



Review

Performance analysis of polymer electrolyte membranes for direct methanol fuel cells



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HIGHLIGHTS

- This review discusses recent advances in polymer electrolyte membranes for DMFCs.
- The PFSA and SAP membranes show remarkable performances at temperatures up to 90 °C.
- The composite membranes appear more suitable for DMFC applications above 100 °C.

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ABSTRACT

The status of research and development of polymer electrolyte membranes (PEMs) for direct methanol fuel cells (DMFCs) is described. Perfluorosulfonic acid membranes, e.g. Nafion, are widely used in fuel cell technology; but, despite their success, they show some drawbacks such as high cost, limited operating temperature range and high methanol crossover. These limit their widespread commercial application in DMFCs. Such disadvantages are inspiring worldwide research activities for developing new PEM materials based on non-perfluorinated polymers as alternative to Nafion for DMFCs. A review of membrane properties is carried out on the basis of thermal stability, methanol crossover and proton conductivity. The analysis of DMFC performance covers perfluorosulfonic acid membranes (PFSA), sulfonated aromatic polymers (SAPs) and composite membranes. PFSA membranes are suitable materials in terms of power density, SAPs are more advantageous regarding the low methanol permeability and cost, whereas composite membranes are more appropriate for operation above 100 °C. DMFC power density values reported in literature show that, although there are remarkable research efforts on this subject, the achieved results are not yet satisfying. Further work is especially necessary on non-perfluorinated polymers to improve performance and durability for an effective application in practical DMFC devices.

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1. Introduction

Low temperature fuel cells are emerging technologies for the electrochemical conversion of the chemical energy of a fuel directly into electric energy with low environmental impact and high-energy efficiency. Nevertheless, before this technology can reach very large scale diffusion, some problems related to poor electrochemical performance, high cost of fuel cell systems, long term stability, etc. must be solved. In a fuel cell system, high costs derive from the use of noble metal catalysts, perfluorosulfonate polymer electrolyte membranes, bipolar plates and auxiliary components. Up to now, Nafion-type polymer electrolyte membranes (Nafion is a perfluorosulfonic acid polymer produced by DuPont) are the most

widely used polymer electrolytes in H₂/air and direct methanol fuel cells. This wide use is due to the high proton conductivity, excellent mechanical and thermal properties, and high chemical and electrochemical stability of Nafion. Other similar perfluorinated polymers commercialized by Dow Chemicals (XUS[®]), Asahi Kasei (Aciplex-S[®]), Solvay (Aquivion[®]), Fumatech (Fumion[®]), Asahi Glass Engineering (FlemionR[®]) are under consideration worldwide. However, although perfluorinated membranes show excellent properties, they have also some disadvantages such as high cost, high methanol crossover, fast dehydration with a decrease of proton conductivity as the temperature increases above 100 °C, and loss of fluorine species in the exhaust gas due to •OH radicals attack. Because of these constraints, there is a strong interest in the R&D of new and cheaper membranes with similar or higher conductivity and lower fuel cross-over for application in the range of temperature from 100 to 150 °C. Most of the new types of PEMs under investigation for DMFC or PEMFC applications are currently

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synthesized by using various approaches, such as the synthesis of new ionic random and block copolymers, graft copolymerization of ionic polymers on hydrophobic membranes, blending of ionic and non-ionic polymers, synthesis of interpenetrating networks of ionic and non-ionic polymers and composite membranes incorporating a large variety of fillers (silica, zeolites, titania, zirconia, etc.).

2. Recent literature regarding polymer electrolytes for fuel cell applications

In the years from 1994 to 2012, wide research activities toward the development of new polymer electrolytes for DMFC applications were carried out as demonstrated by the trend of publications per year in Fig. 1 (the number of publications for the year 2013 is essentially limited to the first four months), and great efforts and progress were made in this topic of research. The number of papers concerning with this subject was performed by searching into Scopus database (www.scopus.com; Scopus® is a registered trademark of Elsevier BV Netherlands) by using a combination of different keywords to identify the current literature in the field of polymer electrolytes and membranes for direct methanol fuel cells. The following keywords were used in TITLE-ABS-KEY (“Fuel cell” OR “Fuel cells”) AND (LIMIT-TO (EXACTKEYWORD, “Methanol”) OR LIMIT-TO (EXACTKEYWORD, “Direct methanol fuel cells (DMFC)”) OR LIMIT-TO (EXACTKEYWORD, “Direct methanol fuel cell”) OR LIMIT-TO (EXACTKEYWORD, “Ethanol”) OR LIMIT-TO (EXACTKEYWORD, “DMFC”) OR LIMIT-TO (EXACTKEYWORD, “DMFCs”)). The keywords used in this search do not allow a complete separation of the papers with a subject regarding the polymer electrolytes and those relative to other types of studies, e.g. catalysts, electrodes, modeling, etc. for DMFCs. The search was performed on 10 May 2013.

With the data extracted from Scopus, a “DMFC membranes” database was created from which a list of published papers per year was generated.

A total of 6890 publications were selected for the analysis, of which 5792 are papers from journals, 887 are publications from conference proceedings (including ECS Transactions), 113 are book series and 98 are trade publications. From Fig. 1, it is evident that there is a gradual increase in publications per year in the range from 1994 to 2000, and that in 2001, 2004 and 2008 there are apparent strong jumps. In 2001, 109 papers have been published with respect to 52 of 2000, in 2004, 417 papers with respect to 231 of 2003, in 2008 710 against 589 of 2007. The peak of productivity has been reached in 2010 with 834 while in 2011 and 2012 the number of

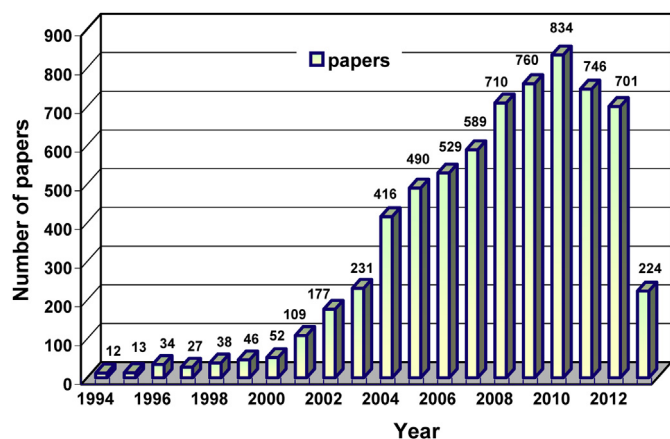


Fig. 1. Summary of the number of papers published per year extracted from Scopus database regarding the polymer electrolyte membranes for direct methanol fuel cells.

papers slightly decreased to 746 and 701, respectively. A detailed analysis of the scientific contents of the publications shows that there is a strong interest in the subject “polymer electrolytes” for DMFCs.

2.1. Highlighting the research in polymer electrolytes for direct methanol fuel cells

In the following sub-paragraphs the most important findings of recent investigations on polymer electrolytes for DMFCs are discussed.

2.1.1. Perfluorosulfonic acid membranes

Perfluorosulfonic polymers, naturally combine in one macromolecule, the very high hydrophobicity of the perfluorinated backbone with the extremely high hydrophilicity of the sulfonic acid functional groups. These polymers, in the presence of water, give rise to some hydrophobic/hydrophilic nano-separation. The sulfonic acid functional groups aggregate to form large hydrophilic domains. When these are hydrated, proton conductivity assisted by water occurs. While the well connected hydrophilic domains are responsible for the transport of protons and water, the hydrophobic domain provides the polymer with an adequate chemical and mechanical stability and avoids that the polymer is dissolved in water [1]. The main advantages of perfluorosulfonic acid (PFSA) membranes are: (i) their strong stability in oxidative and reduction media due to the structure of the polytetrafluoroethylene backbone; and (ii) their proton conductivity, which can be as high as 0.2 S cm^{-1} in polymer electrolyte fuel cells (PEFCs) [2]. Yet, when used at elevated temperatures, PEFC performance decreases due to (i) dehydration of the membrane, (ii) reduction of ionic conductivity, (iii) decrease in affinity with water, (iv) loss of mechanical strength through a softening of the polymer backbone, and (v) parasitic losses (because of a high level of gas permeation). Perfluorosulfonic membranes (Nafion, Flemion, Aciplex, Aquivion, Fumion, etc.) are currently used as electrolytes in DMFCs [3]; yet, since methanol is rapidly transported across these membranes and is chemically oxidized to CO_2 and H_2O at the cathode, there is a significant decrease in coulombic efficiency for methanol consumption by as much as 20% under practical operation conditions. Thus, it is very important to modify these membranes by, for example, developing composites [4–7] or synthesizing alternative proton conductors with the capability of inhibiting methanol transport. The polymer electrolyte should have a high ionic conductivity under working conditions and a low permeability to methanol (less than $10^{-6} \text{ mol min}^{-1} \text{ cm}^{-2}$). Furthermore, it must be chemically and electrochemically stable under operating conditions. Potentially, these requirements appear to be met by new classes of solid polymer electrolytes that show promising properties for applications in DMFCs. A review of these new types of polymers is reported in the following paragraphs.

2.1.2. Poly(styrene)-based electrolytes

A number of sulfonic-acid containing random copolymers was investigated for DMFC applications. Sulfonated poly(styrene) (SPS) [8–11], random copolymers of poly(styrene) and poly(styrene sulfonic acid) (PSSA) [11–13] were the most investigated poly(styrene)-based materials in DMFCs. Additionally, sulfonated crosslinked polystyrene was also used with poly(vinylidene fluoride hexafluoropropylene) copolymer/Nafion® blend [14] and chemically crosslinked poly(vinyl alcohol)/poly(2-acrylamido-2-methyl-1-propanesulfonic acid)/poly(vinylpyrrolidone) blend [15]. SPS can be synthesized either by copolymerizing styrene and styrene sulfonic acid monomers or by post-sulfonation of poly(styrene) with different sulfonating agents (e.g., acetyl sulfate,

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