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Review

Cost effective cation exchange membranes: A review

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ABSTRACT

This paper will look at developments of new polymer electrolyte membranes to replace high cost ion exchange membranes such as Nafion®, Flemion® and Aciplex®. These perfluorinated polymer electrolytes are currently the most commercially utilized electrolyte membranes for polymer electrolyte fuel cells, with high chemical stability, proton conductivity and strong mechanical properties. While perfluorinated polymer electrolytes have satisfactory properties for fuel cell applications, they limit commercial use due to significant high costs as well as reduced performance at high temperatures and low humidity. A promising alternative to obtain high performance proton-conducting polymer electrolyte membranes is through the use of hydrocarbon polymers. The need for inexpensive and efficient materials with high thermal and chemical stability, high ionic conductivity, miscibility with other polymers, and good mechanical strength is reviewed in this paper. Though it is difficult to evaluate the true cost of a product based on preliminary research, this paper will examine several of the more promising materials available as low cost alternatives to ion exchange membranes. These alternative membranes represent a new generation of cost effective electrolytes that can be used in various ion exchange systems. This review will cover recent and significant patents regarding low cost polymer electrolytes suitable for ion exchange membrane applications. Promising candidates for commercial applications will be discussed and the future prospects of cost effective membranes will be presented.

Keywords: Cation exchange membranes; Nafion®; Polybenzimidazole; Fluorinated

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1. Introduction

Ion exchange membranes are highly efficient for use in separation applications, providing cleaner and more energy-efficient alternatives in applications such as water treatment and power generation (Xu, 2005). During the last 50 years, ion exchange membranes have progressed from laboratory scale to applications in commercial industries such as fuel cells (Savadogo, 2004; Smitha et al., 2005). In addition to lowered operational costs and energy demands, environmental and safety issues could push industries towards membrane technology.

A focus on the cost reduction of membrane materials is essential for the development of economically competitive technologies that are more environmentally conscious. A continual challenge in this field is to find lower cost membranes with the desired properties for ion exchange applications. A significant reduction in the capital costs of these membranes without sacrificing performance is an essential criterion for new technologies to become commercially competitive on an industrial scale.

Among fuel cells, proton exchange membrane fuel cells (PEMFCs) are the most promising technology developing for transportation due to their high efficiency and environmentally friendly solution to energy conversion. A proton exchange membrane (PEM) separates the fuel and oxidizer, simultaneously facilitating the transport of positive charges from the anode to cathode to compensate for the transport of electrons.

PEMs are typically based on polymer electrolytes having acidic functional groups attached to the polymer backbone. The efficiency of these fuel cells is highly dependent on their ability to minimize ionic and electronic resistivity. The polymer electrolyte membrane acts as an electrolyte, providing ionic transport between the anode and cathode while separating the reactant gases and performing as an electronic insulator.

Polymer electrolyte fuel cells also offer a promising alternative for portable electronic power using solid polymer membrane direct methanol fuel cells (DMFCs). DMFCs are capable of producing up to 500 W power and have the potential to replace batteries in portable devices such as laptops, phones and cameras (Varcoe and Slade, 2005). The higher energy density in liquid methanol fuel over batteries is a strong advantage but is offset by several electrokinetic issues such as methanol crossover. Where methanol molecules are transported through the membrane from the anode to the cathode, this methanol crossover leads to reduced potential at the cathode and lowers the overall fuel cell voltage. A method used to manage these inefficiencies is to increase the DMFC operating temperature to more than 150 °C. Operation from 100 °C to 200 °C is termed as high temperature operation and can reduce the effect of performance limitations. At these conditions, however, robust membranes are required to achieve long-term stability. Currently, membranes for fuel cells are typically made of perfluorocarbon-sulfonic acid iononmers. These copolymers are formed from tetrafluorethylene and various perfluorosulfonate monomers. Nafion® membranes are the best known commercial membrane materials made by Dupont, using perfluoro-sulfonylfluoride ethyl-propyl-vinyl (Barbir, 2005). These materials have limitations at high temperatures, having high resistance and also being costly (Varcoe and Slade, 2005). Table 1 presents recently obtained costs for Nafion-based ion exchange membranes.

Membranes used in these electrochemical systems require good mechanical and chemical stability in harsh chemically oxidative and physical environments, high proton conductivity and high permselectivity. The development of membranes must also address the issues of low cost, automated processing, performance and reliability.

Ion exchange membranes are suitable for various applications such as electrodialysis, desalination, gas separation processes and water purification. Electrodialysis (ED) transports ions through a membrane under the influence of an applied electrical potential. This technology is primarily used in water treatment and purification systems. Bioelectrochemical systems (BESs) also utilize membranes to provide a novel and promising biotechnological approach for the production of renewable energy or commodity chemicals from wastewater (Rozendal et al., 2008). Based on the current costs of materials used, the capital costs of full scale electrodialysis cells and BESs are orders of magnitude higher than those of current conventional wastewater treatment systems. The most common of bioelectrochemical systems involve microbial fuel cells (MFCs). MFCs are attractive as technologies for off-grid rural or remote power applications in developing countries.

Up until 2003, materials and designs employed for MFCs and MECs were based on similar membranes as used for ion exchange fuel cells, such as Nafion® 117, which has the equivalent weight of 1100 and is 0.17 mm thick (Biffinger and Ringeisen, 2008). However, further research into more optimal materials for these systems has resulted in several cost effective membrane materials more suitable to these specific environments and operational requirements.

Developments are being investigated to produce alternative, low-cost, polymer-based electrolytes with good chemical resistance, good mechanical stability and sufficient proton conductivity. The U.S. Department of Energy has set the following technical targets, as shown in Table 2, for proton exchange membranes and can be used as a general guide to determine the practical viability of newly developed membranes (Bae, 2009). Currently, ionic conductivity comparable to Nafion® membranes of 10^{-3} to 10^{-2} S/cm is sought after for maintaining viable and cost effective alternative membranes.

2. Current membrane materials

2.1. Fluorinated materials

Currently, the most commercially applied cation exchange membranes are based on perfluorinated or partially fluorinated materials. Membranes most commonly used in PEMFCs are perfluorosulfonic polymers, such as Nafion® developed from two patents in 1966 and 1982 and assigned to the then Dow Chemical Company (Connolly and Gresham, 1966; Ezzell et al., 1982). These membranes are classified as perfluorosulfonate ionomer membranes where the fluoropolymer backbone is bonded with sulfonic acid groups.

Nafion® membranes are currently the most commonly used commercial membrane in industrial applications. The current generation of cation exchange membranes used in PEMFCs are based on these sulfonated perfluoropolymers. Perfluorinated membranes have a strong stability in oxidative and reductive environments due to the polytetrafluoroethylene backbone structure and their strong proton conductivity. However, at elevated temperatures, above 80 °C, these membranes