

Trends for fuel cell membrane development[☆]

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ABSTRACT

Fuel cells are considered a promising energy conversion technology of the future owing to inherent advantages of electrochemical conversion over thermal combustion processes. In the polymer electrolyte fuel cell (PEFC) a proton-conducting polymer membrane is utilized as solid electrolyte, having to allow the transport of protons from anode to cathode yet block the passage of reactants (e.g. H₂, O₂) and electrons. Although PEFC technology has matured substantially over the past two decades, technological barriers, such as insufficient durability and high cost, still delay commercialization in many applications. In this contribution, we review current fuel cell membrane technology and outline approaches that are taken to improve the functionality as well as the chemical and mechanical stability of proton conducting polymers in fuel cells.

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1. Low temperature fuel cells

Fuel cells are clean and efficient electrochemical energy conversion reactors. Among the various fuel cell types under consideration, with operating temperatures ranging up to 1000 °C for the solid oxide fuel cell (SOFC), the polymer electrolyte fuel cell (PEFC) is particularly attractive for applications with variable load profile and intermittent operation (portable electronics, remote power sources, vehicle propulsion). The PEFC typically operates at temperatures between 60 and 100 °C, in specific configurations around 180 °C. In a PEFC, the electrochemical reaction of a fuel – typically H₂ – and O₂, commonly taken from ambient air, takes place in two half-cell reactions separated by an electrolyte, which is a polymeric membrane with a thickness of 20 to 200 μm and proton conductivity on the order of 0.1 S cm⁻¹. Methanol can also be used as fuel in the direct methanol fuel cell (DMFC), having the advantage of easy storage, yet with a lower power density compared to the fuel cell operated on H₂. The electrodes consist of porous carbon fiber layer structures with a thickness of a few hundred micrometers (Fig. 1). The hydrogen oxidation and oxygen reduction reactions take place at the anode–membrane and cathode–membrane interface, respectively, within the active layer (thickness ~10 μm) containing highly dispersed Pt nanoparticles, supported on high surface area carbon, as electrocatalyst [1].

In the PEFC, the solid polymer membrane has to fulfill several functions, with concomitant requirements for candidate ion-conducting materials:

Requirements

- transport of protons
- electrical insulator
- oxygen and hydrogen gas barrier

Materials

- chemically stable (against HO / HOO radicals)
- thermally stable
- mechanically robust

Furthermore, the membrane may be part of the gasket system, requiring certain specific mechanical properties. This ensemble of specifications calls for a comprehensive approach in the membrane development for fuel cell application.

2. Membrane materials for fuel cells

In general, PEFC electrolytes are classified into acidic or basic types, yet the acidic proton exchange membrane (PEM) is most widely used owing to its superior chemical stability. Generation of mobile protons is accomplished via the introduction of acid sites into the polymer, yielding an 'ionomer'. As it is desired to have an acid with high dissociation constant, sulfonic acid is predominantly used for this purpose.

Ion exchange membranes are widely used in separation technology (desalination, dialysis, filtration, etc.) and electrochemical processes (electrolysis, fuel cells) [2]. The PEM in the PEFC is subjected to particularly aggressive conditions, because the interaction of H₂ and O₂ on the surface of the Pt catalyst leads to the formation of aggressive HO• and HOO• radical species, which attack the polymer and lead to chain scission and thus membrane degradation [3]. For this reason, the majority of membranes used in fuel cells are perfluorosulfonic acid (PFSA) type membranes, known under the tradenames Nafion[®], Flemion[®], Hyflon[®] Ion, etc.

Substantial efforts are devoted by the academia and industry to the development of novel fuel cell membrane materials, driven by the need for membranes with improved functionality (e.g., conductivity,

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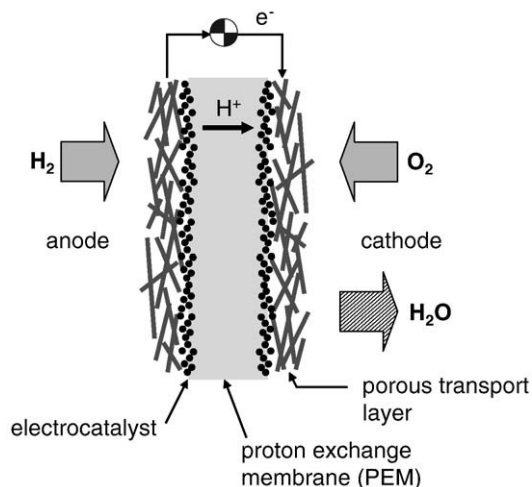


Fig. 1. Operating principle of a H_2 / O_2 fuel cell with acidic electrolyte membrane. Protons are transported from anode to cathode, where water is formed.

robustness) and more cost-efficient polymers [4]. Promising candidate materials are partially fluorinated or non-fluorinated ionomers containing aromatic units with attached $-\text{SO}_3\text{H}$ groups, either in the main polymer chain, or attached to an aliphatic main chain (Fig. 2). Examples of more 'exotic' polymers are polyphosphazenes and silicones.

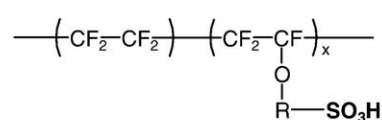
3. Structure–property relationship

The sulfonic acid based PEMs have a common characteristic: dissociation and formation of mobile protons require the presence of water, acting as 'proton solvent'. The structure of water swollen PEMs,

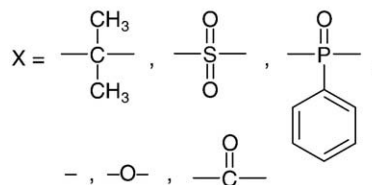
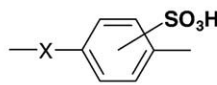
especially Nafion[®], has been subject to numerous investigations. It has been established that Nafion[®], as well as other well-working PEMs, have a nano-phase-separated structure, with a 'polymer' phase and an 'aqueous' phase [5,6]. The proton conduction takes place within water channels lined with sulfonate counter-ions (Fig. 3a). As a consequence, the mobility of the proton is strongly affected by the water content (Fig. 3b). For Nafion[®] a more or less linear increase of conductivity is observed as a function of membrane water content. The dissimilar structure–property relationship for SPEEK membranes leads to a different dependence of conductivity on water content [7].

PFSA type membranes, such as Nafion[®], are copolymers of tetrafluoroethylene and a monomer with pendant $-\text{SO}_2\text{F}$ group, which is later hydrolyzed to yield $-\text{SO}_3\text{H}$. Due to the different chemical nature of the PTFE-like backbone and the pendant acid-bearing chains, the hydrated ionomer forms the phase-separated structure depicted in Fig. 3a. For alternative ionomer materials under investigation, it is important to impart the polymer with a property that will lead to the spontaneous formation of a multi-phase structure. This may be achieved by forming block copolymers with hydrophobic and hydrophilic blocks [9,10] (Fig. 4).

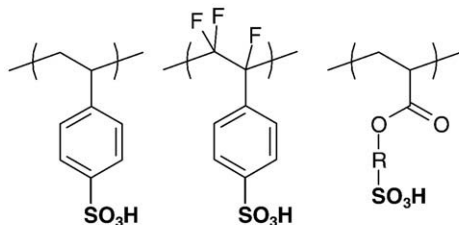
Another approach to obtain phase-separated polymers is the formation of graft copolymers. Grafting involves the introduction of a polymer constituent into a pre-existing polymer film. Grafting can be accomplished by irradiating the base film to introduce radicals, which will serve as starting points for the growth of the grafted polymer [11]. Radiation grafting allows the formation of polymer combinations that are impossible to obtain with other methods, owing to the incompatibility of the constituents, e.g., a hydrophobic and a hydrophilic component. The process offers a broad range of possibilities to design the polymer architecture via careful choice of the base film, grafting monomers, irradiation and grafting conditions [12]. In yet another approach, polymers in solution with different target functionalities may be mixed and cast to yield a polymer blend [13]. One component,



perfluorosulfonic acid
(PFSA)
e.g. Nafion[®], Flemion[®]



aryl main chain polymers



aliphatic main chain polymers

'exotic' polymers

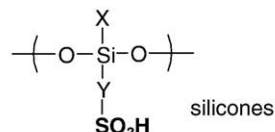
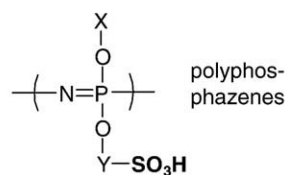


Fig. 2. Polymeric materials used to form proton exchange membranes for fuel cells. The acid functionality is predominantly provided by sulfonic acid.

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