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Review Article

Silica-related membranes in fuel cell applications: An overview

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ABSTRACT

Silica is the most common inorganic filler used in fuel cells, especially for proton exchange membrane fuel cell and direct alcohol fuel cell applications. Silica has played an important role in improving the performance of fuel cells by enhancing their membrane properties. Recently, silica has been widely implemented in different types of membranes, such as fluorinated membranes (Nafion), sulfonated membranes (SPEEK, SPS, SPAES, SPI) and other organic polymer matrixes. The incorporation of silica into membrane matrices has improved the thermal stability, mechanical strength, water retention capacity and proton conductivity of the membrane. This review describes the interactions between silica and different types of polymer matrices in fuel cells and how they boost fuel cell performance. In addition, this review also discusses the current challenges of silica-related membrane-based fuel cells and predicts the future prospects of silica in membrane-based fuel cell applications.

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Introduction

Green technology helps to conserve the natural environment and resources while curbing the negative impacts from human involvement in the progress of the development of the country. Sustainable development is the main concern in green technology due to the continuous increase in energy demand with time. Due to the high risk of nuclear power plants and pollution-creating thermal power plants, alternative renewable energies are needed to overcome those problems [1]. The fuel cell is the most promising renewable energy source compared to solar and wind energy. It can provide a stable and constant energy output as long as fuel is supplied continuously. The proton-exchange-membrane fuel cell (PEMFC) and direct alcohol fuel cell (DAFC) are commonly used in portable electronic applications due to their high power density at low operating temperatures [2]. Apparently, organic-inorganic hybrid proton-exchange membranes (PEMs) are the main choices for current trends in membrane selection in proton exchange membrane fuel cell (PEMFC) and direct alcohol fuel cell (DAFC) applications. Incorporating inorganic materials into organic polymers can cause the membranes to perform better than the original membranes, which will (1) improve the thermal and dimensional stability of the membranes; (2) enhance the proton conductivity of the membranes and fuel cell performance; and (3) reduce methanol transport channel, which in turn will decrease the methanol permeability of the membranes [3].

Organic-inorganic hybrid membranes can be categorized into two major classes based on the type of the chemical bonds formed between the organic phase and inorganic phase. In Class I hybrid membranes, weak bonds such as hydrogen bonding, weak electrostatic interactions and van der Waals forces are formed between organic and inorganic components. In contrast, Class II hybrid membranes consist of strong covalent chemical bonds that chemically graft the organic and inorganic phases together [4].

Inorganic fillers such as silica, metal oxides (TiO_2 and ZrO_2), zirconium phosphate, inorganic nanotubes ($\text{Na}_2\text{Ti}_3\text{O}_7$) and compound inorganic-inorganic fillers such as silica doped with heteropolyacids (HPAs) are popular fillers used in PEM applications [5]. HPA is a class of inorganic proton-conducting material that has redox properties when in a hydrated state [6,7]. Embedding HPA in a filler will provide more proton-exchangeable sites, which in turn will increase the proton-transport capability of the membrane [7]. The presence of inorganic fillers in the membranes gives them greater potential to compete with the original unfilled membranes in terms of thermal and chemical stabilities at intermediate

temperature as they take on the characteristics of inorganic materials that are stable at high temperatures [8]. There are three categories of inorganic fillers, as follows: inert hygroscopic, proton-conducting only and hydrophilic with proton conductivity [9]. Inert hygroscopic fillers are used to reduce the fuel crossover and hold water. The second category includes fillers with a high elastic modulus as they promise high proton conductivity. The third category is a combination of the first and second categories, including fillers that have both hygroscopic and proton-conducting properties [10].

Among these inorganic fillers, silica tends to be the most promising filler for membrane-based fuel cells as it has a large water retention capacity and is able to hold water under high-temperature conditions. High water retention ability of silica has been used in self-humidifying PEMFC by Watanabe et al. [11]. In addition, the porosity of silica will be able to increase the efficiency of fuel utilization in the membrane as more fuel can be utilized during the reaction in the membrane. Arico et al. claimed that for DMFC, surface properties and acid-base properties of silica play a vital aspect in Nafion-based membranes in terms of water adsorption density and water uptake [12,13]. Until now, silica has been widely used as the filler or polymer matrix in the PEMFC and DAFC applications, as it shows improvements in the fuel cell performance compared to non-silica based membranes.

This review is mainly concerned with the study of the recent development of different types of silica-related membrane-based fuel cells. In addition, the challenges that are faced by silica-based membranes and the future developments of the use of silica in membranes for fuel cell applications are discussed at the end of this review.

Silica in different types of membranes

Many studies have specifically reported the effect of the addition of silica into different types of membranes, such as Nafion-based and non-Nafion-based membranes. Silica is well-known as a hygroscopic inorganic filler because it can absorb water into itself even at high temperatures and low RH conditions, which is beneficial to the proton conductivity of the membrane [10,14]. Silica based membranes has been investigated to work well at elevated operating temperature range and high temperature is favourable for better kinetics of methanol oxidation [15].

Nano-size silica particle ranging 1 nm–100 nm can be fitted into swelled Nafion pore. This enhanced the proton conductivity since silica nanoparticles can act as additional water cluster to increase proton conduction. Large silica particle size which exceeded the maximum swelled pore size of polymer

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