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Plasma techniques for the fabrication of polymer electrolyte membranes for fuel cells

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ABSTRACT

Polymer electrolyte membrane, as the indispensable component of a polymer electrolyte membrane fuel cell, serves a bi-function of conducting protons or hydroxide ions and separating fuels and oxidant, largely determining the performance of the corresponding polymer electrolyte membrane fuel cell. Therefore, the development of polymer electrolyte membranes that can efficiently conduct protons (for proton exchange membrane fuel cells) or hydroxide ions (for anion exchange membrane fuel cells) but block fuel permeation through membranes is a promising way to improve the electrochemical performance of polymer electrolyte membrane fuel cells. The plasma technique has shown great advantages in this area. It has been reported that the polymer electrolyte membranes modified or directly synthesized by the plasma technique exhibit superior properties, such as higher ion conductivity, low fuel permeability, high thermal and chemical stability, which provide them with great potentials as promising polymer electrolyte membranes for polymer electrolyte membrane fuel cell applications. However, the plasma polymerization is a very complicated process which involves the degradation of monomers and the formation of polymers. Therefore, the conditions used for the membrane modification and preparation must be well controlled to obtain membranes with desirable properties. This review paper is concerned with applications of the plasma technique in the preparation of polymer electrolyte membranes for uses in polymer electrolyte membrane fuel cells. The various plasma techniques that have been used for the modification and the preparation of polymer electrolyte membranes are reviewed and their associated advantages and disadvantages are discussed.

Contents

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1. Introduction

The ever-increasing global energy consumption due to the continued growth in world population poses serious challenges to the sustainability of natural energy resources [1–5]. This, along with the severe environmental impacts from uses of the traditional fossil-fuel-based energy, has stimulated worldwide efforts to exploit alternative clean sources of energy [6–9]. Among various alternative sources of energy reported to date, polymer electrolyte membrane fuel cells (PEMFCs), which mainly consist of a cathode, an anode and a polymer electrolyte membrane (PEM) with the configuration shown schematically in Fig. 1, have received particular attention [10–12]. Compared with other sources of energy, the distinguishing features of PEMFCs include simple and modular designs, high energy density and energy conversion efficiency, minimal environmental pollution, etc., which make them particularly competitive as energy sources suitable for transport as well as for stationary and portable applications [6,11–21]. Indeed, PEMFCs have been considered as one of the most promising energy sources to alleviate the ever-growing pressure or even solve the problems from energy crisis [12,22–32].

As named, PEMFC is an electrochemical apparatus which turns the chemical energy stored in fuels, such as hydrogen, methanol, ethanol, formic acid, etc., into electric energy without combustion [6,8–10,14,15,25,33–38]. A typical PEMFC at work involves the oxidation of fuels at the anode with the simultaneous release of electrons and protons [26,39–46]. The released electrons then move through external circuit towards the cathode, producing the electrical current, while the protons migrate through the PEM, facilitating the reduction of oxygen, as schematically illustrated in Fig. 1 [26,39–42]. Since the migration rate of protons from the anode to cathode greatly depends on the proton conductivity of the PEM, the development of PEM with enhanced proton conductivity is of great significance in improving the overall performance of PEMFCs [23,41,47–52]. Indeed, except for the conduction of protons, PEM also plays a function of separating fuels and oxidant (usually oxygen), preventing the occurrence of the fuel oxidation and the reduction of oxygen at the same electrode and the possible poisoning of the cathode by the fuels which could lead to the reduction of the utilization of fuels and the overall performance of PEMFCs [11,22,51,53–56]. Therefore, for an ideal PEM, it is generally required to efficiently conduct protons but block the permeation of fuels through the membrane [12,13,16,18,52,57–64].

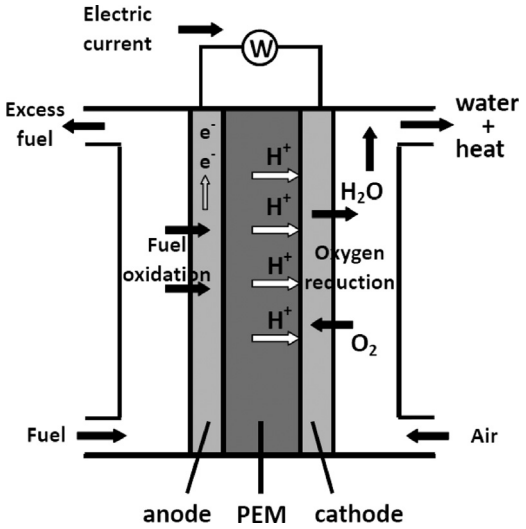

Fig. 1. Schematic configuration of a typical PEMFC.

A typical PEM is made from ionomers containing both electrically neutral units and a fraction of ionized units covalently bonded to the polymer backbone as pendant moieties [23,65,66]. Currently, the most widely used PEMs are sulfonated tetrafluoroethylene based fluoropolymer (commonly referred to as Nafion), which was first reported in the late 1960s by Walther Grot of DuPont [67]. Although these Nafion-based membranes are reported to have significantly high proton conductivity due to their high concentrations of proton exchange groups ($-SO_3H$), their inherent disadvantages such as high cost, high fuel permeability through the membranes, and low activity and poor durability of electrocatalysts, have greatly limited their widespread uses in PEMFCs, which have also been considered as the main source of failure for their commercialization [23,47,57,65]. Great efforts have therefore been devoted to the development of techniques that can modify PEMs or prepare new PEMs to meet the requirements of high proton conductivity, low fuel permeability, low cost, and high chemical and mechanical stability [10–12,23,66,68–72]. Recent advances in the PEM technology have demonstrated great promises of using the plasma technique in this area [13,16,17,73–81].

The application of the plasma technique in the fabrication of PEMs mainly makes use of a plasma polymerization initiated by a plasma discharge to modify or prepare PEMs [71,73,74,76,79,82–105]. The application of the plasma technique for the synthesis of polymers can be traced back to 1870s [106], however these polymers were initially thought of as undesirable by-products associated with electric discharge. Therefore, little attention has been paid to their properties. The usefulness of these plasma polymers was realized until to 1960, when they were found to be able to form flawless thin polymeric coatings on metals [107]. Indeed, the chemical composition and structure of these films could be largely changed by simply selecting the monomer type and the plasma discharge conditions [108–110]. Since the plasma technique can be applied to activate the upper molecular layers on the polymer surface, it enables the tailored surface of membranes with various chemical functionalities, which alters wettability, adhesivity and biocompatibility of the polymers without affecting their desirable bulk properties [22,107,111–114]. Much work has demonstrated that the plasma modification is useful and effective method to prepare high performance separation membranes, such as ultrafiltration, nanofiltration, reverse osmosis and gas separation membranes [22,53,106,111–118]. In addition, the plasma polymerization provides a more versatile technique for the fabrication of polymer membranes with desirable physico-chemical properties. The variation of monomers and its functional groups and the selection of reaction conditions of plasma polymerization can be used to tailor the properties of membranes for the specific applications [67,96,119–125]. It has been demonstrated that the plasma synthesized ion exchange membranes can be widely utilized as active separators in various electrically driven processes such as electro-dialysis for desalting brackish waters, reconcentrating brine from seawater and production of table salt [126–132]. In general, the films formed from this technique are highly branched and highly cross-linked, and well adhere to solid surfaces, which provide them with wide range applications [13,16,17,80,81,83,87,90,97,123,133–138]. The report on the fabrication of PEMs by the plasma technique was