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Functional fluoropolymers for fuel cell membranes

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Abstract

Various routes to synthesize functional fluoropolymers used in membranes for fuel cell applications are presented. They can be separated into three main families of alternatives. The first concerns the direct radical copolymerization of fluoroalkenes with fluorinated functional monomers. The latter are either fluorinated vinyl ethers, α,β,β-trifluorostyrenes or trifluorovinyl oxy aromatic monomers bearing sulfonic or phosphonic acids. The resulting membranes are well-known: Nafion®, Flemion®, Hyflon®, Dow®, Aciplex® or BAM3G®. The second route deals with the chemical modification of hydrogenated polymers (e.g. polyparaphenylenes) with fluorinated sulfonic acid synthons. The third alternative concerns the synthesis of FP-*g*-poly(M) graft copolymers where FP and M stand for fluoropolymer and monomer, respectively, obtained by activation (e.g. irradiation arising from electrons, γ-rays, or ozone) of FP polymers followed by grafting of M monomers. The most used M monomer is styrene, and a further step of sulfonation on FP-*g*-PS leads to FP-*g*-PS sulfonic acid graft copolymers. Other processes such as multilayer membranes or the introduction of fillers to prepare organic/inorganic or 'composite membranes' are reported. The electrochemical properties (ionic exchange capacity, conductivity, swelling-rate or water uptake) of membranes produced from fluoropolymers bearing sulfonic, carboxylic or phosphonic acid are presented and discussed.

Keywords: Fluoropolymers; Perfluorinated sulfonic acid membrane; Direct methanol fuel cell; Copolymerization; Chemical modification; Conductivity; Membranes; PEMFC

Contents

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1. Introduction

Nowadays, much of the production of energy is mainly linked to nuclear generation or the combustion of fossil fuels. These sources are, however, not environmental friendly, since they produce nuclear wastes or carbon monoxide and carbon dioxide. Among cleaner sources of energy arising, for instance, from wind, water, sun and others, a growing interest comes from fuel cells. This process utilizes an electrochemical device, which efficiently converts the chemical energy of a fuel (hydrogen, methanol, ethanol, ethylene glycol, natural gas, etc.) in a reaction with oxygen (from air for example) into electricity, heat and water. It operates like batteries, and is similar in characteristics and components. Several types of fuel cells exist [1–4], normally classified according to the type of electrolyte used, e.g. Solid Oxide Fuel Cell (SOFC), Molten Carbonate Fuel Cell (MCFC), Phosphoric Acid Fuel Cells (PAFC) and the Proton Exchangeable Membrane Fuel Cell (PEMFC). The operating temperature of the fuel cells is connected to the electrolyte used [1].

The development of PEMFC, also called solid polymer fuel cell, has been strongly related to improvements in performance of the polymer electrolyte membrane. The use of an ion-exchange membrane as electrolyte was first suggested by Grubb in 1957, and the first fuel cell system based on a sulfonated polystyrene electrolyte was developed by General Electrical in the 1960s for NASA for application as an on-board power source in the Gemini space program. It was successfully developed using a great amount of noble metal loading per cm^2 of electrode, although the polystyrene sulfonate membrane was not electrochemically stable and the cell exhibited limited power density (less than 50 mW/cm^2).

Fuel cells [1–4] have been involved in the production of stationary electrical energy and as energy sources in fields such as transportation, space, telecommunications, micro combined heat and power (CHP) generators or portable electronic systems (portables, cellular phones), domotics (coproduction of electrical energy and heat, auxiliaries of power (APU) for automotives (board-computer, electrical commands, air conditioning), and computer security. For application in these systems, it is essential that fuel cells exhibit similar performance and comparable cost to thermal engines.

Basically, a polymer electrolyte membrane fuel cell converts hydrogen and oxygen electrochemically into electrical power, heat and water. The electrochemical reaction takes place in the MEA. It typically consists of an ion-conducting polymer membrane sandwiched between the anode and cathode, each