

SPEEK polymeric membranes for fuel cell application and their characterization: A review

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Design of polymeric membranes for fuel cells application requires suitable selection and modification of polymers. This review accounts the various polymeric membranes available for use in fuel cells, advantages of sulphonation of polymers, various sulphonation methods and the characterization techniques. Presently, SPEEK finds extensive application as polymeric membrane in fuel cells. The advantages of SPEEK include good mechanical properties, thermal stability, and toughness and some conductivity depending on degree of sulphonation.

Keywords: Fuel cells, Polymeric membranes, SPEEK

Introduction

A membrane acts as a selective interphase between two bulk phases¹. Research in membrane technology can be roughly divided into two groups²: (i) Membrane process group, which uses membranes with certain specified characteristics as a black box and studies its behavior under certain process conditions as a singular process or, more often, as a hybrid process in combination with other unit operations; and (ii) Material science aspects of membranes, which include morphology of membranes and how this morphology relates to the mass transport characteristics.

Classification of Polymeric Membranes

Polymeric membranes (PMs) can be broadly classified into symmetric and asymmetric membranes¹ (Fig. 1).

Symmetric Membranes

Symmetrical membranes consist of: (i) Homogeneous, dense membranes, with an active layer of thickness (10 μm), are often used for the study of polymer material science aspects in gas separation and pervaporation; (ii) Cylindrical porous membranes, which are normally, used in small size

laboratory experiments like enzyme and DNA separations from dilute solutions; and (iii) sponge-like porous membranes (pore size, 0.2-5 μm), which are used in microfiltration.

Asymmetric Membranes

Asymmetric membranes consist of: (i) Porous membranes, which do not have the same pore size over the whole membrane thickness but have a pore size gradient; (ii) Porous membranes with a top layer, which have normally, atop an open porous support layer, a second layer with much smaller pores (5-500 nm); and (iii) Composite membranes, which have a homogeneous layer placed in a second production step on top of a support membrane.

Application of Polymeric Membranes

PMs have been developed for a variety of industrial applications such as microfiltration (MF), ultrafiltration (UF), reverse osmosis (RO) and gas separation. Each application imposes specific requirements on the membrane material and membrane structure.

Membrane Filtration

Membrane based separation processes are attractive because: (i) Process is simple; (ii) There are diverse applications; (iii) There is no phase change involved, which is measured in commercial applications as energy savings; (iv) Process is generally

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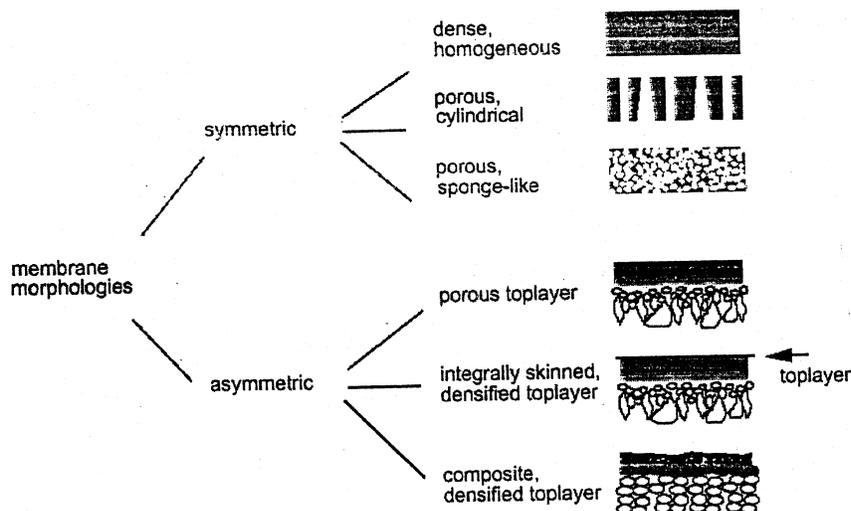


Fig. 1—Schematic representation of different membrane morphologies¹

carried out at atmospheric conditions which, besides being energy efficient, can be important for sensitive applications encountered in pharmaceutical and food industry, and (v) Modules can be added and optimised in a process design to achieve the desired separation.

In MF process, only suspended solids are rejected, while even proteins pass through the membrane freely. In UF process, high molecular weight component, such as protein and suspended solids are rejected, while all low molecular weight components pass through the membrane freely. There is consequently no rejection of mono and disaccharides, salts, amino acids, organics, inorganic acids or sodium hydroxide. RO is the tightest possible membrane process in liquid/liquid separation. Water is in principle the only material passing through the membrane; essentially all dissolved and suspended material is rejected. The more open types of RO membranes are sometimes confused with nano-filtration (NF). True NF rejects only ions with more than one negative charge, such as sulphate or phosphate, while passing single charged ions. NF also rejects uncharged, dissolved materials and positively charged ions according to the size and shape of the molecule in question. In contrast, “loose RO” is an RO membrane with reduced salt rejection³. This effect has proven desirable for a number of applications where moderate salt removal is acceptable since operating pressures and power consumption are significantly lowered. So, in exchange for less than complete salt removal, costs are reduced. Pore sizes³ of different PMs are: MF, 5-0.1; UF, 0.1-0.01; and NF/RO, 0.001 μm .

Major applications of MF include sterile filtration and wastewater treatment, whereas UF is employed in electro-coat paint, juice extraction, pulp and paper and protein purification. Besides using polymers for fabricating porous membranes, ceramic and polymer-ceramic composites are also being used as porous membranes. Inherent thermal and chemical stability observed with these materials are exploited during separation at high temperature and corrosive conditions. Hydrophilic nature of these membranes is sometimes utilized in treating aqueous solutions and emulsions. Recently, molecular sieve membranes have been developed for filtration purposes.

Fuel Cells

Another important application of PMs is the proton exchange membrane fuel cell (PEM-FC), also known as polymer electrolyte membrane fuel cell. This device converts chemical energy directly into electricity. As electrochemical combination of hydrogen (fuel) and oxygen produce water, fuel cell is environmentally clean and is expected to replace gasoline engine or rechargeable battery in current automobiles. This low temperature fuel cell is mainly used in vehicle applications. PEM-FC is the choice of most of the automotive industries, basically due to its convenient operating temperature and the possibility of using air as oxidant medium. The basic principle of this technology is the production of electricity by an electrochemical reaction, which involves the oxidation of fuel at anode, producing protons, which are transported to cathode to react with oxygen forming water. The membrane here plays a decisive

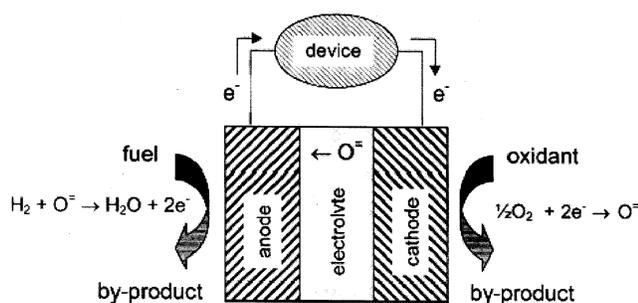


Fig. 2—Working principle of fuel cells

role as electrolyte medium for proton transport and barrier to avoid the direct contact between fuel and oxygen. The electrolyte in this fuel cell is an ion exchange membrane, which is a good proton conductor. The only liquid in this fuel cell is water hence corrosion problems are minimized.

Fuel Cell Models

Physical processes in a comprehensive fuel cell model should ensure equal current distribution via uniform velocity distribution of the reactants at the gas channel/ electrode interfaces. Cell operation must be kept stable by controlling the flow of water within the cell. Polymer membrane must remain hydrated to maintain its protonic conductivity, and water produced by the reaction must be removed from the cathode. The cell temperature must be kept constant. Fuel cells are not constrained by the maximum thermal (Carnot) efficiency as combustion engines are. Consequently, they can have very high efficiencies in converting chemical energy to electrical energy. In the archetypal example of a hydrogen/oxygen, PEMFC, a proton-conducting polymer membrane separates the anode and cathode sides. Each side has an electrode, typically carbon paper coated with platinum catalyst⁴.

On the anode side, hydrogen diffuses to the anode catalyst where it dissociates into protons and electrons. The protons are conducted through the membrane to the cathode, but the electrons are forced to travel in an external circuit (supplying power) because membrane is electronically insulating. On cathode catalyst, oxygen molecules react with the electrons (which have travelled through the external circuit) and protons to form water⁵. In this example, the only waste product is water vapor and/or liquid water⁶ (Fig. 2). Fuel cell must operate under conditions where the by-product water does not evaporate faster than it is produced because the

membrane must be hydrated. The following conditions must be met: (1) Operating temperature of less than 100°C; (2) A H₂-rich gas with little or no CO is used; and (3) A higher catalyst loadings (platinum in most cases) than those used in PAFC required in the anode and cathode.

A fuel cell is an electrochemical device similar to a battery, but differing from the latter in that, it produces electricity from an external fuel supply as opposed to the limited internal energy storage capacity of a battery. Some applications include base load utility power plants, emergency backup power, off-grid power storage, portable electronics, electrically-powered vehicles and cellular phone power (Nokia). Fuel cells cannot store energy like a battery, but in some applications, like stand-alone power plants based on discontinuous sources (solar, wind power), they are combined with electrolyzers and storage systems to form an energy storage system (round-trip efficiency, 30-40%). Ion conducting membranes find application in modern energy conversion technologies, in particular water and hydrogen/oxygen fuel cells, which offer considerable potential for the efficient utilization of solar energy and hydrogen technology. Frequently, energy conversion systems are based on liquid electrolytes as ion conductors, preferentially concentrated acids or bases, which are known to cause severe sealing and corrosion problems at elevated temperature and pressures. Therefore, there is a demand for novel solid proton conducting ion exchange membranes based upon solid polymer electrolytes.

Types of fuel cells^{6,7} include proton-exchange fuel cell, reversible fuel cell, direct-methanol fuel cell, direct borohydride fuel cells and solid-oxide fuel cells. Fuel cells use different materials and operate at a different temperature⁸⁻¹⁴ (Table 1).

Choice of Membranes for Fuel Cells

In order to qualify as membrane materials for electrolysis and fuel cell applications, polymer electrolytes must possess excellent chemical and environmental resistance, especially against attack of oxygen or strong acids, high thermal and dimensional stabilities and high ion conductivity. Introducing sulphonic acid group in the polymeric membranes often brings about this ion conductivity. Perfluorinated polymer electrolytes (Nafion) exhibit a prolonged service life under extreme reaction conditions. However, most of the perfluorinated

Table 1—Fuel cell types and uses

Type	Abbreviation	Operating temp., °C	Electrolyte	Uses
Solid oxide	SOFC	900-1000	Stabilized zirconia	All sizes of CHP
Direct alcohol	DAFC	50-120	Sulphuric acid/polymer	Buses, cars, appliances, small CHP
Proton exchange membrane	PEFC	50-125	Polymer	Buses, cars
Phosphoric acid	PAFC	190-210	Orthophosphoric acid	Medium CHP
Molten carbonate	MCFC	630-650	Li/K carbonate mixture	Large CHP
Alkaline	AFC	50-90	KOH	Used in space vehicles

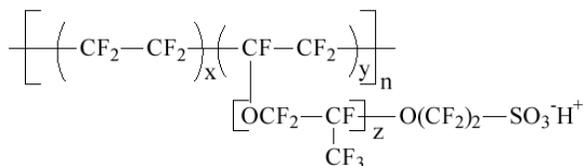
membranes being expensive and difficult to process, there is a demand for novel thermally and chemically stable polymer electrolytes combining membrane properties of perfluorinated polyelectrolyte¹⁵. Disadvantages of perfluorinated ionomers (PFI) membranes stimulated efforts to synthesize poly electrolyte membrane (PEM) based on partially fluorinated and fluorine free hydrocarbon ionomer membranes such as aromatic polyether ether ketone (PEEK)¹⁶.

Polymer/Inorganic Composite Membranes

Polymer inorganic composites can be ionically conductive, ionic polymer with inorganic filler for mechanical support, ionic polymer with water-retaining inorganic filler, ionically conductive inorganic additive with supporting polymer, etc. Polymer inorganic composite membranes are interesting because many of the inorganic additives used are able to operate at higher temperatures than pure polymers¹⁷.

Nafion

Nafion¹⁸, leading membrane in all types of PEM fuel cells, is prepared by the free radical copolymerization of tetrafluoroethylene and the sulphonated co-monomer. Nafion have a pKa of about 6 as compared to an aromatic sulphononic acid moiety in sulphonated PEEK of 1. Implication of difference in pKa values is that there can be a lower ion conductor concentration in Nafion membrane as compared to PEEK to produce the same conductivity under equal conditions.



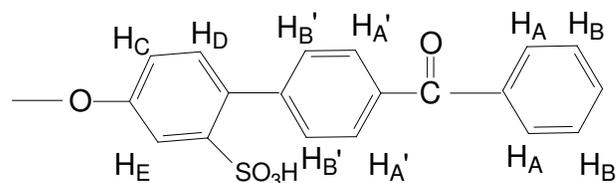
Dais Analytic

Dais Analytic's membranes (ion exchange capacity, 1100 EW) have been primarily based on sulphonated styrene/ethylene-butylene/styrene (S-SEBS) copolymers for ambient temperature low current density systems. These polymers differ from Nafion in backbone composition, hydrocarbon versus fluorocarbon, and the nature of the sulphonate group, aryl sulphonic acid versus perfluorosulphonic acid. Dais materials uptake higher water than Nafion, but lower conductivities at a given weight percent water¹⁹.

Poly(ether ether ketone) (PEEK)

PEEK is a thermostable polymer with an aromatic, non-fluorinated backbone, in which 1,4-disubstituted phenyl groups are separated by ether (-O-) and carbonyl (-CO-) linkages. PEEK is a semi crystalline polymer possessing high thermal stability, toughness, chemical resistance and mechanical properties, which are suitable for aerospace to the medical, electronic industries, MF, UF or RO and ion-conducting membranes. Sulphonation adds proton conductivity as a further feature of PEEK. Conductivity of sulphonated PEEK is large enough to meet the requirements for applications in fuel cells. Sulphonation of PEEK at room temperature in concentrated sulphuric acid places a limit of one sulphonate group per unit, located at one of the four positions²⁰. Sulphonation is an effective method to increase permeation rate of water vapour and the separation factor of water vapor over gases¹⁶.

Perfluorinated ion-exchange polymers (Nafion, Flemion, Aciplex & Neosepta) though very suitable as PEM in hydrogen fuel cells, are not suitable for



direct methanol fuel cell (DMFC) applications due to high methanol permeability through these membranes. Therefore, new materials for direct methanol fuel cells, are wet membranes (ion-exchange materials, such as perfluoro ionomers), dry membranes [heterocyclic homopolymers, such as polybenzimidazole (PBI)], hybrid membranes (polymer blends from a variety of ion-exchange materials, such as sulphonated polysulphone (SPSf), sulphonated polyphenyleneoxide (SPPO) and sulphonated poly(ether ether ketone) (SPEEK) with other materials, such as polyethersulphone (PES), polybenzimidazole (PBI) and polysulphone (PSf).

'Wet' membranes (ion-exchange materials, such as perfluoro ionomers); obtain their properties by dehydration of the ion-exchange group present. These materials seem not to be suitable for DMFC applications since high swelling values enhance transport of methanol. Therefore, dry membranes (heterocyclic homopolymers) that are hardly swollen by water (or methanol) are chosen where proton transport occurs by a kind of an activated diffusion process. Hybrid membranes have better prospective for these applications²¹.

Chemical Modification of PEEK

PEEKs¹⁵ are largely used as construction materials and coating elements of electric transmission wires which may be under operation for long times up to 200°C. Although the cost of PEEK is 5-20 times higher than that of ordinary polymers used as construction materials, excellent properties of PEEKs guarantee a wide use in all branches of the economy.

Sulphonation of PEEK

Sulphonation is a versatile route to polymer modification that is essentially suitable for aromatic polymers. Main purpose of sulphonating an aromatic PEEK is to enhance acidity and hydrophilicity as the presence of water facilitates proton transfer and increases conductivity of solid electrolytes. At 100% sulphonation, SPEEK can dissolve in water²², implying its higher hydrophilicity. Among the attractive properties of engineering thermoplastic PEEKs, good solvent resistance, high thermo-oxidative

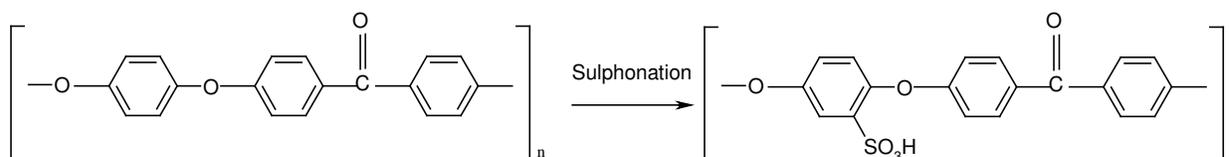
stability and good mechanical properties are significant²³. Sulphonation is an effective method to increase both the permeation rate of water vapor and the separation factor of water vapor over gases²⁴. PEEKs can be sulphonated with a sulphonation degree of 1.0 per repeat unit^{25,26}. However, a greater degree of sulphonation (DS) is difficult to achieve due to insolubility and side reactions such as interpolymer cross-linking and degradation. Sulphonation of PEEK can be performed by concentrated sulphuric acid, chlorosulphonic acid, by pure or complexed sulphur trioxide, by acetyl sulphate and methane sulfonic acid²⁷⁻³¹. Sulphonated polymers can be prepared as free acid form (-SO₃H), salts (-SO₃⁻Na⁺), esters (-SO₂R) and various derivatives. Sulphonation increasingly hindered with decreasing ether group content of polymer chain (PEEK < PEEKK/PEK < PEKEKK)³². Marvel *et al.*^{33,34} have reported sulphonation of various polyether ketones using chloro sulphonic acid or a sulphur trioxide/triethyl phosphate complex. Extensive degradation and cross linking of the polymer was observed with the latter. Chlorosulphonic acid method was more satisfactory although some degradation occurred²⁵. Sulphonation of PEEK^{25,27} in H₂SO₄ (Conc. <100%) is essentially free of degradation and cross-linking reactions. It is believed that the presence of water decomposes pyrosulphonate intermediates to inter- and intramolecular sulphone cross-links. Changing the reaction time and temperature can control sulphonation rate (30-100%) of PEEK in H₂SO₄.

Advantages of Introducing -SO₃H Group

By introducing -SO₃H groups in PMs, ion exchange capacity, hydrophilicity, solubility in polar solvents, proton conductivity and transport number of PMs increases. Important parameter for sulphonated PEEK is its ion exchange capacity and swelling capacity.

Ion Exchange Capacity (IEC)

Dried sample of the membrane is immersed in saturated NaCl solution for 24 h to liberate H⁺ ions. Mixture is then titrated with 0.1 M NaOH or 0.02 M KOH to determine H⁺ and IEC is calculated. Usually,



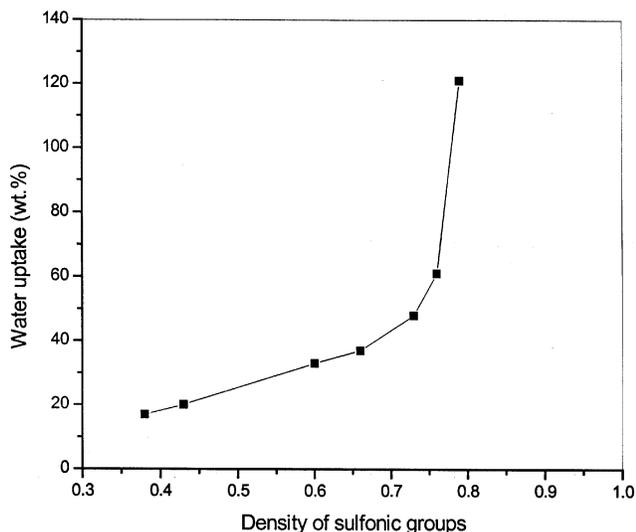


Fig. 3—Water absorption by the SPEEK membranes

the capacity of ion-exchange materials is defined by mmol or meq of functional groups per 1 g of dry substance. IEC depends on the polymer structure (2 phenylene groups for PEK, 3 phenylene groups for PEEK, 4 phenylene groups for PEEKK, 5 phenylene groups for PEKEKK²⁰). PEEK can be functionalized by sulphonation and the degree of sulphonation can be controlled by reaction time and temperature.

$$\text{IEC} = \frac{\text{Consumed ml NaOH} \times \text{molarity of NaOH}}{\text{weight of dried membrane}} \text{ [meq/g]}$$

Swelling

To determine swelling behavior of polymer membrane, dried sample of membrane is immersed in water at 25°C, swollen to equilibrium at 60°C, cooled down to 25°C and removed from the water. Sample is surface dried with a tissue paper and weight of the wet membrane determined. Membrane is then dried to constant weight in an oven at 80-100°C and weighed. The swelling value of the membrane is determined as

$$\text{Water uptake} = \frac{m_{\text{wet}} - m_{\text{dry}}}{m_{\text{dry}}} \times 100$$

In the highly sulphonated SPEEK, density of SO₃H groups is high which may involve clustering or agglomeration. Clustered ionomers absorb more water, which may be suggestive of the presence of ion rich regions²⁰. Polymers (>80% degree of sulphonation) swell and dissolve in water. Zaidi *et al*¹⁶ have shown that water uptake increases with DS. Water absorption of SPEEK membranes increases linearly up to DS of 65% and above that increases rapidly

(Fig. 3). For 80% DS, water uptake of the SPEEK membrane reached 120%.

Solubility of PEEK in Solvents

PEEK due to crystallinity shows little solubility in almost all the solvents except some strong acids (conc. H₂SO₄). Sulphonation improves solubility of PEEK in widely used solvents. Above 30% sulphonation, SPEEK is soluble in hot dimethylformamide (DMF), dimethylacetamide (DMAC), and dimethylsulphoxide (DMSO), or N-methylpyrrolidone; above 40% in the same solvents at room temperature and above 70%, in methanol and at 100% in hot water³⁵. SPEEK-H³¹ (>40% DS) can dissolve in DMF, DMSO, and DMAC at room temperature. But SPEEK-Na (55.5% DS) can dissolve in these solvents at room temperature, however some fiber like residuals probably aggregates of PEEK crystalline network can still be observed in the dilute polymer solution. SPEEK-Na (86.6% DS) is less soluble than SPEEK-H (86.6% DS), indicating that there is a stronger interaction between SPEEK-Na polymer chains³⁶.

Conductivity

Proton conductivity (σ) of samples in the traverse direction can be measured in using ac impedance spectroscopy with potentiostat as $\sigma = l/rs$, where l and s are thickness and area of the membrane, respectively and r is derived from low intersect of high frequency semicircle on a complex impedance plane with re (z) axis³⁷. With increase in DS¹⁶, there is increase in conductivity and solubility of SPEEK membranes in organic solvents.

Characterization of Sulphonated Membranes

Advances³⁸ in synthesis and characterization of polymers eventually resulted in improvements in thermal and mechanical properties of the polymers. A scientific approach, based on (a) structure–property relationship prevailing in the polymers, (b) application of thermodynamics, mass transfer kinetics and (c) surface science (that controls complex morphologies) must be considered in order to ensure satisfactory performance of the membrane³⁹. Methods for characterizing filtration membranes include physical methods that determine pore size and pore size distribution of a membrane and methods based on rejection performance using reference molecules and particles.

Microscopic Characterization

PMs with pores of a wide variety of sizes are frequently used for MU (mean pore diam, $d > 100$ nm) and UF ($d < 100$ nm). These membranes possess a growing significance for various modifications, like enzyme immobilization and as an efficient support for gas separation layers. In each case, shape and size of the pore as well as pore size distribution and porosity are important for separation performance. Scanning electron microscope (SEM) is used to image the cross-section of asymmetric membranes⁴⁰ (Fig. 4). Imaging with field emission SEM (FESEM) is a standard method and is broadly accepted for the investigation of perforated materials⁴¹. The membrane surface shown by FESEM looks either nodular or spongy^{42,43}. A number of methods have been

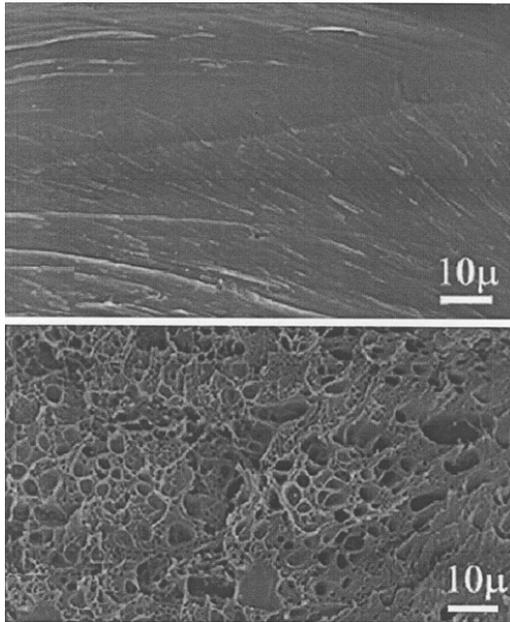


Fig. 4—SEM micrographs of SPEEK membranes

developed for characterization of surface morphology⁴⁴.

Electron Paramagnetic Resonance (ESR)

ESR can be used to study the structure and cast some light to the transport of RO and UF membranes⁴⁵. ESR provides information without disturbing the membrane. Role of paramagnetic radicals in mass transport is also studied by ESR technique. Polymers contain paramagnetic free radicals, which may take part in transportation of gases through the membrane. Froyer *et al.*⁴⁶ prepared poly(phenylene) using two different polymerization procedures. Kaptan & Tatar⁴⁷ reported that ESR spectrum of polymethyl methacrylate depended on the vacuum conditions.

Atomic Force Microscopy (AFM)

Atomic force microscopy (AFM) gives topographic images by scanning a sharp tip over a surface⁴⁸ and has been used to produce atomic resolution images of both conductors and non-conductors⁴⁹ including biological materials⁵⁰. AFM has been used to investigate MF and UF membrane surface structure⁵¹⁻⁵⁵, besides elucidating the mechanisms giving rise to inefficiencies (fouling) in membrane processing⁵⁶. "Non-contact mode", is especially suitable for PMs, which are soft or liable to mechanical damage as the forces used for imaging are also lower.

Nuclear Magnetic Resonance (NMR) Spectroscopy

DS could be determined quantitatively by ¹H NMR using a variation of the method for SPEEK polymers (Fig. 5). In ¹H NMR spectra, presence of sulphonic acid group causes a significant 0.25 ppm downfield shift of the hydrogen H_E compared with H_C, H_D in the phenyl ring. Nomenclatures of aromatic protons for SPEEK repeat unit is given as

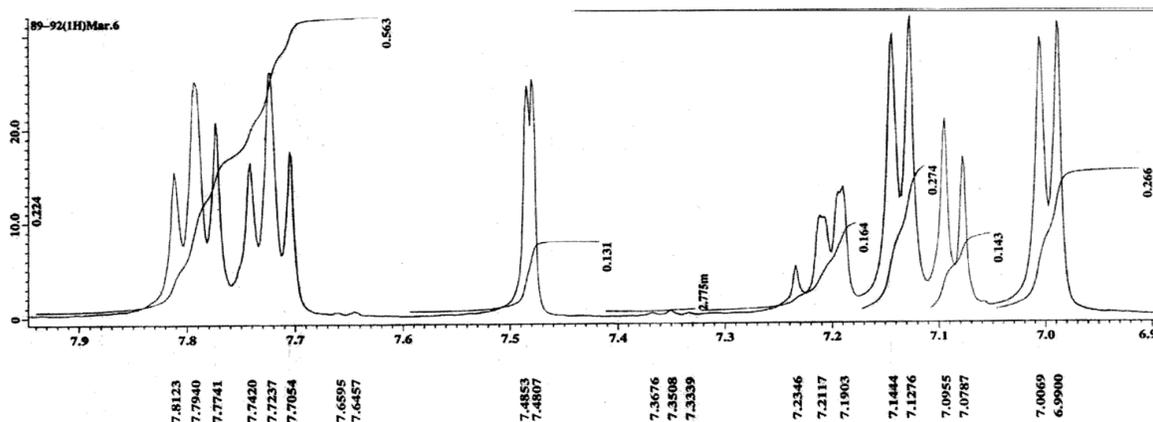
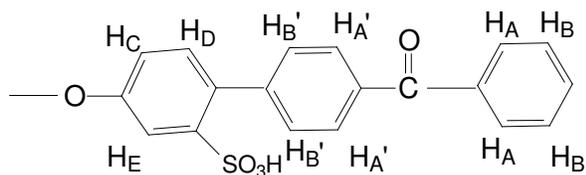


Fig. 5—¹H NMR of a polymeric membrane



The presence of each SO_3H group results in a distinct signals for protons at H_E positions. Intensity of H_E signal yields estimates of H_E content, which is equivalent to SO_3H content. The ^1NMR signal for SO_3H group is less easy to record directly because this proton is labile. The ratio between peak area of distinct H_E signal ($^A\text{H}_E$), and integrated peak area of the signals corresponding to all other aromatic hydrogens ($\text{AH}_{A, A', B, B', C, D}$), is expressed

$$n / (12-2n) = \frac{^A\text{H}_E}{\sum ^A\text{H}_{A, A', B, B', C, D}} \quad (0 \leq n \leq 1)$$

where n is the number of H_E per repeat unit. An estimate of the degree of sulphonation α is obtained as $\alpha = n \times 100\%$ ¹⁶. This method gives DS as mol %.

Infra Red (IR) and Raman Spectroscopy (RS)

IR and RS are widely used to obtain information about the composition, structure and conformation of the polymeric chains⁵⁷. IR spectra of sulphonated PEEK yield several significant differences when compared to the spectrum of PEEK. Presence of absorptions associated with sulphonic acid groups at 3440, 1252, 1080, 1024 and 709 cm^{-1} confirms sulphonation of the polymer. Intensities of these bands increases with increasing level of sulphonation relative to intensities of bands associated with the backbone (e.g. the $\text{C}=\text{O}$ stretch at 1652 cm^{-1}). Broad-band at 3450-3430 cm^{-1} can be assigned as the OH vibration. Asymmetric $\text{O}=\text{S}=\text{O}$ stretch appears at 1252 cm^{-1} and symmetric $\text{O}=\text{S}=\text{O}$ stretch appears at 1080 cm^{-1} , $\text{S}=\text{O}$ stretch at 1024 cm^{-1} and $\text{S}-\text{O}$ stretch at 709 cm^{-1} . Aromatic $\text{C}-\text{C}$ band appears at 1490 cm^{-1} . Intensity of new absorption (1472 cm^{-1}) increased with increased degree of sulphonation. The band at 1414 cm^{-1} will split upon sulphonation (new band at 1402 cm^{-1}). Both PEEK and sulphonated PEEK have a band at ~ 840 cm^{-1} , which is characteristic of the out of plane $\text{C}-\text{H}$ bending of two adjacent hydrogen. In addition, sulphonated polymers have an absorption at 865 cm^{-1} , which is characteristic of the out of plane CH bending of an isolated hydrogen in a 1,2,4- substituted phenyl ring. Intensity of the band at 865 cm^{-1} relative to that of at 840 cm^{-1} increased with increased level of sulphonation⁵⁸.

Other Properties of Polymeric Membranes

Various other mechanical properties, which are of practical importance of PMs are swelling behaviour, viscosity, membrane resistivity, methanol and water permeabilities, compaction, pure water flux (PWF), membrane hydraulic resistance (R_m), molecular weight cut-off, protein rejection, metal ion rejection, etc.

Swelling Behavior of Polymers

Swelling should be considered as an integral factor when developing new membranes, improving cell design and creating models. The existence of two stable ignited states in auto-humidified fuel cells and the cells' responses to dynamic conditions have revealed chemical-mechanical coupling in which the membrane's mechanical properties are changed by its water content which in turn changes cell performance and water production. Swelling behavior can be determined by immersing pre-weighed dry samples in water and the uptake of water calculated by measuring weight gain of samples at a given time interval⁵⁹. Excess surface water can be blotted out with filter paper before weighing. The weight degree of swelling (W_{sd}) is calculated as

$$W_{sd} (\%) = \frac{W_s - W_d}{W_d} \times 100$$

where, W_s and W_d denote the weight of the swollen and dry samples, respectively. Hydrophobic materials show excellent mechanical stability in aqueous environment. For dehydration purpose, membrane materials should exhibit enough affinity to water so that water can be preferentially adsorbed into the membrane, leading to a good membrane performance in terms of a high productivity and high selectivity. Therefore, hydrophobic polymers should first be imparted with some hydrophilicity before it can be applied for this purpose.

Viscosity

PMs are viscoelastic materials, whose mechanical properties depend on time⁶⁰. Viscosity is a measure of the friction and the associated energy dissipation between molecules of fluids. PMs due to their macromolecular (long-chain) structure are expected to have high viscosities. A major focus in the area of PEM development for fuel cells such as in the direct methanol fuel cell is in the optimization of parameters such as membrane resistivity, nanostructure, thermal behaviour, and methanol and water permeabilities.

Table 2—Guidelines to avoid compaction

Pressure	<20 bar	Minimal compaction
Temperature	<15°C	Compaction will be minimal
	15-50°C	Restrict pressure to 30 bar max.
	>50°C	Severe compaction is possible
	>80°C	Keep pressure below 5 bar; some compaction is inevitable

Compaction

Excessive trans-membrane pressure can flatten the membrane excessively (compaction), resulting in an irreversible drop of flux³. Besides the membranes' own ruggedness, it is vital to properly support membrane to prevent pressure squeezing the membrane into the support material. Compaction is a function of pressure and temperature (Table 2).

Flux

A well operating membrane filtration system must have a reasonable and stable flux and the energy consumption should be as low as possible. In order to achieve these goals, process must be optimised with respect to product flux, pressure and temperature⁶¹. Extremely high permeate flux can lead to unstable operation. Pressure can be used as a variable in RO and NF processes to optimise permeate flux, whereas the pressure does not determine the permeate flux in UF and MF processes. Water flux for most membranes increases by 3.3% per °C, and a temperature increase of 30°C will therefore double the water flux. This is unfortunately only true for very few products, because chemical and bacteriological phenomena tend to limit the flux in a number of ways. The full potential flux increase based on temperature is only realized on very pure water, or on effluents from the pulp and paper industry. In most other cases, it is more realistic to calculate with 1% increase per °C.

Molecular Weight Cut-off

Molecular weight cut off (MWCO) is a number expressed in Dalton indicating (cut off value) that 90% of the species with a molecular weight larger than the MWCO will be rejected. MWCO has a clear meaning for RO, but its meaning and value is becoming more and more vague with higher the MWCO is. It depends on the product on which a membrane is tested, and has little meaning for MF. MWCO of the membrane was determined by identifying an inert solute, which has lowest molecular weight and has solute rejection (80-100%) in steady-state UF experiments⁶².

Conclusions

There is ongoing research to find suitable membranes for fuel cell applications. Review presents recent advances made in the field of polymeric membranes for fuel cell applications. The perfluorinated polymer electrolytes used hitherto are being replaced by poly electrolyte membranes owing to the varied advantages of the latter. SPEEK is currently being used as a polymeric membrane in fuel cells extensively. Sulphonation plays a key role in establishing the properties of SPEEK. Various methods of sulphonation along with the methods to determine the degree of sulphonation have been highlighted.

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