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## Review Article

# Sulfonated poly(arylene ether sulfone) nanocomposite electrolyte membrane for fuel cell applications: A review

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## ABSTRACT

Polymer electrolyte membrane (PEM) fuel cells are considered a promising technology for generating power with water as a byproduct. Recently, sulfonated poly(arylene ether sulfone) (SPAES) has emerged as a most suitable alternative for PEM applications because of its high proton conductivity, high CO tolerance, and low fuel crossover. However, the existing SPAES polymeric membrane materials have poor chemical reactivity, mechanical processability, and thermal usability. Thus, the effects of mixing inorganic nanomaterials with SPAES polymers on proton conductivity, power density, fuel crossover, thermal and chemical stability, and durability are discussed in this review. Further, the progress in preparation methods and fuel cell characteristics by the addition of silica, clay, heteropolyacids (HPA), and carbon nanotubes (CNTs) in polymer membrane materials for PEM applications is also discussed.

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**Abbreviations:** AFC, alkaline fuel cells; BPO, benzoyl peroxide; CMB, cross-linked miscible; CNT, carbon nanotube; DFBP, decafluorobiphenyl; DMFC, direct methanol fuel cell; HPA, heteropolyacid; HFB, hexafluorobenzene; IEC, ion exchange capacity; MCFC, molten carbonate fuel cell; MMT, modified montmorillonite; MWNT, multi-walled nanotube; OCV, open-circuit voltage; PAFC, phosphoric acid fuel cell; PBI, polybenzimidazole; PEM, polymer electrolyte membrane; PEMFC, proton exchange membrane fuel cell (polymer electrolyte); RH, relative humidity; SOFC, solid oxide fuel cell; SPAEBI, sulfonated poly(arylene ether benzimidazole); SPAES, sulfonated poly(arylene ether sulfone); SPAEK, sulfonated poly(aryl ether ketone); SPEEK, sulfonated poly(ether ketone); SPES, sulfonated poly(aryl ether sulfone); SPI, sulfonated polynaphthalimide; SWNT, single-walled nanotube; TEOS, tetraethyl orthosilicate; TEP, transparent exopolymer particle; TGA, thermogravimetric analysis.

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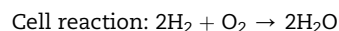
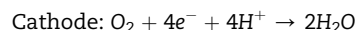
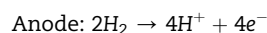
## Introduction

A fuel cell is a highly efficient electrochemical energy converter that directly converts the chemical energy stored in the fuel and oxidant into DC electricity with water and heat as the only byproducts. Fuel cell technology for electricity generation has received considerable attention in the 21st century because of the limited fossil fuel resources available on earth and the need for clean energy and because fuel cells generate electricity with no moving mechanical parts. However, the high cost required for the commercialization of fuel cells has limited their applications. The scientific community has focused on developing new materials and fabrication processes to improve the functionality of fuel cells and to optimize and simplify fuel cell components. Models of fuel cell systems have been used to reduce membrane cost and improve the performance, durability, and reliability of the cells, thereby enabling them to compete with the conventional combustion engine [1,2]. Classification of fuel cells is based on various factors such as operating conditions (e.g., temperature, pressure, and relative humidity), structure of fuel cell (e.g., scale of application and system), and nature of the polymer electrolyte in the fuel cell [3]. Based on the different electrolytes, fuel cells are categorized into five different types as follows:

- (i) PEMFCs: Proton exchange membrane fuel cells (polymer electrolyte)
- (ii) PAFCs: Phosphoric acid fuel cells (acidic solution)
- (iii) AFCs: Alkaline fuel cells (alkaline solution)
- (iv) SOFCs: Solid oxide fuel cells (ceramic ion-conducting electrolyte)
- (v) MCFCs: Molten carbonate fuel cells (molten carbonate salt electrolyte)

Comparatively, PEMFCs and direct methanol fuel cells (DMFCs) have more advantages than other types of fuel cells

in terms of portable electronics. They can also be used for smaller-scale products such as automotive mobile power generation and stationary equipment. The electrochemical reaction at the anode and cathode for power generation in a PEMFC involves hydrogen, methanol, and ethanol gases [4,5]. The reactions occurring in the PEMFC are as follows:



The hydrogen ions move from the anode to the cathode through the electrolyte membrane in fuel cells. As previously mentioned, the key component of PEMFCs is the polymer electrolyte membrane (PEM), which not only behaves as an electrolyte to transfer the protons from the anode to the cathode but also restricts the flow of electrons and fuel through the membrane [2]. The working principle of the fuel cell is schematically illustrated in Fig. 1.

In the mid 1960, DuPont Company developed a cation-exchange membrane called Nafion<sup>®</sup>, which has a polytetrafluoroethylene backbone and perfluorinated vinyl ether pendant side chains terminated by sulfonate ionic groups [7]. Currently, Nafion<sup>®</sup> is used commercially because of its high proton conductivity and good thermal and chemical strength. However, Nafion<sup>®</sup> also has some drawbacks such as high cost, low CO tolerance, and exhaustion of proton conductivity at higher operating temperatures. Therefore, researchers are trying to achieve a stable polymer electrolyte membrane with high proton conductivity, low fuel/water crossover, good thermal and chemical stability, good mechanical properties, and low cost of fabrication of the membrane electrolyte and assembly [8,9]. The main characteristics desired of PEMs are high

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