

Review

A review of polymer electrolyte membranes for direct methanol fuel cells

Vladimir Neburchilov, Jonathan Martin, Haijiang Wang*, Jiujun Zhang

Institute for Fuel Cell Innovation, National Research Council Canada, Vancouver, BC, Canada V6T 1W5

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Abstract

This review describes the polymer electrolyte membranes (PEM) that are both under development and commercialized for direct methanol fuel cells (DMFC). Unlike the membranes for hydrogen fuelled PEM fuel cells, among which perfluorosulfonic acid based membranes show complete domination, the membranes for DMFC have numerous variations, each has its advantages and disadvantages. No single membrane is emerging as absolutely superior to others. This review outlines the prospects of the currently known membranes for DMFC. The membranes are evaluated according to various properties, including: methanol crossover, proton conductivity, durability, thermal stability and maximum power density. Hydrocarbon and composite fluorinated membranes currently show the most potential for low cost membranes with low methanol permeability and high durability. Some of these membranes are already beginning to impact the portable fuel cell market.

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Keywords: Polymer electrolyte membrane; DMFC; Methanol crossover; Proton conductivity; Durability; Thermal stability

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* Corresponding author. Tel.: +1 604 221 3038; fax: +1 604 221 3001.
E-mail address: haijiang.wang@nrc.gc.ca (H. Wang).

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1. Introduction

The market for mobile fuel cells, with DMFC technologies expected to account for a large portion, is projected to reach US\$2.6 billion by 2012 [1]. The US Department of Energy (DOE) has forecasted commercialization of portable fuel cell in 2010. The DOE also gave 2010 targets for portable fuel cells, which will be necessary to achieve the aforementioned forecasts. The DOE 2010 targets are [2]:

- power density, 100 W l⁻¹
- energy density, 1000 Wh l⁻¹
- lifetime, 5000 h
- cost, \$3 W⁻¹

There are substantial technology gaps between the current DMFC technology and the DOE targets. Such technology gaps for DMFC – the main alternative to Li-ion batteries in portable electronics – are impossible to bridge without significant improvements in the economical and technical efficiency of polymer electrolyte membranes. Currently, based on a 50 kW polymer electrolyte membrane fuel cell (PEMFC) for automotive applications, Nafion[®] polymer membranes account for 20% of the total cost of Nafion[®] based membrane electrode assemblies (MEAs) [3]. A Nafion[®] membrane based MEA for DMFC is expected to cost much more due to the thicker membranes needed for reduced methanol crossover. Nafion[®] membranes for DMFC applications typically have a price in the range of \$600–1200 m⁻², depending on the thickness. Alternatives to Nafion[®], on the other hand, are often significantly cheaper (i.e. sulfonated poly(ether ether ketone) membranes (sPEEK) have a price of \$375 m⁻²) [4].

In recent years, significant progress has been made in the development of polymer electrolyte membranes for DMFCs in terms of cost reduction and improvement of functionality, together with other associated technology advancements. An analysis of the DMFC technology development shows that some currently developed DMFC materials approach the DOE requirements. The following highlights some specific technologies that have significantly narrowed the technical gaps between the current technology and the DOE targets:

- cheap and durable membranes, such as the hydrocarbon membranes produced by polyfuel (5000 h lifetime in a passive DMFC);
- high performance non-platinum or low platinum anode catalysts (<0.2 mg cm⁻²);
- high performance non-platinum cathode catalysts with low precious metal loading (0.2–0.5 mg cm⁻²), i.e. palladium alloys;
- non-carbon cathode supports that are more resistant to oxidation, i.e. porous titanium.

1.1. Requirements for DMFC membranes

Although varying for different applications, common requirements for a polymer electrolyte membrane in DMFC applications include:

- operation at high temperature;
- low methanol crossover (MCO) (<10⁻⁶ mol min⁻¹ cm⁻¹) or low methanol diffusion coefficient in the membrane (<5.6 × 10⁻⁶ cm² s⁻¹ at T = 25 °C) [5];
- high ionic conductivity (>80 mS cm⁻¹) [5];

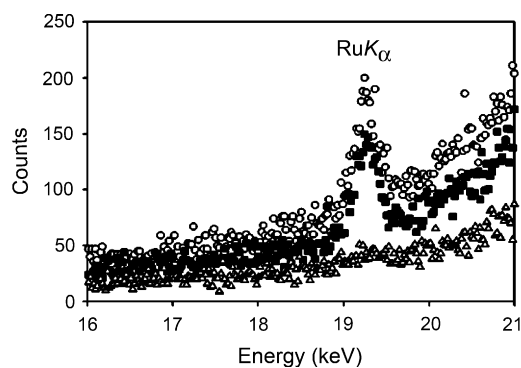


Fig. 1. XRF traces showing ruthenium crossover to the cathode for two used membranes (open circle and square) vs. an unused membrane (open triangle) [9]. Reproduced by permission of The Electrochemical Society.

- high chemical and mechanical durability especially at $T > 80^\circ\text{C}$ (for increased CO tolerance);
- low ruthenium crossover (in the case that the anode catalyst contains Ru);
- low cost ($< \$10\text{ kW}^{-1}$ based on a PEMFC) [6].

The most commonly used membranes for DMFCs, the DuPont's Nafion[®] membranes do not satisfy all of these requirements and have the following disadvantages:

- high cost, $\$600\text{--}1200\text{ m}^{-2}$ [4];
- high cost per unit power, 300 € kW^{-1} at 240 mW cm^{-2} [7];
- high MCO [3,5];
- high ruthenium crossover (in the case that the anode catalyst contains Ru) from the anode and its re-deposition on the cathode [8,9].

Only discovered recently, Ru crossover has a large impact on performance for DMFCs that utilize Ru at the anode. Piela et al. confirmed the presence of Ru in Nafion[®] 117 after use in a DMFC, as shown in Fig. 1 [9]. After crossover, the ruthenium re-deposits on the cathode, decreasing the performance of the DMFC.

An analysis of the DMFC market reveals four main types of membranes, which are or could be used in commercial DMFCs (Table 1). The first two groups of fluorinated commercial membranes, including Nafion[®] [10], were not specifically developed for DMFC applications. Nevertheless, Nafion[®] is now one of the main membranes for commercial DMFC use despite many inherent disadvantages for this application. Based on the Nafion[®]

Table 1
Classification of DMFC polymer membranes

1	Nafion [®] membranes
2	Non-Nafion [®] fluorinated membranes
3	Composite fluorinated membranes Organic–inorganic composite Acidic–basic composite
4	Composite non-fluorinated membranes Organic–inorganic composite Acidic–basic composite

analogy, the use of other fluorinated commercial membranes (second group) for DMFC applications should also be possible. This second group (some of which were analyzed for PEMFC applications in [11]) consists of membranes from the firms: Dow Chemical (USA) [12], Asahi Glass Engineering (Japan) (Flemion[®]R, IEC $1.0\text{ mequiv. g}^{-1}$ dry resin, $50\text{ }\mu\text{m}$ dried film thickness) [13], Asahi Kasei (Japan) (Aciplex-S[®], based on a weak functional acid ($-\text{COOH}$) instead of the SO_3H groups in Nafion[®]) [14], W.L. Gore & Associates (USA) (Gore-Tex[®], Gore-Select[®]) [15,16], and 3P Energy (Germany) [17]. The third and fourth groups contain membranes that are in various stages of development. Some examples are still in the laboratory stage, while a few others have been, to a degree, commercialized.

Some of the above mentioned membranes are only stable for a narrow temperature range. The upper limit of temperature is partially dictated by the degree to which membrane conductivity is affected by humidification. For membranes that require high humidity conditions, the maximum operating temperature is typically lower than those that do not.

Improvements to the structure and functionality of membranes are usually made by adding inorganic–organic and/or acidic–basic constituents to produce composite membranes (third and fourth groups). The water uptake of the membranes typically determines the proton conductivity and methanol permeation based on the ionomer microstructure, cluster and channel size [18]. MCO, in Nafion[®]-based membranes, likely also occurs via ion-cluster pores and ion channels within the hydrophobic polymer backbone [19]. Thus the change in membrane structure also changes the MCO. Some details of the current approaches used to improve DMFC membrane characteristics are given in the following sections.

1.1.1. Conductivity

Proton conductivity is determined two mechanisms: “proton hopping”(Grotthus) and migration of hydrated protons [$\text{H}^+(\text{H}_2\text{O})_n$ species] [20]. The main approaches for addressing the issue of proton conductivity in membranes is the use of additives. The electronic conductor, polyaniline, is a prospective additive because it increases the conductivity of Nafion[®]-based membranes due to the formation of a hydrophobic phase, alignment of the hydrophobic backbone structure of the membrane, and the subsequent alignment of the hydrophilic cluster by a secondary orientation effect [20]. The following lists the types of additives that have been utilized:

- catalysts for proton transport: Pd [21], Pt–Pd and Pt–Ag [22];
- electronic conductors: electronically conductive polyaniline (simultaneously reduces MCO) [23];
- acid sites: molybdophosphoric acid [24], phosphotungstic and silicotungstic acid [25,26];
- water retention amplifier: zirconium phosphate [27,28];
- structure modifier: hydroxyapatite [29] and Zeolite [30].

Table 2
Effect of DMFC parameters on methanol crossover [3]

Parameters increased	Reduction of methanol crossover	Effect on DMFC performance	
		High current	Low current
Membrane thickness	+	–	+
Equivalent weight	+	–	+
Temperature	–	+	+
Cathode pressure	+	+	+
Current density	+	–	–
Methanol concentration	–	+	–

1.1.2. Methanol crossover

MCO decreases the performance of DMFCs in three main ways, poisoning of the cathode catalyst, fuel efficiency reduction and electrode potential reduction due to methanol oxidation at the cathode. Some passive approaches to MCO reduction, such as the use of diluted methanol and operation at low temperatures, negatively affect DMFC performance [6,17]. Table 2 [3] shows the effect that increases in various parameters have on both MCO and performance.

An active approach to the reduction of MCO is the modification of fluorinated and non-fluorinated membranes (PBI, sPEEK, AMPS (asymmetric based acrylic), etc.) through the addition of inorganic components. This approach can dramatically reduce the MCO without lowering the proton conductivity.

1.1.3. Thermal stability

Nafion[®] based membranes have a limited range of working temperatures. However, high operation temperatures provide the following advantages:

- improved tolerance of the electrodes to carbon monoxide;
- simplification of the cooling system;
- possible use of co-generated heat;
- improved proton conductivity;
- improved kinetics of methanol oxidation.

The limited temperature range of fluorinated membranes can be addressed by the use of proton-conducting hydrocarbon and heterocyclic-based polymer membranes that are more stable at high operating temperatures. These membranes are often developed on the basis of acidic and basic polymers such as: poly(ether ketones) (PEK) or their derivations (sPEEK, etc.) [31–43], poly(arylene thioethylene sulfone) [44], sulfonated polysulfones (sPSU) [45–47], polystyrene sulfonate (PSS) [48], poly(phenyl quinoxaline) (PPQ) and polybenzimidazole (PBI) [49–53], and styrene grafted and sulfonated poly(vinylidene fluoride) (PVDF-g-PSSA) [54,55].

Another factor that limits the operating temperature of DMFCs is water-assisted nature of the majority of proton-conducting polymer membranes. For instance, at an operating pressure of 3 atm, the upper limit of operating temperature for a water-saturated environment is ca. 135 °C [39].

1.1.4. Lifetime

The stability of Nafion[®] membranes in DMFC conditions is insufficient for the long operational lifetime required for commercial DMFCs. This has led to the development of non-fluorinated membranes with higher durability and lifetime ranging from 500 to 4000 h [39]. Polyfuel, for instance, announced their new hydrocarbon membranes for DMFC applications with a 5000 h lifetime [56]. Several hydrocarbon membranes are able to maintain long lifetimes during operation at high temperatures ($T > 100$ °C) at which Nafion[®] is not stable. Modification of hydrocarbon membranes with inorganic components also increases their durability, i.e. sPEEK membranes modified by silica (See Section 5.1.2). The inorganic component fixes the heteropolyacid within the membrane and correspondingly increasing the stability [72].

1.1.5. Membrane compatibility with Nafion[®]-bonded electrodes

Unfortunately, promising membranes such as sPEEK and BPSH (with low MCO and high proton conductivity) have low compatibility and adhesion with Nafion[®]-bonded electrodes [57,58]. For sPEEK, this behavior is determined by the high water uptake, which increases with degree of sulfonation [57]. Alternately, the surface fluorine enrichment (38%) for hexafluoro bisphenol A-based poly(arylene ether benzonitrile) membrane (6FCN-35) provides better adhesion with Nafion[®]-bonded electrodes and lower interfacial resistance [33].

2. Nafion[®] membranes (DuPont)

Nafion[®] (with the structure shown in Fig. 2) is the major type of commercially available membrane for DMFC and PEMFC technologies [20,59]. The Nafion[®] membrane is relatively durable (unsurpassed longevity >60,000 h in the PEMFC [39]) and has high ionic conductivity and chemical stability. The hydrophobic polytetrafluoroethylene (PTFE) backbone of Nafion[®] provides thermal and chemical stability, whereas, the perfluorinated side chains terminating with hydrophilic sulfonic acid ($-\text{SO}_3\text{H}$) provides the channels for proton conduction. Protons migrate through the hydrophilic phase from anode to cathode with a relatively high conductivity of 90–120 mS cm^{-1} at 80 °C in the relative humidity (RH) range of 34–100% [60,61].

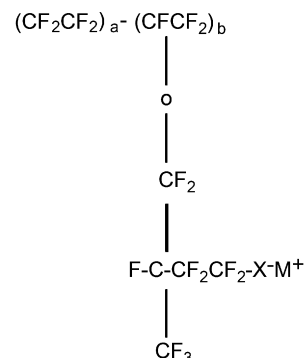


Fig. 2. Nafion[®] structure [3].

Nafion[®] membranes also have disadvantages in DMFC applications: high methanol and ruthenium (for Pt–Ru anodes) crossover, high cost, low temperature limit (<80 °C), and high humidification requirements, among which MCO, which reduces the efficiency of the oxygen reduction reaction (ORR) by the known mixed potential effect, is the major barrier preventing Nafion[®] membranes from being used successfully in DMFCs. Although Nafion[®] 112 is the most commonly used membrane for PEM fuel cells, Nafion[®] 117 is preferred for DMFC applications, in spite of higher ionic resistance, due to the significant reduction in MCO [32]. A study of the crossover behavior of Nafion[®] 117, Nafion[®] 1135, Nafion[®] 1035, and Nafion[®] 112 was conducted using cyclic voltammetry [62]. It was shown that the concentration of crossed methanol decreases with increasing thickness and equivalent weight.

Increasing competition from alternative proton-conducting membrane technologies has led to improvements in DuPont's Nafion[®] products. In 2005, DuPont announced its latest technology for DMFC applications, the Gen IV MEA. The new technology demonstrated a 20% increase in power density, twice the durability and significantly lower catalyst loading requirements than their previous MEA [10].

3. Non-Nafion[®] fluorinated membranes

3.1. Dow chemical XUS[®] membranes

The Dow membrane is prepared by the co-polymerisation of tetrafluoroethylene with a vinylene monomer. With its short side-chain the Dow membrane functions very different from Nafion[®]. The specific conductance of the 800 and 850 EW (equivalent weight, grams of dry polymer per mole of ion exchange sites) membranes is 0.2 and 0.12 $\Omega^{-1} \text{ cm}^{-1}$, respectively [11]. They have higher MCO than Nafion[®] 117 but, with a thickness of 125 μm , are 50 μm thinner. Expressed in terms of ionic current, tests showed approximate values of MCO to be 4×10^{-10} and $2.7 \times 10^{-10} \text{ A cm}^{-2}$ for the XUS and Nafion[®] membranes, respectively [12].

There is no DMFC performance data for the Dow membrane known to the authors. Performance testing of a Dow membrane in a six cell Ballard Power Systems PEMFC MK4 stack in 1988 showed better performance than with Nafion[®] (at $E = 0.5 \text{ V}$, $j = 5000$ and 1400 A ft^{-2} , respectively) [11].

3.2. 3P energy membranes

The German firm 3P-energy developed a perfluorinated sulfonic acid (PFSA) membrane. The 3P-membranes have 20 times lower MCO than commercially available Nafion[®] membrane. A DMFC fabricated with the 3P-membrane could operate with a higher methanol concentration, resulting in a higher power density [14]. Unfortunately, other properties such as mechanical durability and lifetime data for the 3P-membranes were not available in the open literature.

The membranes of other known firms such as Asahi Glass Engineering (Flemion[®] membranes) [13], Asahi Kasei

(Aciplex[®] membranes) [14], Gore & Associates [15,16] have been recommended by their manufacturers for PEMFC, but may also be modified for use in DMFC applications.

4. Composite fluorinated membranes

One of the main approaches taken to improve the performance of perfluorinated membranes is the creation of composite membranes. Both organic–inorganic composites (which reduce methanol crossover) and acidic–basic polyaryl composites (which reduce methanol crossover and increase conductivity) have been investigated.

4.1. Organic–inorganic composite membranes

4.1.1. Zirconium hydrogen phosphate modified Nafion[®]

Nafion[®]-zirconium membranes can be prepared by starting with an extruded film such as Nafion[®] 115. The film is then impregnated with zirconium phosphate (ZrP) via an exchange reaction involving zirconium ions followed by precipitation of zirconium phosphate by immersion of the membrane in H_3PO_4 solution. The result is an insoluble ZrP entrapped in the pores of the Nafion[®] membrane.

Nafion[®]-zirconium membrane is stable at $T = 150 \text{ °C}$ with dry oxidant. The membrane resistance was measured as $0.08 \Omega \text{ cm}^2$ and maximum power densities of 380 and 260 mW cm^{-2} for a DMFC with this membrane were achieved with oxygen and air feeds, respectively. The ZrP additive enhanced water retention characteristics, raised the maximum working temperature, and increased the dry weight and thickness of the membrane by 23% and 30%, respectively [28]. The membrane resistance decreased from $0.12 \Omega \text{ cm}^2$ at 90 °C to $0.08 \Omega \text{ cm}^2$ at $140\text{--}150 \text{ °C}$. The OCV of the DMFC cell was measured between 0.86 and 0.87 V during the operation between 120 and 150 °C with oxygen or air [27].

Crystallinity and surface morphology play an important role in determining the conductivity of ZrP modified membranes. The distribution of ZrP particles inside the membrane is uniform and the particle size is 1161 nm, which is larger than the pore size of the bare Nafion[®] membrane under complete hydration. The surface area of the Nafion[®] membrane increases by two orders of magnitude when modified by ZrP. Nafion[®]-zirconium membranes also have comparable proton conductivity to that of Nafion[®] ($10^{-2} \text{ S cm}^{-1}$) at room temperature and 100% relative humidity [28].

4.1.2. Silica and molybdophosphoric acid modified Nafion[®]

Modification of Nafion[®] through the addition of silica is a common approach utilized for the improvement of membrane performance in DMFC applications. Nafion[®]-silica membranes have been prepared according to several methods by casting mixtures such as: silica powder [24], diethylenetriamine (DETA) [63], sol–gel reaction with tetraethylorthosilicate (TEOS) followed by solution casting of the Nafion[®] solution [64], phosphotungstic acid (PWA)-doped composite silica/Nafion[®]/PWA [65] and silica oxide [25,66].

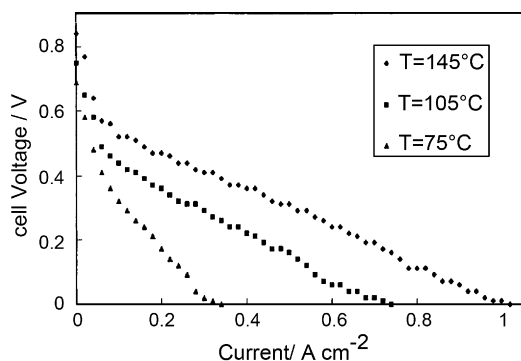


Fig. 3. Effect of operating temperature on DMFC performance with Nafion[®]-SiO₂ membrane (oxygen feed) [25]. Reprinted from Solid State Ionics, 125, P.L. Antonucci, A.S. Aricò, P. Cretí, E. Ramunni, V. Antonucci, Investigation of a direct methanol fuel cell based on a composite Nafion[®]-silica electrolyte for high temperature operation, 431–437, Copyright (1999), with permission from Elsevier.

Nafion[®]-silica membranes show good performance at $T > 100^\circ\text{C}$ due to low levels of dehydration. Nafion[®]-silica membranes were prepared by mixing Nafion[®] ionomer (5%) with 3% SiO₂ followed by a regular membrane casting procedure. In the final stage, the membranes were heat-treated at 160°C for 10 min to achieve both a high crystallinity and high mechanical stability [25].

A DMFC utilizing these membranes was tested under galvanostatic conditions at 500 mA cm^{-2} . The voltage initially decreased from 0.42 to 0.36 V but then remained stable for 8 h. The performance decrease is due to adsorption of poisoning species, which appears to be a reversible process at 145°C (removed by short circuit discharging in the presence of water). The effect of the operating temperature on performance of DMFCs with this membrane (conditions as mentioned above) is given in Fig. 3, demonstrating higher performance with increasing temperature [25].

Nafion[®] membranes with 10–20 wt% DPS have a nanolayered microstructure that results in low MCO. The proton conductivity increases with increasing DPS content, as the phenyl group can impact hydrophobic characteristics and reduces water adsorption. The increase in the hydrophobic properties of the membrane reduces flooding at the DMFC cathode [63]. DMFC performance with this membrane is dominated by MCO at high methanol concentrations and by resistance at low concentrations (1 M). The methanol crossover current density (mA cm^{-2}) and conductivity ($\times 10^{-2}\text{ S cm}^{-1}$) for the different membranes were: 329 and 2.89 for Nafion[®], 183 and 2.39 for

Nafion[®]/10 wt% DPS, and 160 and 2.16 for Nafion[®]/20 wt% DPS [63].

Nafion[®]/5 wt% silica membranes utilizing TEOS, fabricated according to the sol-gel method, have a methanol permeability of $4.17 \times 10^{-7}\text{ cm}^2\text{ s}^{-1}$ in a two glass compartment cell at 20°C in 1 M methanol, compared to $9.7 \times 10^{-7}\text{ cm}^2\text{ s}^{-1}$ for Nafion[®]. The membranes with 3 and 5 wt% silica have a MCO of 215–245 mA cm^{-2} in a DMFC at 60°C and fuelled with 3 ml min^{-1} of 1 M methanol, versus 273 mA cm^{-2} for Nafion[®]. The conductivity of a Nafion[®]/10% SiO₂ membrane was found to be slightly lower than for pure Nafion[®] 112 [64].

A DMFC with the Nafion[®]-SiO₂ membrane (80 μm thick) could be operated at $T = 145^\circ\text{C}$ and reach a maximum power density of 240 and 150 mW cm^{-2} with an oxygen and air feed supply, respectively. MCO was $4 \times 10^{-6}\text{ mol min}^{-1}\text{ cm}^{-1}$ at $j = 0.5\text{ A cm}^{-2}$ with 2 M methanol. A Pt-Ru/C catalyst with a loading of 2 mg cm^{-2} was used at the anode and a 20% Pt/C catalyst with a 2 mg cm^{-2} loading was used at the cathode. The operating pressure at the anode was 3.5 and 5.5 atm O₂ was supplied to the cathode. Fig. 3 shows the performance of this membrane at various operating temperatures [25].

The modification of Nafion[®] membranes through the addition of molybdophosphoric acid (MoPh-a) has been shown to increase the proton conductivity 2–2.5 times, but with slightly increased MCO [24]. As shown in Table 3, Nafion[®] membranes modified by 3.3% MoPh-a and 4.3% SiO₂ have slightly higher MCO than Nafion[®] 117 but much higher conductivity.

A polyaniline coating was used to create Polyaniline-Nafion[®]-Silica nanocomposite membranes (PaniNC), a modified membrane with decreased MCO. Polyaniline, an electronically conductive polymer, modifies the membrane structure and correspondingly reduces the MCO while the silica nanocomposite improves the conductivity. One approach to prepare PaniNC membrane is through the sol-gel method. This method embeds the silica in the hydrophilic clusters of Nafion[®] first. Polyaniline was then deposited on the silica-Nafion[®] membranes by redox polymerization [23].

4.1.3. Nafion[®]-polyfurfuryl alcohol nanocomposite membranes

Nafion[®]-polyfurfuryl alcohol (PFA) nanocomposite membranes can be synthesized by in situ polymerisation of furfuryl alcohol within commercial Nafion[®] membranes. Furfuryl alcohol is miscible with mixtures of water and alcohols (it penetrates into the hydrophilic channels of Nafion[®]) and becomes hydrophobic following polymerization via acid catal-

Table 3
Effect of the composition of Nafion[®] composite membranes on conductivity and methanol crossover

Membrane type	Conductivity (S cm^{-1})		Equivalent methanol permeation, ($\text{mol s}^{-1}\text{ m}^{-1}$) in 1.5 M methanol at $T = 65^\circ\text{C}$
	$T = 60^\circ\text{C}$	$T = 90^\circ\text{C}$	
Nafion [®] 117 + 4.3% SiO ₂	0.23	0.29	7
Nafion [®] 117 + 3.3% H ₃ PO ₄ ·12 MoO ₃ ·H ₂ O (MoPh-a)	0.27	0.39	7.5
Nafion [®] 117	0.09	0.15	5.9

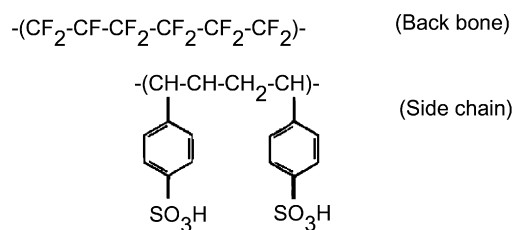


Fig. 4. Structure of Pall membrane R-1010 [70]. Reproduced by permission of The Electrochemical Society.

ysis. The chemically stable PFA is responsible for the low MCO through homogenous Nafion[®]-PFA nanocomposite membranes at PFA concentrations varying from 3.9 to 8%.

The Nafion[®]-8 wt.% PFA membrane has a MCO of $1.72 \times 10^{-6} \text{ mol min}^{-1} \text{ cm}^{-1}$ and a proton conductivity of 70.4 mS cm^{-1} at room temperature. The corresponding properties of Nafion[®] 115 are $4.66 \times 10^{-6} \text{ mol min}^{-1} \text{ cm}^{-1}$ and 95.3 mS cm^{-1} [67]. The 26% lower conductivity of Nafion[®]-8% PFA is offset by almost three times lower MCO. The Nafion[®]-4.7% PFA (290 mV) has much higher cell performance than the plain Nafion[®] 115 (58 mV) at $j = 40 \text{ mA cm}^{-2}$, $T = 60^\circ\text{C}$, 1 M methanol and ambient air. The OCV for Nafion[®]-4.7% PFA is 705 mV compared to 624 mV for Nafion[®].

4.2. Acid–base composite membranes

4.2.1. Nafion[®] polypyrrole based membranes

Nafion[®] polypyrrole based membranes had been prepared by two methods [66]: the impregnation of polypyrrole by in situ polymerization and polymerization in hydrogen peroxide with Fe(III) as the oxidizing agent. Pyrrole has good solubility in water, which simplifies the preparation procedure for these membranes. The membranes modified via Fe(III) oxidation have low MCO but high resistance and poor performance in comparison with Nafion[®]-based DMFCs due to poor electrode bonding.

The methanol permeation of poly(1-methyl pyrrole) coated Nafion[®] 117 changes with time. The value decreased (as measured by gas chromatography) from 1.47×10^{-9} to $6.63 \times 10^{-12} \text{ mol cm}^{-2} \text{ s}^{-1}$ after 24 h of conditioning. The conditioning procedure was conducted at OCV, $T = 25^\circ\text{C}$, in 1 M sulfuric acid plus 1 M methanol, 1 mg cm^{-2} of PtRu(1:1) at the anode, and 0.4 mg cm^{-2} of 20% Pt/C at the cathode. The methanol permeation further decreased from 6.63×10^{-12} to $1.47 \times 10^{-12} \text{ mol cm}^{-2} \text{ s}^{-1}$ after 6 days of conditioning at OCV [68]. The effect of methanol fluid convection within the membrane by protonic flow induced electroosmotic drag was reduced by the presence of 1 M sulfuric acid.

4.3. Pall IonClad[®] membranes

Pall Gelman Sciences Inc. produces Pall IonClad[®] membranes, which are based on tetra-fluoroethylene/perfluoropropylene. IonClad[®] R-1010 (36 μm thick, shown in Fig. 4) and IonClad[®] R-4010 (63 μm thick) have 2.5–3 times lower MCO than Nafion[®] 117 (180 μm thick) [69]. A comparison of all three membranes studied is shown in Table 4. The stability

Table 4
Comparison of the membrane parameters [64]

Temperature, °C	Pall R-4010	Pall R-1010	Nafion [®] 117
Conductivity, (mS cm^{-1})			
20	73	80	79
Methanol permeability ($\times 10^7$), $\text{cm}^2 \text{ s}^{-1}$			
60	9.4	13.7	34.4

of the Pall membranes for a PEMFC was estimated to be 500 h [70].

The complex parameter ϕ (ratio of proton conductivity to methanol crossover) has been suggested for the evaluation of the performance of membranes for DMFC. This parameter contains two physical factors: the diffusion of protons and methanol and the concentration of protons and methanol. Apparently, the higher the value of ϕ is, the better the performance of the membrane. The Pall R4010 membranes at $T = 80^\circ\text{C}$ have $\phi = 130$, compared to $\phi = 37$ for Nafion[®] 117.

5. Non-fluorinated membranes

Non-fluorinated membranes seem to have a promising future for DMFCs as replacements for the expensive fluorinated membranes that have high methanol and ruthenium crossover. We will now discuss this type of membranes.

5.1. Organic–inorganic composite membranes

5.1.1. Polyvinylidene fluoride + SiO₂ (or SiO₂ gel) + acid membranes

The modified polyvinylidene fluoride (PVDF) membranes (24% PVDF–16% SiO₂ with 60%–3 M H₂SO₄ (vol%)) are nanoporous proton-conducting membranes (NP-PCM). The membranes, which utilize PVDF as the polymer binder to implant SiO₂ powder and acid into the polymer matrix to provide proton conductivity, can have very high surface area and thus two to four times higher ionic conductivity than Nafion[®]. Meanwhile, the MCO of PVDF membranes are two to four times lower than Nafion[®] due to smaller pore sizes (1.5–3 nm compared to 3 nm for Nafion[®]) [71].

Impregnation of the NP-PCM pores with Na₂SiO₃ solution and hydrolyzing the silicate in sulfuric acid (forming silica gel) decreases the MCO further to almost an order of magnitude lower than Nafion[®]. Table 5 shows a comparison between two modified PVDF membranes and Nafion[®] [71].

Table 5
Effect of temperature and membrane composition on (a) MCO (mA cm^{-2}) and (b) conductivity (mS cm^{-1})

Temperature (°C)	PVDF + 16% SiO ₂ (300 μm)	PVDF + silica gel (225 μm)	Nafion [®] 117
60 a	53	22	125–150
80 a	74	37	–
90 a	–	42	250–300
25 b	200	70	–

These membranes operate in a wider temperature range than Nafion[®] (from 0 to over 90 °C). They are also less sensitive to iron impurities (Fe > 500 ppm) than Nafion[®], which allows for the use of Pt–Fe catalysts or stainless steel fuel cell hardware. MEAs utilizing these membranes have achieved power densities of 85 mW cm⁻² (at $T = 80$ °C, 1 M methanol, and a Pt–Ru anode with a loading of 4–6 mg cm⁻²). At about \$4 m⁻², the cost of modified PVDF is significantly lower than Nafion[®] [71].

Modified PVDF membranes have good mechanical properties and can be bent 180° without breaking (at membrane thicknesses 30–1000 μm). They can be manufactured with 50–90% (by volume) acid solution, have a high thermal stability (from subzero to over 100 °C) and have stable dimensions which do not change with absorption of water.

5.1.2. Silanes/silica modified sulfonated poly(ether ether ketone)

SPEEK-based membranes were developed to contain heteropolyacids and an oxide phase that was either produced by hydrolysis of amino-modified silanes or by dispersion of a surface-modified fumed silica. The degree of sulfonation ranged from 65 to 66%. The heteropolyacid was based on lacunary divacant [γ -SiW₁₀O₃₆]⁻⁸ and contained epoxy groups. The reaction provided a covalent bond between the heteropolyacid and the insoluble oxide phase, resulting in its fixation within the membrane [72].

The organic–inorganic materials are mechanically more stable than membranes without inorganic compounds in alcohol solutions. Heteropolyacid has good proton conductivity but degradation was shown to be an issue for DMFC applications due to its dissolution in water. The stability has usually been increased through silica modification, which increases the strength of the covalent bonds or columbic interactions but reduces the acid strength. Heteropolyacid bleeding can also be reduced through the addition of silanes (S66/RSiO_{3/2}/H4) and the dispersion of surface-modified, fumed silica (S66/Aerosil 380/H4) [72]. In comparison with non-modified sPEEK S66 (with 65–66% sulfonation and IEC: 1.66 mequiv. g⁻¹) the modified membranes have:

- lower methanol permeability (0.3×10^{16} m² s⁻¹ Pa⁻¹ for silane modified and 0.8×10^{16} m² s⁻¹ Pa⁻¹ for silica modified) at $T = 55$ °C and 20% methanol (MCO is lower than that of the plain membrane when alkoxysilane was used to generate the oxide phase);
- proton conductivities of 4, 10, and 12 mS cm⁻¹, respectively (at RH = 100% and $T = 70$ °C).

The silane modified sPEEK membrane has lower methanol crossover but also lower conductivity than that modified by silica. The inorganic phase decreases the water and methanol crossover, in addition to fixing of the heteropolyacid to the membrane. The stability of these membranes is higher than unmodified sPEEK due to their higher stability in alcohol solution.

The modification of sPEEK by ZrP (10%) and PBI (5.6%) produces a membrane with [73]:

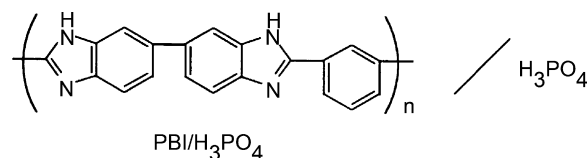


Fig. 5. Phosphoric acid doped PBI structure [37]. Reprinted from Progress in Polymer Science, M. Rikukawa, K. Sanui, Proton-conducting polymer electrolyte membranes based on hydrocarbon polymers, 1463–1502, Copyright (2000), with permission from Elsevier.

- maximum power density of 50.1 mW cm⁻² at $j = 250$ mA cm⁻² and $T = 130$ °C;
- improved chemical stability and DMFC efficiency over unmodified sPEEK.

5.1.3. Polybenzimidazole based membranes

The PBI based membranes were cast from a solution of high molecular weight PBI in dimethylacetamide (DMAc) followed by immersion into an 11 M solution of phosphoric acid. PBI is a basic polymer ($pK_a = 5.5$) and doping with acid forms a single-phase polymer electrolyte that has a good oxidative and thermal stability, and mechanical flexibility at elevated temperatures $T < 200$ °C [49]. At $T > 100$ °C, these membranes have the following advantages in comparison with Nafion[®]:

- high proton conductivity;
- low electroosmotic drag (ca. 0 compared to 0.6 for Nafion[®]) [49] with minimal effect of water content on proton transport through the PBI;
- operation at high temperature ($T = 200$ °C) and low gas humidification;
- low MCO at 80 μm thick it is 1/10 of 210 μm thick Nafion[®];
- low cost (165 £ kg⁻¹) in comparison with Nafion[®] [3].

The major disadvantage is leaching of the low molecular weight acid (H₃PO₄, shown in Fig. 5) in hot methanol solutions. These problems were solved by the addition of high molecular weight phosphotungstic acid as a replacement of the low molecular weight acid. At $T > 130$ °C the conductivity of the doped PBI membrane is similar to Nafion[®] (30 mS cm⁻¹ at 130 °C and 80 mS cm⁻¹ at 200 °C). The methanol crossover at different methanol concentrations is as shown in Table 6 [49].

The maximum methanol crossover from Table 6 (10.7 mA cm⁻² at 100% methanol) is in good agreement with Wainright et al. [50]. The DMFC used by Wainright et al. achieved a power density of 210 mW cm⁻² at $T = 200$ °C,

Table 6

Effect of methanol concentration on MCO in a DMFC $E = 0.9$ V (RHE), $T = 180$ °C, PBI doped in 5 M H₃PO₄, air flow, anode feed (24.7 ml min⁻¹), anode (Pt/C, 0.5 mg cm⁻²) and cathode (Pt/C, 4 mg cm⁻²)

Water:methanol	Methanol crossover (mA cm ⁻²)
3	4.5
2	6.4
1	10.4
0 (pure methanol)	10.7

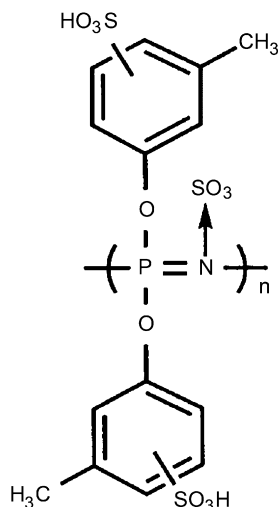


Fig. 6. Structure of sPPZ [39]. Reprinted, with permission, from the Annual Review of Materials Research, Volume 33, Copyright (2003) by Annual Reviews www.annualreviews.org.

atmospheric pressure, a water/methanol ratio of 2:1, and $j = 500 \text{ mA cm}^{-2}$.

Recently, a PBI-based membrane was commercialized by PEMEAS (USA) for DMFC applications. The Celtec[®] V membrane has operating temperatures that range from $T = 60$ to 160°C without humidification, can be produced much cheaper than Nafion[®], has low methanol crossover and possesses good mechanical properties [74]. However, quantitative data on the lifetime and durability of PBI-based membranes were not found in the literature.

5.2. Acid–base membranes (direct modification of a polymer backbone)

5.2.1. Acid–base composite membranes (direct modification of a polymer backbone)

5.2.1.1. Sulfonated polyphosphazene membranes. The sulfonated polyphosphazene (sPPZ) membranes (Fig. 6) were prepared by dissolving benzophenone (a photo-initiator) in the membrane casting solution and then the resulting films, after solvent evaporation, were exposed to UV light. The films of ethane cross-linked polyphosphazene can be sulfonated from the surface inward. This prevents dissolution in water, thus allowing sulfonation to proceed through the material. sPPZ has some of the highest thermal and chemical stability and low methanol crossover in DMFC operation. Its modification, sulfonated poly[bis(3-methylphenoxy) phosphazene], also has a high proton conductivity and the methanol diffusion coefficient ($1.6 \times 10^{-8} \text{ cm}^2 \text{ s}^{-1}$) was much lower than for Nafion[®] ($6.5 \times 10^{-6} \text{ cm}^2 \text{ s}^{-1}$) at $T = 30^\circ\text{C}$ and 1 M methanol [75]. The advantages of these membranes, at $200 \mu\text{m}$ thick, are:

- low cost;
- good proton conductivity at higher sulfonation, only 30% lower than Nafion[®] 117;

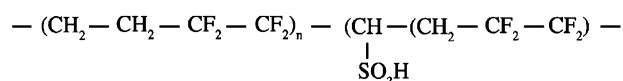


Fig. 7. ETFE-SA structure [76]. Reprinted from Electrochimica Acta, 50, V.Saarinen, T. Kallio, M. Paronen, P. Tikkanen, E. Rauhala, K. Kontturi, New ETFE-based membrane for direct methanol fuel cell, 3453–3460, Copyright (2005), with permission from Elsevier.

- low water and methanol diffusivities in the crosslinked polyphosphazene ($1.2 \times 10^{-7} \text{ cm}^2 \text{ s}^{-1}$);
- crosslinked sPPZ membranes have good mechanical properties, without failure (softening) up to 173°C and a pressure of 800 kPa;
- high chemical stability in a hot hydrogen peroxide/ferrous ion solution.

5.2.2. Acid–base membranes (direct modification of a polymer backbone)

5.2.2.1. Irradiated sulfonated poly(ethylene-alt-tetrafluoroethylene) membranes. Nowofol GmbH manufactures an irradiated and sulfonated poly(ethylene-alt-tetrafluoroethylene) (ETFE) polymer known as ETFE-SA (Fig. 7). The ETFE-SA membranes are prepared by irradiation (with a total dose of 500 kGy and dose rate of 2.7 kGy s^{-1}) followed by sulfonation without grafts of other polymers. The membranes are typically semi-crystalline and the cross-linking effects of the crystallites result in the low swelling of the sulfonated membranes [76].

Sulfonation and adsorption of water into the amorphous structure decreases the initial crystallinity from 34% to 22% (Nafion[®] has 3–12% crystallinity). ETFE-SA has a larger number of chemical cross-links formed during sulfonation and irradiation than Nafion[®]. The conductivities of ETFE-SA and Nafion[®] 115 at 25°C are 10 and 40 mS cm^{-1} , respectively. For 1 and 2 M methanol solutions and at $T = 25^\circ\text{C}$, the MCO (in $\text{mol min}^{-1} \text{ cm}^{-1} \times 10^8$) are 0.3 and 0.6 for ETFE, respectively. Under the same conditions the MCO of Nafion[®] 115 are 6.7 and 12. ETFE-SA membranes ($35 \mu\text{m}$ thick) are cheaper than Nafion[®] 115 ($127 \mu\text{m}$ thick) and have the following advantages [76]:

- at $T = 25^\circ\text{C}$ the water and methanol uptake are 70% lower than Nafion[®] 115 and methanol permeability is 10% lower;
- a lifetime of over 2000 h in a DMFC without any performance loss (1300 h at $T = 30^\circ\text{C}$, 400 h at 50°C , 300 h at $70\text{--}85^\circ\text{C}$, completely broken at 100°C);
- cost of $\$30\text{--}100 \text{ m}^{-2}$ (in contrast to $\$500\text{--}2000 \text{ m}^{-2}$ for other commercial perfluorinated membranes).

The main disadvantage of ETFE-SA is a lower maximum power density (4.5 mW cm^{-2}) than Nafion[®] 115 (10.5 mW cm^{-2}) at $T = 30^\circ\text{C}$ in 1 M methanol.

5.2.2.2. Sulfonated poly(ether ether ketone). A SPEEK membrane with 38% sulfonation (the structure is shown in Fig. 8) was prepared by casting a 10 wt% SPEEK in a dimethylformamide (DMF) solution on a glass plate and then drying at

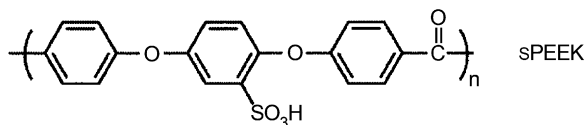


Fig. 8. sPEEK structure [39]. Reprinted, with permission, from the Annual Review of Materials Research, Volume 33, Copyright (2003) by Annual Reviews www.annualreviews.org.

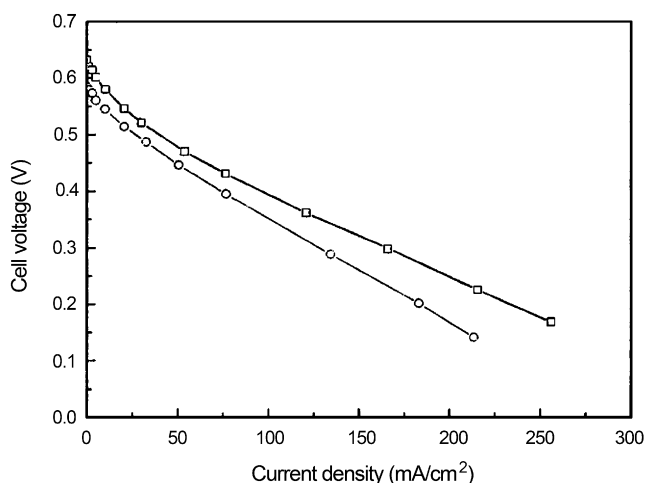


Fig. 9. Polarization curves for two MEAs equipped with sPEEK membranes prepared by two different methods ($T=80^{\circ}\text{C}$, oxygen feed, 2 M methanol) [77]. Reprinted from Journal of Materials Science Letters, 22, 2003, 1595–1597, Sulfonated polyether ether ketone membranes cured with different methods for direct methanol fuel cells, L. Li, J. Zhang, Y. Wang, Figure 3, Copyright (2003) Kluwer Academic Publishers, with kind permission of Springer Science and Business Media.

60°C for 6 h or 100°C for 4 h. SPEEK membranes ($78\ \mu\text{m}$) in DMFCs have lower methanol crossover and proton conductivity at $T=25^{\circ}\text{C}$ in 2 M methanol solution than Nafion[®] 115 (2.03×10^{-8} compared to $1.32 \times 10^{-6}\ \text{cm}^2\ \text{s}^{-1}$ and 0.9 compared to $21.4\ \text{mS}\ \text{cm}^{-1}$, respectively). The performance of a single DMFC with this membrane was $j=25\ \text{mA}\ \text{cm}^{-2}$ at $E=0.5\ \text{V}$ ($T=80^{\circ}\text{C}$, 2 M methanol, oxygen feed). The polarization curves are shown in Fig. 9 [77].

The electroosmotic drag of a $70\ \mu\text{m}$ thick sPEEK membrane is lower than that of Nafion[®] 115 at $T=85^{\circ}\text{C}$. The stability of the sPEEK membranes decrease with the degree of sulfonation. Instability can be addressed through cross-linking of the polymer. Suitable compounds for the desired cross-linking are

aliphatic and cyclic diamines such as diazobicyclooctane and aminopyridine. The chain length of the diamines can be varied and optimized so as to minimize the methanol flow through the membrane [39].

5.3. Acid–base composite membranes (direct polymerization from monomer units)

Non-fluorinated membranes can be improved by the direct synthesis of a new polymer from monomer building blocks functionalized with sulfonic acid or sulfonate groups. Control of the position, number, and distribution of protogenic functions along the polymer backbone could potentially provide access to more thermohydrolytically stable sulfonated polymers and allow tuning of the microstructure for high conductivity and low swelling [3]. However, the cost of such modified membranes can be higher than membranes produced by direct sulfonation.

5.3.1. Poly(arylene ether sulfone) based membranes

Los Alamos National Laboratory and Virginia Polytechnic Institute created the bi-phenol based poly(arylene ether sulfone) (PES) membrane BPSH-40 (40 refers to the molar fraction of sulfonic acid by percent) and a poly(arylene ether benzonitrile) membrane 6FCN-35 (Fig. 10).

6FCN-35 consists of disulfonated poly(arylene ether benzonitrile) copolymers containing hexafluoroisopropylidene diphenol. The membranes were prepared by direct aromatic nucleophilic substitution and polycondensation of 4,4'-hexafluoroisopropylidene diphenol (6F), 2,6-dichlorobenzonitrile, and 3,3'-disulfonate-4,4'-dichlorodiphenylsulfone under basic conditions in *N*-methyl-2-pyrrolidione at 200°C . During the preparation process a 65:35 mole ratio was maintained between unsulfonated benzonitrile and the disulfonated sulfone monomer [33].

As is typically the case, water uptake correlated proportionally with ion exchange capacity (IEC), with both decreasing in the order of BPSH-40, 6FCN-35, and Nafion[®]. Nevertheless methanol permeability, which is typically proportional to water uptake and IEC, was two times higher for Nafion[®] than the other two membranes. Kim et al. [33] explain the situation by the presence of less loosely bonded and/or free water in BPSH membranes than Nafion[®] membranes (due to structural differences), even at the higher total water uptake.

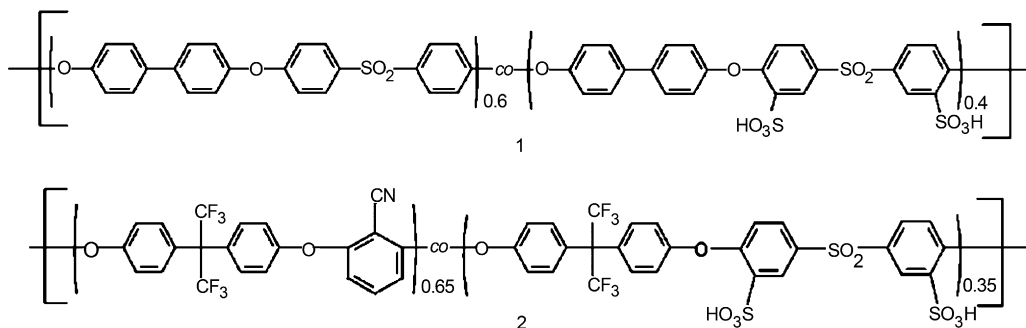


Fig. 10. Structures of 1: BPSH-40 and 2: 6FCN-35 [33]. Reproduced by permission of The Electrochemical Society.

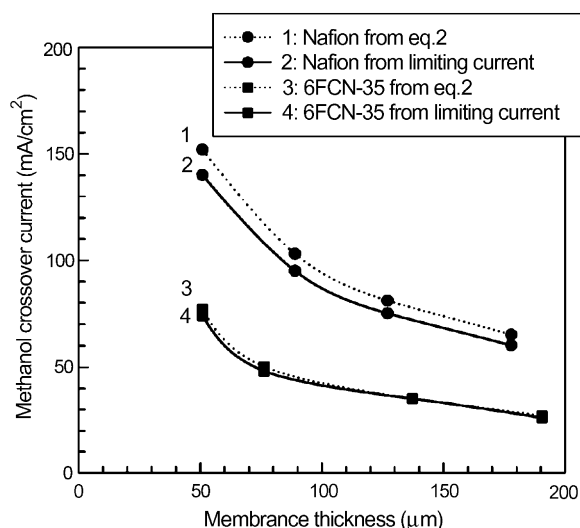


Fig. 11. Effect of thickness on MCO for Nafion[®] and 6FCN-35 membranes: dotted line, electro-osmotic drag corrected value; solid line, uncorrected value [33]. Reproduced by permission of The Electrochemical Society.

Another interesting feature of the 6FCN-35 membranes was fluorine enrichment of the air-contacting surface (38%), which had over twice the fluorine concentration of the bulk material (17%). It was hypothesized that the surface fluorine enrichment was the source of high adhesion to Nafion[®] bonded electrodes [33].

The MCO of 6FCN-35 and BPSH-40 are nearly equal (81×10^{-8} and $87 \times 10^{-8} \text{ cm}^2 \text{ cm}^{-1}$) with 0.5 M methanol at $T=30^\circ\text{C}$. At a slightly higher (10%) membrane resistance, the MCO is a factor of two lower than for Nafion[®] ($167 \times 10^{-8} \text{ cm}^2 \text{ cm}^{-1}$) (Fig. 11) [33]. The combination of MCO and resistance properties results in a 50% improvement in selectivity, regardless of membrane thickness, and a DMFC with this membrane has shown a performance of $j = 200 \text{ mA cm}^{-2}$ (compared to 150 mA cm^{-2} for Nafion[®]) at 0.5 V, $T = 80^\circ\text{C}$ and ambient air pressure [9].

Another prospective DMFC membrane (originally developed for PEMFC) composed of modified PES is sulfonated poly(arylene thioether sulfone) (sPTES) [45]. This membrane was synthesized at the Air Force Research Laboratory (AFRL) by dissolving the sodium for 6F-sPTES-50 copolymer (50% sulfonation) in DMAc followed by direct casting on a glass dish. Sulfonation increases the acidity and hydrophilicity, improving the conductivity but also increasing the water uptake. The latter problem was resolved by incorporation of $[-\text{CF}_3]$ groups into the backbone of the polymer resulting in a new sPTES modification with comparable water-uptake in the backbone to Nafion[®]. With the major disadvantage of sPTES membranes resolved, they have the following advantages:

- high chemical and thermal stability;
- higher proton conductivity ($>100 \text{ mS cm}^{-1}$) than Nafion[®] 112 (80 mS cm^{-1}) at $T=65^\circ\text{C}$ and $\text{RH} = 85\%$;
- comparable performance to Nafion[®] in DMFC applications;
- specific area resistance (ASR) of $0.13 \Omega \text{ cm}^2$ at 80°C and H_2/air feed (compared to $0.18 \Omega \text{ cm}^2$ for Nafion[®]);

Table 7

Comparison of Nafion[®] and sPEEK + (sPSU) + (PBI) membranes

Parameters DMFC	Methanol permeation equivalent (mA cm^{-2})		
	Nafion [®] 117	Nafion [®] 105	sPEEK + PBI + bPSU (E504)
OCV	163	343	195
$j = 200 \text{ mA cm}^{-2}$	103	257	150
$j = 500 \text{ mA cm}^{-2}$	–	135	–

- retains large amounts of water over a wide temperature range;
- cheaper than Nafion[®].

Lifetime data, however, for sPTES membranes was not found in the literature.

5.3.2. Composite membranes of sPEEK (or sPSU) with P4VP (or PBI)

The composite membranes (Fig. 12) have been prepared by blending main-chain polymers, sulfonated PEEK Victex or sulfonated PSU Udel (sPSU), with basic polymers, poly(4-vinylpyridine) (P4VP) or PBI. The membranes show comparable performance to Nafion[®] 105 (500 mV) at $j = 0.5 \text{ A cm}^{-2}$ and $T = 110^\circ\text{C}$. However, these membranes have higher methanol crossover than Nafion[®] 117 (150 mA cm^{-2}), as shown in Table 7. The testing parameters were: 5.3 mg cm^{-2} Pt black cathode, 5.2 mg cm^{-2} Pt/RuOx E-TEK anode, 4 ml min^{-1} of 1 M methanol at 2.5 bar, 1.5 ml min^{-1} of air at 4 bar [42].

5.3.3. Asymmetric acrylic membranes

The National University of Singapore developed a novel asymmetric membrane (Fig. 13) composed of a three-component acrylic polymer blend (TCPB). The membrane was prepared by polymerization of an acrylic polymer blend consisting of 4-vinylphenol-co-methyl methacrylate (P(4-VP-MMA)), poly(butyl methacrylate) (PBMA) and Paraloid B-82 acrylic copolymer resin. The membrane was designed on the basis of the following considerations [78]:

- the acrylic polymer has low solubility in methanol;
- the Paraloid B-82 acrylic copolymer resin acts as a methanol barrier;
- the Paraloid B-82 resin and PBMA provide a flexible and structurally stable framework;
- the hydrophilic 4VP segments in P(4-VP-MMA) form the proton conducting channels within the TCPB.

To maintain membrane homogeneity the hydrophilic monomers, 2-acrylamido-2-methyl propanesulfonic acid (AMPS), 2-hydroxyethyl methacrylate (HEMA) and poly(ethylene glycol) dimethylacrylate (PEGDMA) are polymerized only after they have been embedded in the TCPB matrix. The resulting membrane has a novel asymmetric structure in which the hydrophilic network is sandwiched between two layers of matrixes containing high percentages of TCPB. The two exterior layers in this asymmetric membrane primarily provide methanol-blocking with some proton-conducting

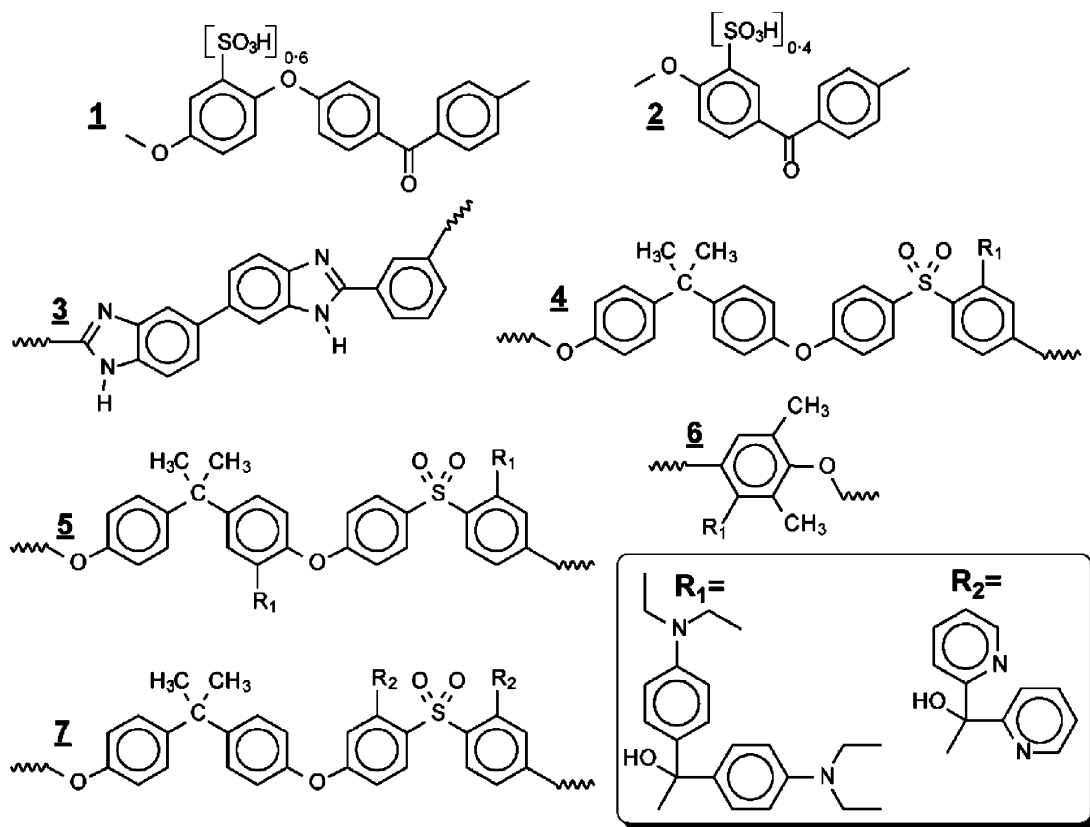


Fig. 12. Arylene-chain polymers used for the preparation of an acid–base blend membrane [42]. Reprinted from Journal of Power Sources, 105, L. Jörissen, V. Gogel, J. Kerres, J. Garche, New membranes for direct methanol fuel cells, 267–273, Copyright (2002), with permission from Elsevier.

functionalities, while the middle layer supplies protons and conserves water [78].

The proton conductivity of AMPS-based membranes (1.2 mS cm^{-1}) is lower than Nafion[®] (80 mS cm^{-1}) due to lower sulfonic group content (0.7 mmol g^{-1} compared to 0.91 mmol g^{-1} for Nafion[®]). The methanol permeability, however, of the membranes is lower ($10^{-8} \text{ cm}^2 \text{ s}^{-1}$). The clusters strain the carbon bonds and link them with polymer main chains. The high water uptake of this membrane is determined by the PEGDMA component in the hydrophilic network (it is responsible for 75% of the water uptake).

These membranes have high thermal stability (up to 270°C) and good mechanical properties due to the association of the AMPS sulfonic acid groups via ionic interaction, which forms heavy clusters. Lifetime data, however, was not found in the literature.

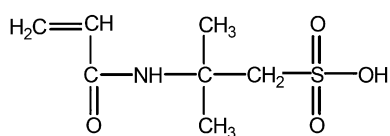


Fig. 13. Structure of asymmetric acrylic membranes [78]. Reprinted from Journal of Membrane Science, 270, H. Pei, L. Hong, J.Y. Lee, Embedded polymerization driven asymmetric PEM for direct methanol fuel cells, 169–178, Copyright (2006), with permission from Elsevier.

5.3.4. Polyvinylidene fluoride or low density polyethylene + styrene membranes

Grandfield University developed membranes based on copolymers of polyvinylidene fluoride (PVDF) ($50 \mu\text{m}$ thick) and low-density polyethylene (LDPE) ($125 \mu\text{m}$ thick) with styrene. The membranes were produced through radiation grafting with a cobalt source (Co-60). The radiation was carried out in air and resulted in the formation of peroxy radicals on the polymer backbone. The membranes were then polymerized with styrene in an inert gas, sulfonated, and then hydrolyzed in hot water. The grafting process incorporates the styrene or its derivatives into substrates with subsequent conversion into sulfonate or other functional groups.

These membranes have a factor of 10 higher resistance than Nafion[®] (Table 8), but have lower cost and lower methanol diffusion coefficients at 2 M methanol and $T = 20^\circ \text{C}$ ($< 0.05 \times 10^6 \text{ cm}^2 \text{ s}^{-1}$ compared to 0.11×10^6 for Nafion[®]) [3,79]. Lifetime and mechanical durability data, however, was not found.

5.3.5. Sulfonated poly(arylether ketone) membranes

The German company FuMA-Tech GmbH developed cost-effective sulfonated poly(arylether ketone) membranes (FKE[®] Series, $50 \mu\text{m}$ thick) that have higher mechanical stability while also demonstrating increased efficiency and significantly higher power density, due to the considerably lower methanol perme-

Table 8
Characteristics of several commercial and grafted radiation membranes

Membrane/supplier	Material	Thickness (μm)	Resistivity ($\Omega \text{ cm}^2$)	IEC (mequiv. g^{-1} Na form)	Methanol diffusion coefficient ($\text{cm}^2 \text{ s}^{-1} \times 10^6$)
Nafion [®] 117/DuPont	Perfluorinated polymer	170	0.04	0.9	1.72
CRA/Solvay	Radiochemically grafted	160	1–4	1.4–2.2	0.58
CRS/Solvay	Fluorinated film	160	1–3	1.7–2.2	0.92
R4010/Pall	PTFE	20	0.6	1.2	1.2
R1010/Pall	PTFE	40	0.3	1.2	0.6
3553P/Granfield University	LDPE-PSSA	125	0.454	0.81	<0.05

ability, than Nafion[®] membranes. FKE membranes operate in the 100–160 °C temperature range. Inorganic or polymer materials will be blended with these membranes to increase stability [80].

5.3.6. Polyfuel polycarbon membranes

In 2005, PolyFuel, Inc. developed novel polycarbon membranes (the exact composition is unavailable) for passive DMFCs with power densities of 60 and 80 mW cm^{-2} for thicknesses of 62 and 45 μm , respectively (at 0.28 V, $T = 40$ °C, and 8 mg cm^{-2} catalyst loading). The lifetime for a nearly constant runtime is 5000 h, which is longer than the lifetime required for a commercially viable portable fuel cell (2000–3000 h). In comparison, the runtime of a 4 h LiIon laptop battery decreases to 2.5 h after 3000 h of operation [56]. Additional characteristics of the polyfuel membrane include:

- water crossover is unchanged and remains less than 1/2 of competing fluorocarbon membranes;
- MCO of $\sim 57 \text{ mA cm}^{-2}$ at OCV;
- back diffusion of water has been improved by 30%, which helps mediate the dissolution of the methanol concentration in a passive DMFC.

PolyFuel is now working with six major corporations that are developing DMFC systems, including NEC and SANYO Electric. Of these six, five are already evaluating the 45 μm membrane for near-term commercial use [56].

6. Other prospective membranes for DMFC applications

The following membranes have only been developed for PEMFC applications, but may also be prospective contenders for DMFC.

6.1. Ballard membranes

Ballard Power System Inc. has developed trifluorostyrene based composite membranes for PEMFC applications [81,82]. However, the membranes were also tested in DMFC cells. A Ballard Mark IV single cell with a membrane of *para*-methyl- α,β , β -trifluorostyrene (p-Me-TFS) grafted poly(ethylene-*co*-tetrafluoroethylene) (Tefzel.RTM) was tested at DMFC conditions ($T = 110$ °C, 0.5 M methanol, 3 bar oxygen

pressure, 2.0 oxidant stoichiometry and 3.0 methanol stoichiometry). The cell had a current density of 263 mA cm^{-2} at the cell voltage of 0.5 V. This current density at 0.5 V was higher than those for BPSH-40 and 6FCN-35 membranes at similar conditions but less than that for sPEEK-PSU + PBI.

6.2. Fluorocarbon membranes of Hoku Scientific Inc.

Hoku Scientific Inc. developed a butadiene/stryrene rubber membrane that contains an inorganic cation exchange material, aluminosilicates-kaolin, and a silica-based binder, LUDOX or tetra ethyl orthosilicate (TEOS). A PEM fuel cell with this composite electrolyte membrane exhibited a cell voltage of 13–30% higher than that with a Nafion[®] membrane. The roles of the various ingredients of the composite membrane are [83]:

- Aluminosilicates: stabilize the proton conductivity and reduce the degree of dimensional fluctuations caused by variations in electrochemical cell temperature and/or variations in water content of the composite electrolyte membrane.
- Silica-based binder: increases the cation exchange capacity of kaolinite, in some cases, by 200% and increases the proton conductivity.
- Polymer-based binders: increase both the mechanical strength and the proton conductivity during operation.

6.3. Resin modified polystyrene sulfonate

A new polystyrene sulfonate (PSS) has low cost and high water absorption, swelling, and proton conductivity in comparison to Nafion[®] 115. It does, however, have a low tensile modulus and is susceptible to chemical degradation in the oxidizing environment of a fuel cell. Polarization curve measurements showed fast degradation of the membranes: the cell potential decreased by 60% in 55 h for a PSS membrane and in 340 h for a composite membrane with resin [48].

7. Analysis of and comparison of different membranes

We have carried an analysis of the major properties of different DMFC membranes. The results are shown in Table 9. Table 9 allows comparison of different membranes and selection of the best properties for every group. But comparison of the efficiency of different membranes is very difficult, as the tests were carried out at different conditions.

Table 9
Comparison of the major operational parameters for various DMFC membranes

Polymer (thickness, μm)	Methanol crossover (mA cm^{-2} or $\text{mol min}^{-1} \text{cm}^{-2} \times 10^6$ or $\text{cm}^2 \text{s}^{-1} \times 10^7$), conditions	Ratio, Nafion®/ membrane of interest	Conductivity, conditions	Ratio, Nafion®/ membrane of interest	Lifetime (h)	Current density, conditions	Max. power density, conditions	Ratio, Nafion®/ membrane of interest	Thermal stability ($^{\circ}\text{C}$)	Cost ($\text{US\$ m}^{-2}$)	References
Target parameters	$<10^{-6} \text{ mol min}^{-1} \text{cm}^{-2}$ or $<5.6 \times 10^{-6} \text{ cm}^2 \text{s}^{-1}$		$>80 \text{ mS cm}^{-1}$ (60°C and 100% RH)								[5]
1. Nafion® 117 (170–180 μm)	$125\text{--}150 \text{ mA cm}^{-2}$ ($60\text{--}90^{\circ}\text{C}$ and 1 M) [71] $14.1\text{--}17.2 \text{ cm}^2 \text{s}^{-1}$ at 60°C ; 3.48 and $0.78 \text{ mol min}^{-1} \text{cm}^{-2}$ (65 and 25°C , 1.5 M, and OCV) [24] $65 \text{ cm}^2 \text{s}^{-1}$ (30°C and 1 M) [75]		$90\text{--}120 \text{ mS cm}^{-1}$ (80°C and 34–100% RH) [60]			50 mA cm^{-2} (80°C and 1 M) [28]			80	790 (150) [11]	[24,28,60,71,75]
2. Nafion® 115 (127 μm)	$19.8 \text{ cm}^2 \text{s}^{-1}$ (25°C and 2 M) [76] $4.66 \text{ mol min}^{-1} \text{cm}^{-2}$ (25°C and 1 M) [67]		41 mS cm^{-1} (25°C)		800–1300 [76]	20 mA cm^{-2} (238 mV 60°C 1 M and air) [30] 150 mA cm^{-2} (80°C , 0.5 M, and 1.5 atm) [33]	10.5 mW cm^{-2} (30°C and 1 M) [76]		80		[67,76,33]
3. Nafion® + 4.7% PFA	$1.72 \text{ mol min}^{-1}$ cm^{-2} (25°C)	2.7 (vs. Nafion® 115)	70.4 mS cm^{-1} (25°C)	1.4 (vs. Nafion® 115)		20 mA cm^{-2} (0.349 mV)					[67]
4. Nafion® + ZrP	$4 \text{ mol min}^{-1} \text{cm}^{-2}$ (145°C , 2 M, 500 mA cm^{-2}) [25]		$24\text{--}60 \text{ mS cm}^{-1}$ (25°C , 100% RH) [28] ARS ($\Omega \text{ cm}^2$)-0.12 (90°C) and 0.08 (150°C) Ratio = 1.4 [27]	0.35 [28]		12 mA cm^{-2} (80°C and 1 M) [28]	360 mW cm^{-2} (O_2) and 260 mW cm^{-2} (air) (150°C and 2 M) [27]		150		[25,27,28]
5. Nafion® 117 + 9.2% MoPh-a ($\text{H}_3\text{PO}_4 \cdot 12\text{MoO}_3 \cdot \text{H}_2\text{O}$)	2 and 7.5×10^{-5} $\text{mol s}^{-1} \text{m}^{-1}$ (25 and 65°C , 1.5 M and OCV)	0.65 (25°C)	230 and 290 mS cm^{-1} (60 and 90°C)	0.39 and 0.51							[24]
6. Nafion® + SiO_2	5% SiO_2 $4.17 \text{ cm}^2 \text{s}^{-1}$ (20°C , 1 M) 245 mA cm^{-2} (60°C , 1 M)[64] 10% DPS 183 mA cm^{-2} [63] $4 \text{ mol min}^{-1} \text{cm}^{-2}$ [25]	2.3 and 1.1 (vs. Nafion® 112) [64]	270 and 390 mS cm^{-1} (60 and 90°C) [24] 183 mS cm^{-1} (in-cell resistance)[63]	0.33 and 0.38 [24]		120 mA cm^{-2} (105°C and 2 M) [25]	240 mW cm^{-2} (145°C) [25]		145 [25]		[64,25,63]
7. Nafion® + SiO_2 + polyaniline (Nafion®-Pani)	37 and $27 \text{ cm}^2 \text{s}^{-1}$ (65°C , 50 and 100% methanol)	3.51 and 2.2 at 50 and 100% methanol	15 mS cm^{-1} (22°C and 100% RH)	0.83							[23]
8. Nafion® + poly(1- methyl pyrrole)	$6.63 \times 10^{-12} \text{ mol}$ $\text{cm}^{-1} \text{s}^{-1}$ [25°C , 1 M sulfuric acid + 1 M methanol (after 24 h)]	220 (at 25°C)									[68]
9. BPSH-40 (138 μm)	43 mA cm^{-2} (80°C , 0.5 M, OCV); $81 \text{ cm}^2 \text{s}^{-1}$ (30°C) $8.1 \text{ cm}^2 \text{s}^{-1}$ (30°C)	1.9, 2				150 mA cm^{-2} (80°C , 0.5 M and 1.5 atm)					[33]

10. 6FCN-35 (137 μm)	35 mA cm ⁻² (80 °C and 0.5 M) 8.7 cm ² s ⁻¹ (30 °C)	2.3, 2								225 mA cm ⁻² (80 °C, 0.5 M and 1.5 atm)	[33]
11. sPEEK, sulfonated poly(ether ether ketone) + silanes/silica (75 μm)											
S66/RSiO _{3/2} /H4[γSi(4)] (sPEEK + silane)	0.8 × 10 ¹⁶ m ³ m m ⁻² s ⁻¹ Pa ⁻¹ (55 °C and 20% methanol)		5 mS cm ⁻¹ (90 °C and 100% RH)	30 at 90 °C							72
S66 (sPEEK)	–		21 mS cm ⁻¹ (90 °C and 100% RH)	7.1 at 90 °C							
12. sPEEK, sulfonated poly(ether ether ketone) (78 μm)	0.2 cm ² s ⁻¹ (20 °C and 2 M)	66	0.9 mS cm ⁻¹ (20 °C)	23.8 at 25 °C						25 mA cm ⁻² (0.5 V, 80 °C, and 2 M)	[77]
13. PBI, poly(benzimidazole) (75 μm)	10.7 mA cm ⁻² [180 °C and 0.9 V (RHE)]		10–40 mS cm ⁻¹ (130–180 °C)							200 mW cm ⁻² (200 °C and 500 mA cm ⁻²)	160–200 [49,50]
14. sPPZ, sulfonated poly(phosphazene)	0.16 cm ² s ⁻¹ (20 °C)	123	40 mS cm ⁻¹ (25 °C)	1.98							[75]
15. sPEEK + PBI + sPSU (60 μm)	150 mA cm ⁻² (110 °C, 1 M, OCV)	0.84	Resistance 66.6 Ω cm ² (110 °C)							500 mA cm ⁻² (110 °C, 0.5 V, 1 M and 3 bar)	[42]
16. AMPS, asymmetric based acrylic membrane (50 μm)	0.1 cm ² s ⁻¹ (90 °C)	~14 (Nafion® 117 at 60 °C)	42 mS cm ⁻¹ (90 °C)								270 [78]
17. PVDF + styrene membrane (50 μm)	1.1 cm ² s ⁻¹ (20 °C and 2 M)	17	Resistance 0.454 Ω cm ²	10							[79]
18. PVDF + SiO ₂ or SiO ₂ gel	22 mA cm ⁻² (SiO ₂) and 53 mA cm ⁻² (gel) (60 °C and 1 M)		70 mS cm ⁻¹ (SiO ₂) and 200 mS cm ⁻¹ (gel) (25 °C)								[71]
Commercial non-Nafion® membranes											
19. Tetra-fluoroethylene with poly(styrene sulfonic acid) (Pall Gelman Sciences)											
Pall R1010 (36 μm)	6 and 13.6 cm ² s ⁻¹ (20 and 60 °C)	2.53 (60 °C)	80 and 146 mS cm ⁻¹ (20 and 60 °C) [64]	1 (20 °C)	–	–	–	–	–	–	[69]
Pall R4010 (63 μm)	4.2 and 9.6 cm ² s ⁻¹ (20 and 60 °C)	3.6 (60 °C)	73 and 132 mS cm ⁻¹ (20 and 60 °C) [64]	1.1 (20 °C)	–	–	–	–	–	–	
20. Sulfonated poly(arylether ketone) (FuMA-Tech GmbH)											
FKE®	Methanol crossover of FKE is lower than for Nafion®	Several times									100–160 [80]
21. Polyfuel hydrocarbon membranes (for passive DMFC)	57 mA cm ⁻² (40 °C)									5000	60 (62 μm) and 80 (45 μm) mW cm ⁻² (40 °C and 0.28 V) [56]
22. Ballard sulfonated sulfonated p-Me-TFS grafted poly(ethylene-co-tetrafluoroethylene) Tefzel.RTM											263 mA cm ⁻² (110 °C, 0.5 V, 0.4 M MeOH at 3 stoich, 3 bar oxidant at 2 stoich) [81]
23. Dow Chemical fluorinated membranes XUS®, (125 μm)	4 × 10 ⁻¹⁰ A [12]	1.5									>10000 in PEM [11] \$150 ft ⁻² [11] [11,12]
24. Asahi Glass fluorinated membranes Flemion®											>50000 in PEM [11] [11]
25. Asahi Kasei fluorinated membranes Aciplex-S1002®											>50000 in PEM [11] 95–120 [14] [11,14]
26. 3P Energy membranes		20									[17]
27. Nowoful (Germany) irradiated sulfonated poly(ethylene- <i>alt</i> -tetrafluoroethylene)											

Table 9 (Continued)

Polymer (thickness, μm)	Methanol crossover (mA cm^{-2} or $\text{mol min}^{-1} \text{cm}^{-2} \times 10^6$ or $\text{cm}^2 \text{s}^{-1} \times 10^7$), conditions	Ratio, Nafion®/ membrane of interest	Conductivity, conditions	Ratio, Nafion®/ membrane of interest	Lifetime (h)	Current density, conditions	Max. power density, conditions	Ratio, Nafion®/ membrane of interest	Thermal stability ($^{\circ}\text{C}$)	Cost (US\$ m^{-2})	References
ETFE-SA (35 μm)	0.03–0.06 mol $\text{min}^{-1} \text{cm}^{-1}$ (30 $^{\circ}\text{C}$, 1–2 M)	22.3 (30 $^{\circ}\text{C}$, 1M) 20 (30 $^{\circ}\text{C}$, 2 M)	10 mS cm^{-1} (20 $^{\circ}\text{C}$)	4	2000	4.5 mW cm^{-2} (30 $^{\circ}\text{C}$, and 1M)		2.3	<85	30–100	[76]
28. PEMEAS PBI-based membranes Celtec®V	Lower than Nafion®								60–160	Cheaper than Nafion®	[74]
29. FuMA-Tech GmbH sulfonated poly(arylether ketone) FKE® Series (50 μm)	Lower than Nafion®								110–160		[80]

Note: the performance of some of the commercial membranes in PEMFC conditions was given in [11], at 0.5 V in a Ballard Power Systems MKSE single PEMFC showed the current densities (j) for BAM3G® (Ballard hydrocarbon membrane), Nafion® 105, XUS®, Aciplex-S®, Nafion® 115, Nafion® 117 to be: >1100, 950, 950, 900, 800, and 785 (mA cm^{-2}), respectively.

7.1. Methanol crossover

MCO has been the major issue for Nafion® membranes in DMFC applications. As a result of the high MCO, 40% methanol losses have been experienced [69]. The ratio of the MCO for Nafion® membrane and other membranes was used for comparison, since different conditions were used by different researchers. The membranes with the lowest MCO ratio have been poly(1-methyl pyrrole) modified Nafion®, sPPZ, and the membranes developed by the companies 3P Energy and Pall. Their corresponding MCO ratios are lower than Nafion® by factors of 215, 123, 20 and 2.5. The irradiated EFTE membranes have factors of 20 lower MCO than Nafion®. The MCO of Pall membranes is only a factor of two lower than Nafion®, but its proton conductivity is similar.

An analysis of the literature shows that the water uptake of the membranes largely determines the methanol permeation through the ionomer microstructure and clusters [18,64]. For Nafion®/silica membranes, for example, at low hydrophobic silica content, the silica surrounds the hydrophilic ion-clusters and ion-channels. The newly formed new tortuous Nafion® structure alters the methanol transport. High silica content increases the contribution of the backbones to methanol permeability and increases proton conductivity and water uptake [64].

7.2. Proton conductivity

Membranes with higher conductivity than Nafion® include Nafion® membranes modified by the addition of inorganic compounds such as SiO_2 , MoPh, and ZrP. The conductivity ratio between Nafion® and these modified membranes is 0.33–0.38 (for the same conditions, see Table 9). One of the reasons for such high conductivity in these membranes, i.e. Nafion® + ZrP, is the higher proton mobility on the surface of ZrP particles and good water retention capabilities [28]. The irradiated EFTE membranes and sPEEK membranes have a factor of 4 and 23 lower proton conductivity than Nafion®, respectively.

7.3. Durability

Data on the durability of DMFC membranes are very limited. Polyfuel membranes in a passive DMFC (40 $^{\circ}\text{C}$, 0.28 V) have reached a lifetime of 5000 h. Alternately, the 35 μm thick ETFE-SA membranes have shown no decrease in performance over 2000 h of testing (the test cycle included 1200 h at 30 $^{\circ}\text{C}$, 400 h at 50 $^{\circ}\text{C}$, 300 h at 70–85 $^{\circ}\text{C}$). The efficiency of the DMFC utilizing ETFE-SA was, however, 40–65% lower than the DMFC with a Nafion® membrane [76].

The lifetime of the partially fluorinated Pall membranes was found to be 1000 h. Lastly, for the composite Nafion® + silica membranes, the cell voltage decreased 60 mV to 0.36 V during an 8.5 h test at $j = 500 \text{ mA cm}^{-2}$ and $T = 145 \text{ }^{\circ}\text{C}$ with 2 M methanol [69].

7.4. Thermal stability

AMPS (asymmetric based acrylic) [78] and PBI [49] based membranes have the best thermal stability, being able to oper-

ate at up to 270 °C and 160–200 °C, respectively. AMPS based membranes also have lower methanol crossover and conductivity than Nafion[®] membranes by factors of 14 and 2, respectively.

7.5. Power density

Polyfuel's 45 μm thick polycarbonate membrane simultaneously has one of the highest power densities (80 mW cm⁻²) at 40 °C, the best lifetime (5000 h) and low MCO. At temperatures as high as $T=200$ °C the highest power density has been achieved with 75 μm thick PBI based membranes (200 mW cm⁻²) [56].

8. Conclusions

Analysis of the various DMFC membranes showed few potential membranes for satisfying the DOE requirements. The following membranes are comparatively promising:

- Polyfuel's 45 and 62 μm thick hydrocarbon membranes with a 5000 h lifetime in a passive DMFC at power densities of 80 and 60 mW cm⁻², respectively (at 40 °C, 0.28 mV).
- Pall's 63 μm thick IonClad[®] R-4010 membrane (tetrafluoroethylene poly(styrene sulfonic acid)) has a factor of 3.6 lower methanol crossover than Nafion[®] with similar conductivity and has shown stability for 1000 h.
- Promising membranes from 3P Energy, FuMA-Tech GmbH (sPES-membranes), and PEMEAS (PBI-based Celtec membranes).

Composite fluorinated and non-fluorinated (hydrocarbon) DMFC membranes have been reported with low cost, methanol and ruthenium crossover (for Pt–Ru anodes), wider temperature range (80–180 °C) and higher ionic conductivity in comparison to Nafion[®] membranes. The traditional Nafion[®] membranes for DMFC applications do not satisfy all of the DMFC requirements. In hydrogen PEMFC applications, unlike DMFCs, thinner membrane materials are preferred as they offer reduced ionic resistance and increased MEA performance. In DMFCs, however, thin membranes (such as Nafion[®] 112) result in a high methanol crossover. These disadvantages exceed the advantage of low ionic resistance and thus thicker membranes like Nafion[®] 117 are typically used. However, Nafion[®] 117 in a DMFC at $j > 0.3$ A cm⁻² has a very low cell voltage. Hydrocarbon membranes are the main candidates for the replacement of the expensive Nafion[®] membranes commonly used.

The improvement of Nafion[®] based membranes through the addition of inorganic compounds (SiO₂, silanes, Zr, MoPha, etc.) and acidic-basic composites (polyaryl) decrease the methanol crossover but do not reduce cost.

The hydrocarbon membranes are cheaper and more technically effective for DMFC than Nafion[®] membranes. They have lower methanol crossover and higher conductivity and stability. A general comparison between the main hydrocarbon membranes and Nafion[®] for DMFC applications is given in Table 10.

Some prospective hydrocarbon membranes are sPTES, sPEEK + PBI blend, and sPPZ. SPPZ has low MCO

Table 10
Comparison of hydrocarbon membranes to Nafion[®]

Parameter	Membranes					
	sPEEK	sPEEK + PBI	PBI	sPSU + PBI	sPTES	sPPZ
Methanol crossover	+	+	+	+	+	+
Conductivity	–	+	–	=	+	+
Stability	–	+	+	+	+	=
Cost	+	+	+	+	+	+

(0.7×10^{-7} cm² s⁻¹) and high chemical stability, PBI has high thermal stability 160–200 °C, and sPTES has high conductivity (>100 mS cm⁻¹ at $T=85$ °C and RH=85% compared to 80–112 mS cm⁻¹ for Nafion[®]). The PBI membranes have the best thermal stability along with high power density (250 mW cm⁻² on air at $T=110$ –130 °C).

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