INTERNATIONAL JOURNAL OF HYDROGEN ENERGY 36 (2011) 3187–3205

Available at www.sciencedirect.com

ScienceDirect

journal homepage: www.elsevier.com/locate/he

Review

Overview on nanostructured membrane in fuel cell applications

H.S. Thiam [a], W.R.W. Daud [a], S.K. Kamarudin [a,b,*], A.B. Mohammad [a,b], A.A.H. Kadhum [a,b], K.S. Loh [a], E.H. Majlan [a]

[a] Fuel Cell Institute, Universiti Kebangsaan Malaysia, 43600 UKM Bangi, Selangor, Malaysia

[b] Department of Chemical and Process Engineering, Universiti Kebangsaan Malaysia, 43600 UKM Bangi, Selangor, Malaysia

ARTICLE INFO

Article history:
Received 14 July 2010
Received in revised form
8 November 2010
Accepted 16 November 2010
Available online 11 January 2011

Keywords:
Fuel cell
Nano-structure membrane
Nafion membrane
Proton conductivity
Permeability

ABSTRACT

Fuel cells are expected to soon become a source of low- to zero-emission power generation for applications in portable technologies and electric vehicles. Allowing development of high quality solid electrolytes and production of smaller fuel cells, significant progress has been made in the development of fuel cell membranes using nanotechnology. Nanostructures have been recognized as critical elements to improve the performance of fuel cell membranes. This paper provides an overview of research and development of nanostructured membranes for different fuel cell applications and focuses on improvement of fuel cell membranes by these nanostructures. Theoretical studies using molecular-scale modeling and simulation of fuel cell membranes have also been included in this review. Other issues regarding the technology limitations, research challenges and future trends are also reviewed.

1. Introduction

In the recent years, the issues of global warming, ozone layer depletion, ecological devastation topics have received great discussion because of their harmful effects to environment. One of the reasons of these issues is resulting from fossil fuel burning, which is the main energy source for human activity. Thus the need of the hour is about significant breakthroughs on alternative energy conversion devices with low pollution level for environment protection, low costs, and high efficiency of energy conversion such as fuel cell system [1]. Nowadays, nanotechnology is playing an important role in increasing the efficiency of current technology; it also has great potential to deliver environmental benefits and reduce the impact of energy production, storage and use [2]. Nanotechnology, with its unique capability to fabricate new structures at the atomic scale, resulting in materials and phenomena at the nanoscale, offers improvement of advanced materials and manufacturing techniques.

Fuel cells are electrochemical devices in which the chemical energy stored in fuel is converted directly to electrical currents through an electro-catalytic process; this technology has been the focus of new energy technology development because of its noteworthy features. Fuel cells are adaptable,

* *Corresponding author*. Fuel Cell Institute, Universiti Kebangsaan Malaysia, 43600 UKM Bangi, Selangor, Malaysia. Tel.: +60389216422; fax: +60389216148.

E-mail address: ctie@vlsi.eng.ukm.my (S.K. Kamarudin).

0360-3199/$ – see front matter

doi:10.1016/j.ijhydene.2010.11.062

have a high theoretical efficiency, do not need to recharge and unlike batteries, can produce electricity continuously as long as they are supplied with fuel. The main components of a fuel cell, together referred to as the membrane-electrode assembly (MEA), are an ion-conducting electrolyte, a cathode and an anode [3]. Fuel cell technologies can be classified in many ways, for example by the operating temperature, fuel type, oxidizer type, or charge carrier. Each type of fuel cell has its own advantages and disadvantages compared to the others; however, they represent a promising option to replace existing electricity production technologies when the Earth is subjected to severe environmental damage one day and oil has become scarce [4].

Over the past few years, fuel cells have demonstrated increased reliability and lower costs because of the incorporation of nanomaterials. Use of nanotechnology in the manufacturing process results in increased surface area and high aspect ratio, which creates in large power and energy densities, a long shelf life, and ease of miniaturization; these features are important for the development of a more powerful fuel cell for portable electronic devices [5,6]. Nanomaterials are also increasingly used in the production, purification and storage of hydrogen for use with fuel cells [7]. For example, carbon nanotubes [8] have been used in fuel cell applications, such as a carbon nanotube-based gas diffusion layer [9,10], carbon nanotube-supported electrocatalysts [11–14], nanocomposite bipolar plates consisting of multi-walled carbon nanotubes [15,16], and Nafion membranes modified by multi-wall carbon nanotubes [17].

This review covers the basic applications of nanostructured membranes in fuel cells, a technology that has received much attention, especially for use in Proton Electrolyte Membrane (PEM) fuel cells. The proton-conducting membrane, as the “heart of the fuel cell,” has to fulfill several demanding requirements simultaneously: high proton conductivity with electrical isolation; adequate mechanical, thermal and chemical stability; low fuel permeability; and enhanced water management characteristics over wide temperature and humidity ranges [18]. These requirements should furthermore be combined with a low manufacturing cost and easy start-up and processing. The most widely implemented electrolyte in PEM fuel cells is Nafion, which consists of a perfluorinated polymer [19–22]. However, there are a number of barriers that hamper commercialization of this common membrane and that must be overcome. Driven by the need for membranes with improved functionality, mechanical and chemical durability and cost effectiveness, substantial efforts have been made to develop alternative membranes that are composed of partially fluorinated and non-fluorinated ionomers [23].

2. Application of nanostructured membranes in fuel cells

2.1. *Proton electrolyte membrane fuel cell (PEMFC)*

PEMFCs are a clean and efficient energy system and are well suited to be a power source by virtue of their energy conversion efficiency, relatively simple design, environmentally friendly nature, and high energy and power densities [24,25]. Much effort has been made in to overcome the two big challenges for commercialization of PEMFCs, which are the high cost of the Pt/support electrodes [26,27] and the poor performance of the membrane under low humidity and elevated temperatures [22,28]. Introduction of nanosized materials in the fuel cell components has been used to overcome the latter issue.

Modification of conventional PEMFC polymers by the use of nanosized inorganic materials or through the development of alternative polymer systems is one of the contributions of nanotechnology in PEMFC membrane performance [29]. There are two main types of polymer electrolytes, perfluorinated polymer membranes and non-fluorinated membranes (e.g. hydrocarbon polymer, aromatic polymer), each of which performs respectably. The most commonly used perfluorinated polymer membrane in PEMFCs is Nafion, which has entitled with high conductivity and substantial chemical and electrochemical stability but is limited by its high cost, mechanical instability at high temperatures and water-dependent conductivity [30]. Nanocomposite membranes based on Nafion capable to improve its performance and to increase water retention at higher temperatures.

Addition of nanosized inorganic oxides to Nafion improved water uptake and enabled fuel cell operation at temperatures above 100 °C and conditions of approximately 70% relative humidity (RH) [31]. The composite membrane was prepared by the recasting method and consisted of nanosized inorganic additives, such as silicon oxide (SiO_2), titanium dioxide (TiO_2), tungsten oxide (WO_3) and SiO_2/phosphotungstic acid (PWA), along with the Nafion solution; all of these modified membranes delivered higher current density than the pure Nafion membrane. Meanwhile, Jalani et al. [29] prepared nanocomposite membranes with the *in situ* sol–gel method, in which the host PEM acts as a template that directs the particle growth and controls the morphology and size of the oxide particles in the PEM matrix. Nanosized inorganic additives were successfully incorporated into these membranes and were found to be homogeneously distributed, as seen in the scanning electron microscopy (SEM) image of the nanostructured membrane in Fig. 1. Good dispersion of fillers can introduce better behavior than the unfilled matrix, as shown in Fig. 2, which demonstrates the conductivity of the nanocomposite membrane at 120 °C, as a function of water vapor activity. Amjadi et al. [32] sought to improve the performance of a PEMFC at high operating temperatures by employing the sol–gel synthesis method to prepare membranes composed of TiO_2 nanoparticles and Nafion. An even distribution of fine TiO_2 particles in the Nafion matrix was achieved, and the morphology of the nanoparticles, which was affected by the doping level, as revealed by SEM, is shown in Fig. 3. Unfortunately, the proton transport blocking effect of TiO_2 by the Grotthuss mechanism and vehicular transport may contribute to a decrease in proton conductivity in spite of the increased water uptake.

Zhao et al. [33] proposed a somewhat different approach, in which a $MnO_2/SiO_2–SO_3H$ nanocomposite is dispersed into the Nafion membrane in an attempt to mitigate the degradation of membrane under fuel cell conditions. This nanocomposite can maintain fuel cell performance and improve membrane durability by decompose hydrogen peroxide and quench the free radicals effectively, especially under low