Abstract

The proton exchange membrane (PEM) is considered the key component of a fuel cell. It is acting as a solid electrolyte for proton transfer and prevents fuel crossover between the cathode and anode. Fuel cells use environmentally friendly technology to provide pollution-free operation and excellent energy conversion efficiency. Nafion®, a perfluorosulfonated ionomer membrane with outstanding chemical and physical stability and strong proton conductivity, is now regarded as the state-of-the-art membrane for fuel cell applications. However, their use is limited due to the complicated synthetic technique, low glass transition temperature, restricted working temperature (>80 ^{o}C), and high fuel crossover. This instigated the researchers to look for alternative PEM material with better properties. In this regard, a variety of sulfonated polymer membranes with wide-ranging molecular designs had been inspected to cope with the deficiency of state-of-the-art materials.

Copper-induced azide-alkyne click polymerizations have been used to make sulfonated polytriazole-based PEM materials in recent years. However, the low chemical stability, poor water management, and inadequate mechanical stability are some major issues in sulfonated polytriazoles. In this context, the incorporation of phosphine oxide moieties into polytriazole backbones is an interesting approach to obtain a higher-quality polymer membrane with efficient proton transport, high thermal and mechanical stability, and adequate water retention with unique chemical resistance towards the peroxide attack. Accordingly, phosphorus-containing sulfonated polytriazole membranes with polar phosphine oxide moiety (–P=O), trifluoromethyl groups (–CF_3), bulky phosphophenanthrene system, and the pendant diphenylphosphine oxide unit have been designed and prepared. Their PEM properties were investigated systematically. The –P=O units, flexible ether linkages, and –CF_3 groups in the polytriazole backbone ascribed the general solubility of the polymers. The inclusion of fluorinated groups and phosphorus-based moieties in the sulfonated polytriazoles occasioned good phase-separated morphology, improved dimensional stability under hydrated conditions, and facilitated the generation of the interconnected proton transportation channels. The effect of the high content of phosphorus on PEM properties has also been studied by integrating a pendant diphenylphosphine oxide containing dialkyne monomer along with a triarylphosphine oxide-based diazide. The possible peroxide decomposition mechanisms of the triarylphosphine oxide systems were proposed. Additionally, the detailed microstructural alterations of the polytriazoles were elucidated as a function of DS. Finally, we correlated various PEM properties with molecular design, chemical functionality, phosphorus content, the proportion of sulfonated monomer, and ion exchange capacity.

Keywords: *Phosphorus-containing polymer, Click polymerization, Sulfonated polytriazole, Oxidative stability, Phosphine oxide, Proton conductivity, Phase-separated morphology.*