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Review

A review of radiation-grafted polymer electrolyte membranes for alkaline polymer electrolyte membrane fuel cells

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HIGHLIGHTS

- A comprehensive reviews on radiation-grafted alkaline membranes (RGAMs).
- Alkaline polymer electrolyte fuel cells.
- RGAM synthesis/fabrication/characterization, membrane material selection, and theoretical approaches.
- Alkaline polymer electrolyte fuel cells.
- RGAM challenges and possible research directions.

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ABSTRACT

The past two decades have witnessed many efforts to develop radiation-grafted alkaline membranes for alkaline PEM fuel cell applications, as such membranes have certain advantages over other kinds of alkaline membranes, including well-controlled composition, functionality, and other promising properties. To facilitate research and development in this area, the present paper reviews radiation-grafted alkaline membranes. We examine their synthesis/fabrication/characterization, membrane material selection, and theoretical approaches for fundamental understanding. We also present detailed examinations of their application in fuel cell in terms of the working principles of the radiation grafting process, the fabrication of MEAs using radiation-grafted membranes, the membranes' corresponding performance in alkaline PEM fuel cells, as well as performance optimization. The paper also summarizes the challenges and mitigation strategies for radiation-grafted alkaline membranes and their application in PEM fuel cells, presenting an overall picture of the technology as it presently stands.

1. Introduction

Fuel cells, particularly polymer electrolyte membrane (PEM) fuel cells, are considered one of the most promising energy technologies due to their high energy efficiency, high energy/power densities, and low/zero emissions, as well as their wide application potential in the areas of portable, stationary, and automotive powers. However there are some major challenges still hinder their commercialization: insufficient durability and high cost. These factors are mainly due to two major components—the electrocatalyst and the polymer electrolyte membrane (PEM). For alkaline PEM fuel cells, the dominant limiting factor is the PEM, whereas for acid PEM fuel cells it is the electrocatalyst. In this article, the focus will be alkaline PEM fuel cells. Thus, the PEM—in particular, radiation-grafted PEMs—will be reviewed in terms of current research and development on their synthesis, characterization, performance validation, and application.

1.1. Overview of alkaline PEM fuel cells

In general, PEM fuel cells operated at low temperatures (normally < 90 °C) can be classified into two categories, according to the PEM they use: alkaline and acidic [1–7]. The membranes used in alkaline PEM fuel cells conduct hydroxide ions (OH^-), while those in acidic PEM fuel cells conduct protons (H^+) [8–15].

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Recently, alkaline PEM fuel cells have garnered great interest because several potential advantages over acidic PEM fuel cells have also been recognized, such as: a faster oxygen reduction reaction, which allows the use of cost-effective, non-Pt-based catalysts, including nickel- and silver-based materials [16–19]; a less corrosive environment allowing inexpensive component materials to be used [20]; decreased fuel crossover rates [21–23] allowing the possibility of using low-cost membranes [24–28]; the improved water management because the electro-osmotic drag transports water away from the cathode; the reduced alcohol "crossover" problem because OH^- anions move across the membrane as opposed to H^+ ions in an acidic membrane [29]; as well as the mitigated CO poisoning. In addition, alkaline PEM fuel cells can use many different fuels such as H_2, CH_3OH, CH_3CH_2OH, $CH_3CHOHCH_3$, $(CH_3OH)_2$, $NaBH_4$,, although hydrogen and methanol are still considered the two major ones.

Although alkaline PEM fuel cells have several advantages over their acidic counterparts, several challenges still remain: (1) insufficient membrane ionic conductivity; (2) high membrane resistance leading to low fuel cell performance; (3) lower mechanical and chemical stability of the membrane; (4) CO_2 poisoning; and (5) water-related issues. It can be seen that all of these challenges are more or less related to the PEM membrane. But the membrane is one of the necessary and performance-determining components in fuel cells because it is a carrier for ions and a barrier to gases and electrons. Hence, synthesizing membranes to improve OH^- conductivity and mechanical/thermal/chemical stability has become the central focus in alkaline PEM fuel cell development.

Although various efforts have been made to prepare high-performance membranes [30], there is still no significant progress which has been made. In recent years, a physical/chemical modification method using simultaneous irradiation to make alkaline PEM fuel cell membranes, called the radiation grafted membranes, has been developed [31–36], and the resulting membranes have promising properties and are cost-effective for use [37].

1.2. Overview of radiation-grafted PEM fuel cell membranes

In general, the process of radiation-induced grafting can be summarized in two steps: (1) creating active sites in the pre-existing polymer using physical/chemical techniques; and (2) initiating a polymerization reaction with a monomer according to an expected requirement. Depending on the chemical nature of the monomer, membranes with desired properties can be fabricated through this grafting process. Moreover, if the monomer possesses ionic groups, the grafted membrane acquires an ionic character with only limited influence from its inherent characteristics. The grafting process can be controlled to yield desirable architectures.

Many types of polymers can be used for the base matrix when synthesizing alkaline fuel cell membranes. The functionalization of these base polymers by radiation grafting with appropriate monomers has been demonstrated to be effective and feasible in developing alkaline membranes. During radiation grafting, the ionic nature, water absorption, and conductivity of the membrane can be changed, resulting in high-performing membranes [38–44]. In the grafting reaction, some cationic groups—such as ammonium, phosphonium, sulfonium, pyridinium, guanidinium, and imidazolium (see Fig. 1)—can be created within the entire membrane [45]. To uniformly distribute these functional groups throughout the whole membrane, the membrane bulk must be activated. In this case, high-energy radiation is necessary, as it can penetrate and induce the ionization of the entire polymer matrix. Various types of high-energy radiation, such as X-rays, gamma rays, beta particles, electrons, UV, as well as plasma, are often utilized to graft functional monomers into polymer films via copolymerization [2,46]. In the development of alkaline PEM fuel cell membranes, radiation-grafting methods have shown significant advantages in terms of reducing both cost and environmental pollution.

1.3. Advantages and remaining issues of radiation-grafted alkaline PEM fuel cell membranes

The attractiveness of radiation grafting method lies in its versatility: the available base polymers and graft monomers are virtually unlimited, one can accurately tailor and tune membrane composition by adjusting the process parameters, and it is easy to combine the desired properties in the polymer backbone and graft components. For fuel cell applications, low-cost raw materials for the base polymers and graft monomers can be selected, yielding cost-competitive ion-exchange membranes.

Besides the above, radiation-grafting methods also have other advantages:

(1) *Uniformly distributed reaction sites created within the bulk membrane.* The radiant energy can effectively penetrates the polymer bulk and thoroughly activates the matrix, so the reaction progresses to completion and the grafting efficiency is enhanced [31,34,36]. Furthermore, the membrane non-selectively absorbs the ionizing radiation, so the grafting reaction is more extensive. In addition, the reaction can be controlled by adjusting radiation power, radiation time, dose, monomer concentration and so on; consequently, the velocity, ratio, and depth of grafting can easily be controlled to meet actual needs;
(2) *Simple and effective.* The radiation-grafting method is simple and effective, and the reaction can be completed at room temperature or even at low temperatures, unlike chemical polymerization with catalysts and initiators [47];
(3) *Cost-effective.* Radiation grafting is initiated by rays, so in many instances initiators and catalysts can be omitted, further reducing the cost and yielding a purer and cleaner grafted copolymer [48];
(4) *Fewer requirements in terms of base polymer materials and shape/structure.* The radiation-grafting process can be carried out on a base polymer irrespective of its shape or form. This circumvents the difficulty of shaping a grafted polymer bulk into a thin foil [49,50].

Despite considerable progress in the development of radiation-grafted membranes, several aspects require further attention, including: (1) mechanical/thermal/chemical stability; (2) chemical and physical interactions between the membrane base reaction sites and the monomers; (3) chemical incompatibility between the radiation-grafted membrane and the ionomer in the catalyst layer; (4) scale-up and the costs of production; (5) optimization of the structures and morphologies of radiation-grafted membranes with respect to their performance (i.e., conductivity and stability); (6) tool and test protocol development for validating conductivity and stability in real fuel cell tests; and (7) fundamental understanding of the ionic conductive mechanisms and their correlation with fuel cell performance.

The literature on radiation-grafted membranes comprises many publications, including several review articles and book chapters, but nothing specifically focused on their application as fuel cell membranes, particularly for alkaline PEM fuel cells [2,14,15,30,48–64]. A comprehensive review that surveys the most recent progress—with a focus on the preparation of anionic exchange membranes by radiation-induced graft copolymerization using different monomers on various polymer films, and the