization, Proton exchange membrane, Phosphine oxide, Pyridinyl, Oxidative stability, Proton conductivity, Sulfonated polytriazole.