Review

Cost effective cation exchange membranes: A review

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ABSTRACT

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

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

Contents

1. Introduction

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

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

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

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

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

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

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

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

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

2. Current membrane materials

2.1. Fluorinated materials

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

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

Table 1 – Costs of Nafion® membranes.

| Membrane classification	Cost	Normalised cost ($USD/cm^2)
Price list from Fuel Cell Store (Fuel Cell Store, 2011)		
Nafion® NRE212 Membrane 100 cm^2	$24	$0.24
Nafion® NRE212 Membrane 900 cm^2	$130	$0.14
Nafion® 115CS Membrane 100 cm^2	$30	$0.30
Nafion® 115CS Membrane 900 cm^2	$175	$0.19
Nafion® 117CS Membrane 100 cm^2	$35	$0.35
Nafion® 117CS Membrane 900 cm^2	$200	$0.22
Price list from Fuel Cells (Electrochem Inc., 2006)		
Nafion® N115 Membrane 900 cm^2	$282	$0.31
Nafion® N117 Membrane 900 cm^2	$340	$0.38
Price list from Ion Power, Inc. (Ion Power Inc., 2007)		
Nafion® N115 Membrane 900 cm^2	$193	$0.21
HYDRion™ N115 25 cm^2 Electrolysis Membrane	$103.50	$4.14
Nafion® N117 Membrane 900 cm^2	$221	$0.25
HYDRion™ N117 25 cm^2 Electrolysis Membrane	$117	$4.69

Table 2 – Technical targets of proton exchange membranes set by the U.S. Department of Energy.

PEM conductivity (S/cm)	Operating temperature (°C)	Area-specific resistance (Ω cm^2)	Cost ($/m^2)	Durability with cycling (h)
At ≤ 120°C 0.07 (at room temperature) 0.01 (at -20°C)	≤ 120	0.02	40	5000 (at ≤ 80°C) 2000 (at >80°C)

decrease in performance (Savadogo, 2004). When operating at temperatures of around 100 °C, per-fluorinated membranes lose their mechanical properties and have lowered swelling properties. They are also limited by low proton selectivity, relatively low mechanical stability, high methanol crossover, low conductivity at a low humidity or a high temperature, and, most significantly, high cost (Varcoe and Slade, 2005). The Nafion® series membranes are expensive due to the fluorochemistry involved in synthesis. At costs of US$700/m^2 (Biffinger and Ringeisen, 2008; Smitha et al., 2005) these membranes limit the broader and large-scale commercial applications when compared with other current technologies. The basic structure of the Nafion® membranes is shown in Fig. 1.

Well established commercial membranes can also be found with trade names of Flemion® (manufactured by Asahi Glass Co., Ltd.) and Aciplex® (Asahi Kasei Co., Ltd.). Though not as commonly used as Nafion®, these membranes also have the proton conductivity and chemical stability required for an electrolyte membrane, but are similarly limited by high cost. Modified composites of these commercial membranes have shown improved performance and properties, however, little progress has been made to significantly reduce manufacturing or materials costs (Savadogo, 2004).

In addition to cost and performance limitations, safety during manufacture and operation, as well as
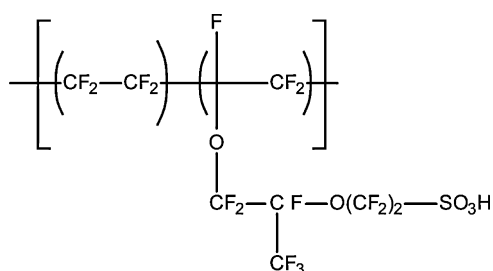
environmental considerations regarding disposal render any fluorinated membranes less appealing. Safety concerns derive from the toxic intermediates and corrosive gases released above 150 °C (Smitha et al., 2005). These materials will remain costly due to the use of fluorine and the severe reaction conditions needed to prepare these polymers. They also cause considerable environmental concern with regard to disposal of halogenated materials. Decomposition of the fluorinated material is also of concern and limits the recycling options of this material. At high temperatures (>90 °C) and low relative humidity, performance and conductivity of these materials are compromised. In addition to high cost and high methanol permeability, these limitations are non-trivial for commercial viability.

Gore and Associates Inc. are developing novel fluorinated ionomer membranes based on polytetrafluoroethylene (PTFE). This membrane provides good resistance to tear, dimensional stability, low membrane resistance and durability under fuel cell operation for vehicle applications (Savadogo, 2004). This membrane is a composite based on PTFE porous sheet reinforcement and is trademarked under the name Gore-Select® (Bahar et al., 2001, 2002). With a lower shrinkage rate upon dehydration, higher mechanical strength and more effective water management, Gore-Select® is a reasonable alternative to Nafion® in fuel cell applications. Gore-Select® with PTFE reinforcement has been shown to outlast Nafion® commercial membranes three times its thickness and can also provide significantly higher power density (Savadogo, 2004). These factors indicate Gore-Select® may be a more durable alternative to Nafion® when considering capital and operational cost aspects.

2.2. Partially perfluorinated materials

An alternative family of materials that can be used for ion exchange membranes involves partially per-fluorinated polymers. A sulfonated copolymer incorporating α,β,β-trifluorostyrene monomers has been patented under Ballard
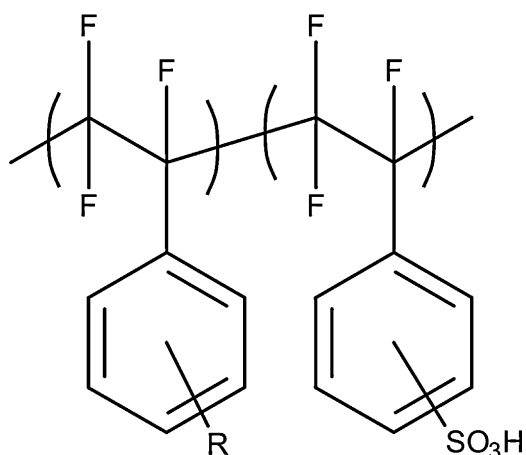

Fig. 1 – Basic Nafion® chemical structure.

Fig. 2 – Basic BAM3G chemical structure, where R = alkyls, halogens, alkoxy, CF=CF$_2$, CN, NO$_2$, and OH.

Advanced Materials 3rd Generation (BAM3G) from Ballard Advanced Materials and have been recognized as membranes suitable for PEMFC applications. BAM3G is a partially fluorinated polystyrene-like electrolyte membrane where the C–F bonds are substituted at the benzylic position, as shown in Fig. 2.

The presence of the electron-withdrawing group (–CF–) on the aromatic ring renders the sulfonic acid group a stronger acid. These membranes have shown superior PEFC performance than that of conventional fluorinated membranes (Savadogo, 2004). BAM3G is considered a promising membrane in terms of performance and stability.

The high cost and limited availability of trifluorostyrene monomers used to produce BAM3G limits the practical application of this material in commercial membranes. Subsequently, BAM3G composites have been investigated where a porous substrate has been impregnated with a polymeric composition comprising of various combinations of the following:

i. Sulfonated α,β,β-trifluorostyrene and *m*-trifluoromethyl-α,β,β-trifluorostyrene.
ii. Sulfonated polymer of α,β,β-trifluorostyrene.
iii. Copolymer of α,β,β-trifluorostyrene, *m*-trifluoromethyl-α,β,β-trifluorostyrene and *p*-sulfonyl fluoride-α,β,β-trifluorostyrene.
iv. Sulfonated copolymer of α,β,β-trifluorostyrene and *p*-fluoro-α,β,β-trifluorostyrene.
v. Copolymer of α,β,β-trifluorostyrene, *p*-fluoro-α,β,β-trifluorostyrene and *p*-sulfonyl fluoride-α,β,β-trifluorostyrene.

These modifications can further improve the mechanical strength of the material in the dry state and its dimensional stability when wet. The modified composites of BAM3G have reduced costs compared to the initial membrane material (Savadogo, 2004). These composite materials are still in early stages of development and have not yet been patented for commercialization. A further study of the chemical and mechanical properties of these materials is recommended to determine if these are viable membranes for commercial applications.

While the use of fluorinated materials in the development of new membrane materials increases costs of production, Cooray et al. (2006) argue that perfluorinated or partially perfluorinated materials are indispensible. Non-fluorinated

materials may be capable of controlling methanol crossover but are claimed to have insufficient proton conductivity as they do not form appropriate ion channel structures. These materials are also subject to chemical degradation in strong acidic and oxidative conditions due to the –C–H– bonds within these materials. Partially fluorinated materials show excellent resistance to acids, low methanol crossover and high proton conductivity. However, these are still unable to produce low-cost membranes due to their use of expensive fluorinated materials.

3. Non-fluorinated hydrocarbon membranes

The most promising alternative materials that are capable of producing low cost membranes are non-fluorinated or acid–base blends. Other materials such as composite membranes also show significant promise. Hydrocarbon membranes provide distinct advantages over perfluorinated membranes in terms of reducing cost and allowing for easier manufacture by eliminating fluorinating steps. Reducing the fluorinate species significantly reduces costs of manufacture, as well as improving environmental viability with minimal halogenated materials.

Low cost cation exchange membranes can be produced from functionalized polymers, which are readily available or able to be produced from inexpensive materials. In order to enhance stability at higher temperatures, aromatic hydrocarbons can be incorporated directly to the hydrocarbon polymer backbone. Due to these inflexible and bulky aromatic groups, polyarylenes are stable at high temperatures of more than 200 °C (Soczka-Guth et al., 2002). Aromatic rings also allow for electrophilic as well as nucleophilic substitution. Functionalization is typically by sulfonation or phosphonation, either directly or by polymerizing functionalized monomers. These reagents are inexpensive and readily available (Meier-Haack et al., 2007).

Earlier sulfonation treatments mainly focused on improving the hydrophilicity of membranes. Concentrated sulfuric acid and chlorosulfonic acid are typically employed as sulfonating agents. It is known that chlorosulfonic acid is a stronger solvent due to the weaker Cl–S bond. This causes the sulfonation reaction to be less controllable, with side reactions often occurring. Sulfonation is an electrophilic substitution reaction, with the active site for substitution determined primarily by electron density, preferably taking place on the aromatic ring.

Thermoplastic polymers such as polystyrenes, polyethersulfones, polyetherketones, and polybenzimidazole have been proposed as substitutes of perfluorinated materials, provided an acidic functional group has been introduced to the unit structure. For cation exchange materials, it is preferable that the solid electrolyte has an acidic functional group, with sulfonic acid most commonly used, phosphonic acid, carboxylic acid or phosphoric acid groups are also currently being investigated (Zaopo et al., 2009).

3.1. Polystyrene membrane materials

Polystyrene is a very low cost thermoplastic and is readily available for large-scale commercial uses. Ehrenberg et al. (1995, 1997) describes such membranes developed from sulfonated polystyrene. This material is composed of hydrogenated and sulfonated styrene copolymers, obtained
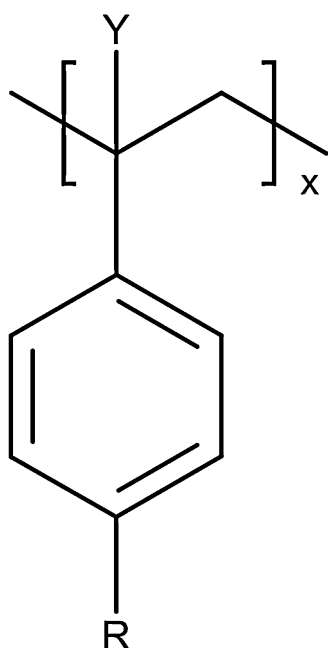
Fig. 3 – Basic structure of modified polystyrene.

by sulfonating styrene-(ethylene-butylene)-styrene (SEBS) copolymer. However, at higher sulfonation levels, the strength of these membranes decreases when they become hydrated.

A proton exchange membrane with improved stability has been developed by Fan and Hussain (2004) with a sulfonated and phosphonated polystyrene material having a covalently bonded tertiary hydrogen replacement group. The base structure of this polymer is shown in Fig. 3, where the Y is a covalently bonded group and R is a group of $-SO_3H$, $-PO_3H_2$, or mixtures thereof. The produced membrane has high chemical and mechanical stability suitable for use in fuel cells.

Fan and Hussain (2004) argues that the tertiary hydrogen atoms contribute to the instability of current sulfonated polystyrene membranes. By replacing the tertiary hydrogen atoms with covalently bonded groups, a more stable membrane can be produced.

Further improvements to the selectivity of polybenzoxazole membranes have used poly(styrene sulfonic acid) polymers as a polymer backbone such as described by Liu et al. (2009). These membranes are prepared from aromatic polyimide membranes for gas, vapor, and liquid separations. Thermally treating these membranes with poly(styrene sulfonic acid) polymer showed 95% improvement in selectivity for CO_2/CH_4 and H_2/CH_4 separations (Liu et al., 2009).

Typical polystyrene contains phenol groups distributed randomly along the hydrocarbon chain. Syndiotactic polymers are ordered, with phenol groups alternating on each side. Syndiotactic polystyrene (s-PS) is a commercially available and inexpensive engineering plastic. Bae (2009) investigates several sulfonation synthesis techniques based on polystyrene-like materials.

Tanioka et al. (2003) has patented a polyelectrolyte material comprising a syndiotactic polystyrene configuration. This material was found to be suitable for fuel cell use or wastewater treatment. This inexpensive membrane material also exhibits good long-term stability. Typical sulfonated styrene resins are copolymerized with divinylbenzene to maintain the film configuration when hydrated, however, this resin has poor long-term stability. Previously published syndiotactic configurations of polystyrene have low sulfonation

degrees of up to 6.3 mol%. When formed into electrolyte membranes, this gives a maximum ion exchange capacity of only 0.6 mequiv./g if all sulfonic groups are effectively functioning. This performance of such materials leaves them as insufficient for use in industrial fuel cells. However, Tanioka et al. (2003) investigated the use of sulfonated polystyrene (s-PS) in blends, utilizing the good crystallizability of this polyelectrolyte to effectively form pores in the resin. The preferred styrene polymers include polystyrene, poly(p-methyl styrene), poly(m-methyl styrene), poly(p-tertiary-butyl styrene), poly(p-chlorostyrene), poly(m-chlorostyrene), poly(p-fluorostyrene), hydrogenated polystyrene and copolymers containing these constituting units. The membrane blends retained their configuration due to the good crystallizabilty of s-PS, while also having high sulfonation from resins more readily sulfonated than polystyrene. The resulting membrane showed good electric conductivity, low water-permeability and good retention of the film's configuration in water and is ultimately inexpensive.

Simplified processing methods also assist in reducing the overall cost of a membrane. Bae (2009) presents several methods for post-sulfonation of aromatic polymers via transition metal-catalyzed polymerization followed by post-sulfonation. This novel synthesis procedure is more cost effective, though less controllable, than methods where the monomer is pre-sulfonated. The presence of the electron-withdrawing group enhances the polymerization rate and increases the molecular weight of the polymer, while also making the sulfonic acid group a stronger acid. The mix of *meta-* and *para-* configurations also provides for improved solubility and easier film processing.

Recently, the use of sulfonated polystyrene grafted to a polyethylene backbone has shown promise for low cost membranes for DMFCs. Baglio et al. (2010) recently produced a low cost fluorine-free proton conducting polymer electrolyte for application in DMFC mini-stacks. This membrane material was based on sulfonated polystyrene grafted onto a polyethylene backbone. The mini-stack structure improves the utilization of this fluorine-free membrane. A power density of $18 \, mW \, cm^{-2}$ was achieved and, while low compared to Nafion® 117 of $31 \, mW \, cm^{-2}$, the fluorine-free membrane showed good characteristics for application in DMFCs especially with regard to significant cost reduction.

3.2. Poly(arylene ether sulfone) membranes

Poly(arylene ether)s are promising candidates for ion exchange membranes due to their outstanding chemical and thermal stabilities, high glass-transition temperature, as well as their good solubility in dipolar aprotic solvents for film forming (Meier-Haack et al., 2007). Sulfonated poly(arylene ether sulfones) in random copolymer form is a highly promising material being investigated (Klaysom et al., 2010, 2011a,b,c). Sulfonated arylene-main-chain polymers such as poly(ether sulfone)s and poly(etherketone)s are the next preferable materials as they show the best chemical stability compared to Nafions and are relatively cheaper (Koter et al., 1999).

Victrex Manufacturing Ltd. has examined sulfonated polyarylethersulfones as ion conducting membranes for PEMFC, although greater ion exchange capacities are needed to achieve similar conductivities to perfluorosulfonic acid Nafion® polymers.
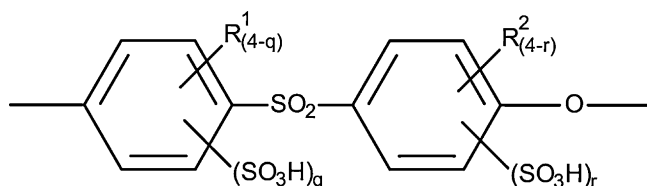
Fig. 4 – Chemical structure described by Hibino et al. (2006).

Hibino et al. (2006) discusses a method to provide a solid electrolyte that can be formed into an electrolyte membrane that has restricted fuel crossover even at high ion exchange capacity. The solid electrolyte displays the structure shown in Fig. 4, where the functional group –SO$_3$H is bound to any position of the benzene ring. This three armed, trifunctional compound structures allows for control of the cross-linking density and cross-linking positions in solid electrolyte to restrict fuel crossover.

Cooray et al. (2009) describes an electrolyte composed of a sulfonic acid group-containing polymer having at least one structure unit of those shown in Fig. 5. These membranes are cross-linked by irradiation treatment and can be used in DMFCs as they are stable in strong acid environments, give low methanol crossover and have high proton conductivity.

3.3. Poly(arylene ether ketone) membranes

Poly(arylene ether ketones)s (PAEKs) are regarded as high performance engineering thermoplastics due to their good solvent resistance, high thermooxidative stability and excellent mechanical properties (Wang et al., 1998). Depending on the sequences of ether and ketone units, this class of materials can include various types of polymers such as PEK, PEEK, PEKK and PEEKK. The sulfonated derivates of these polymers are low cost alternatives to Nafion® membranes that may also help reduce problems with high methanol crossover (Kreuer, 2001). SPEK materials are inexpensive and are environmentally friendly alternatives to fluorinated materials (Soczka-Guth et al., 2002). For such materials, it is crucial to achieve a balance between high proton conductivity and the degree of sulfonation, which in turn affects the mechanical strength of the polymer.

Sulfonated PEEKs can be prepared via modification, where sulfonate groups are incorporated onto the polymer chains by a sulfonating agent. Alternatively, direct copolymerization of pre-sulfonated monomers enables easier control of the degree of sulfonation by controlling the ratio of the sulfonated monomers. This method also avoids cross-linking and other side reactions associated with post-sulfonation that can reduce thermal and mechanical stability. Several papers have described this direct sulfonation technique and the subsequent polymerization to attain sPEEK polymers (Gil et al., 2004; Harrison et al., 2003; Li et al., 2004, 2005; Muthu Lakshmi et al., 2005; Park et al., 2008; Wang et al., 1998).

Helmer-Metzmann and Osan (1993) produced a sulfonated aromatic polyether ketone where the ratio of sulfonated monomer to non-sulfonated monomer varied from 0.2 to 1. Subsequently, Helmer-Metzmann and Schneller (1998) identified a homogeneous polymer alloy comprising of SPEK and at least one aromatic polysulfone. This membrane was found suitable for electrochemical cells at operating temperatures above 100 °C. By copolymerization, properties of the polymer materials can be improved or controlled.
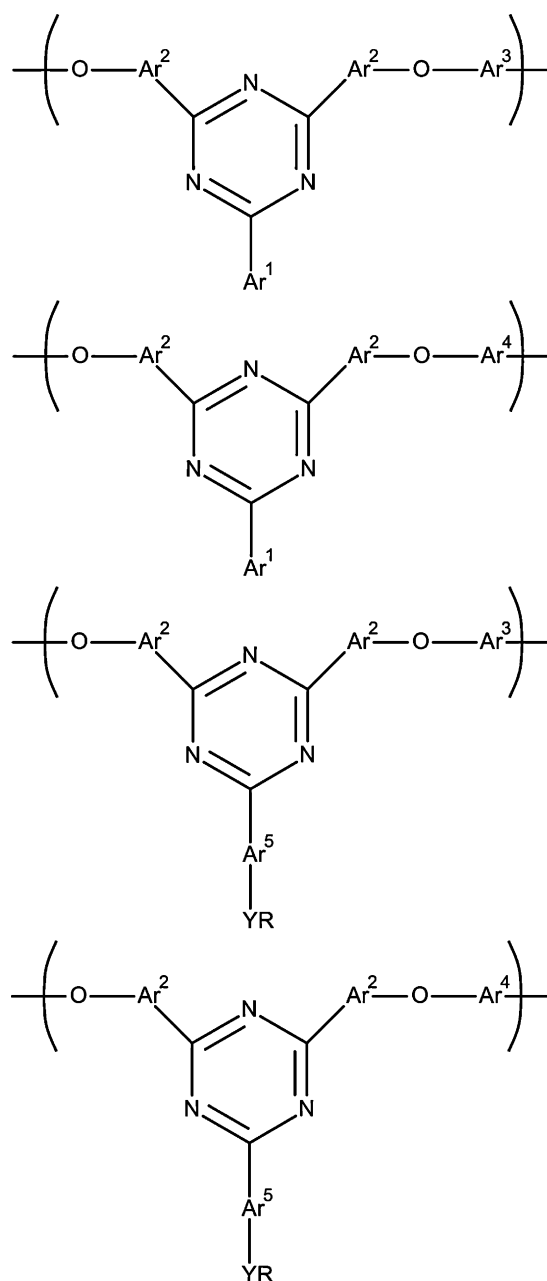

Fig. 5 – Chemical structure of polybenzimidazole.

While the direct synthesis of SPEEK from sulfonated monomers has been shown to be more advantageous from a materials perspective than that of post-sulfonation (Gil et al., 2004), the simplicity and lower cost of post-sulfonation is preferable for ease of large-scale commercialization. Despite the limitations of cross-linking, mechanical and thermal degradation, the post-sulfonation procedure described in various reports (Balster et al., 2005; Basile et al., 2006; Dai et al., 2001; Do and Kim, 2008; Drioli et al., 2004; Gohil et al., 2006; Hu et al., 2004a,b; Li et al., 2003; Xing et al., 2004; Zhang et al., 2005) provides for a noticeably much simpler and hence, more cost effective, method for SPEEK synthesis. The differences with regard to the mechanical and transport properties of hydrated perfluorinated polymers such as Nafion® and low cost sulfonated polyaryls is described succinctly by Kreuer (2001).

SPEEK polymer membranes are characterized by lower permeability to water, methanol, O$_2$ and H$_2$ when compared to Nafion® (Fontananova et al., 2010). They also present good chemical, high thermal resistance and mechanical stability

(Soczka-Guth et al., 2002). These materials have high heat resistance, excellent hydrophilicity and good solubility in organic solvents, which allows them to be cast into thin film membranes. SPEEK membranes show promise as commercial ion-exchange membranes with sufficient stability in many processes (Koter et al., 1999).

Conventional sulfonation processes for polyether ketones are described by Rose (1980, 1981), and through a more novel process by Helmer-Metzmann and Osan (1993). The post-sulfonation of polyether ether ketones has also been described by Rose (1980) and Helmer-Metzmann and Osan (1993), while the more recent work of Bauer (2004) describes the synthesis route of PEKK sulfonation. Under mild conditions, the sulfonation reaction proceeds very slowly, while under vigorous conditions sulfonated products are difficult to obtain pure, with high degrees of cross-linking or decomposition of the polymer main chain. Helmer-Metzmann and Schneller (1998) describe a process that permits the rapid and mild post-sulfonation of aromatic PEK. The manufacture and casting of SPEK thin films has also been described (Brown, 2008).

More recently, various synthesis techniques that provide SPEEK membranes with reduced methanol crossover for use in direct methanol fuel cells have been reported (Gil et al., 2004; Gohil et al., 2006). These show much lower methanol diffusion coefficients than the currently used Nafion®. The ion exchange capacities and proton conductivities of these alternative membranes shows good potential for use in proton exchange membrane fuel cells.

Recent inventions have allowed for homogenous SPEEK electrolyte membranes to be developed by organic solvent casting. Reduced methanol permeability down to a tenth that of Nafion® has been achieved while still maintaining ion conductivity. These membranes act as effective alternatives to more expensive commercial membranes (Kim et al., 2009). Variations on these materials such as SPEEKK have also been prepared using inexpensive commercially available monomers (Gao et al., 2010).

Other recent patents have investigated modifications of SPEKs that contain cycloalkenyl groups as candidates for PEMFCs (Chang et al., 2010). Composite polymer electrolyte membranes have recently been produced which show significant promise as inexpensive materials for use in such applications as PEMFCs. These include a blend of PEEK and poly(amide imide)s (Ma et al., 2008) giving reduced methanol permeability while maintaining good proton conductivity. A monomer comprising of phthalazinone and a phenol group has also been used to produce a sulfonated poly(phthalazinone ether ketone) membrane that can be used particularly for direct methanol fuel cells (Xiao et al., 2008). A composite material comprising of silica dispersed in a polymer matrix based on poly(aromatic ether ketones), poly(benzoyl phenylene) or derivatives of these have also been characterized with good water retention capabilities, good impermeability to the gas and liquid fuels commonly used in fuel cell technology, obtained due to the presence of silica particles. Good mechanical properties of this composite allows for straightforward casting into thin films, suitable for use as proton exchange membranes for fuel cells (St-Arnaud and Bebin, 2006).

3.4. Acid-doped polybenzimidazole membranes

Polybenzimidazoles (PBIs) refer to aromatic heterocyclic polymers containing benzimidazole units as shown in Fig. 5, that
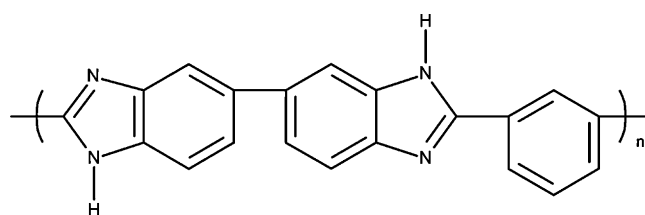

Fig. 6 – Phosphoric acid-doped poly(benzimidazole).

may provide a low cost alternative as a base for composite membranes.

Acid–base complexation is an effective method for the development of proton conducting membranes as the basic polymer acts as a proton acceptor, where an ion pair can be formed. With a lower permeability for hydrogen, they also retain high temperature oxidative stability, good chemical and mechanical properties as well as high ionic conductivity when acid-doped (Savadogo, 2004). PBIs doped with high acid concentrations can result in high ionic conductivities of 2×10^{-3} and 6×10^{-2} S/cm. These conductivities are comparable with commercial Nafion® 117, while being significantly more cost effective than perfluorinated options (Fig. 6).

Doped PBI shows great potential for fuel cells operating at moderate temperatures. A review by Smitha et al. (2005) looks at several journal articles that examines the potential of doped PBI membranes to replace commercial Nafion® in DMFCs as they are known to have lower methanol permeability. The ease of fabrication of such composites membranes is also increasingly appealing for low cost membrane production. While these materials are promising, they are relatively novel and require further studies into long-term stability and reliability if they are to be commercialized. Several journal articles have examined these materials (Asensio et al., 2002, 2004) but there have been few patents relating this material to commercial applications.

The first patent filed regarding doped PBI membranes was by Savinell and Litt (1996), after which numerous patents on PBI membranes and fuel cells have been issued to Savinell's group (Savinell and Litt, 1998), Hoechst Celanese and Aventis (Onorato et al., 2000, 1999; Yamamoto, 2004), and Honda among others (Akita et al., 2000; Okamoto et al., 2004).

Modified PBI membranes have high ionic conductivity and are suitable for solid polymer electrolytes in electrochemical applications. US Patent No. 6987163 describes the synthesis and performance of modified PBI polymer membranes (Cabasso et al., 2006). This invention relates to PBIs modified by phosphonylation and sulfonation.

Phosphoric acid-doped polybenzimidazole membranes have been shown to be highly successful in PEMFCs, with demonstrated performance and high ionic conductivity at temperatures up to 200 °C (Li et al., 2009).

Lee et al. (2009) claim that PBI membranes doped with phosphoric acid have insufficient proton conductivity to replace Nafion® membranes, and instead propose a novel polybenzimidazole-benzamide copolymer for fuel cell use with higher proton conductivity than conventional PBI polymer electrolyte membranes. The polymer electrolyte composed of repeating benzimidazole and benzamide units has improved proton conductivity and excellent mechanical strength, as compared with conventional polybenzimidazole membranes. High thermal and chemical stability was also shown under operating capacities in a wide temperature range. Further improvement to PBI membranes can be made

on the thermal and chemical stability of the polymer (Li et al., 2009).

3.5. Poly(vinyl chloride) membranes

Ion exchange membranes are also relevant for electrodialysis applications. Anion exchange membranes Neosepta AMX and cation exchange membranes Neosepta CMX have been used (Długołęcki et al., 2009). These membranes are homogeneous ion-exchange membranes based on poly(vinyl chloride) and are manufactured commercially by Tokuyama Soda Co. (Japan). Neosepta AMX contains quaternary ammonium groups as fixed charges while Neosepta CMX contains sulfonic acid groups. The anion and cation membranes are stacked in pairs, separated by spacers.

4. Future progress

Non-fluorinated membrane materials offer a competitive alternative to current high cost ion exchange membranes. Though the lower costs of non-fluorinated membranes is significant, large-scale applications of these materials over fluorinated membranes is still disputed in current literature. In the author's opinion, developments on hydrocarbon membranes show promise to produce economically viable membranes. Appropriate membrane materials are sought with key factors involving appropriate conductivity, thermal, mechanical and chemical stability as well as low cost manufacturing ability. It is suggested that polymer membranes should be focused on, as the lack of fluorination is a crucial component in reducing costs. In particular, poly(aryl ether)s are promising candidates due to their chemical and thermal stabilities. These materials are also readily available and can be functionalized and easily cast to specific parameters. Improvements to ion exchange capacities will make these materials highly competitive to current high cost membranes. Given the steadily improving performances documented by recent literature, these materials show strong potential to replace fluorinated materials as PEMs.

With the fuel cell market rapidly developing, demand for inexpensive membrane materials is also expected to boom. Growing technologies such as electrodialysis and bioelectrochemical systems are also encouraged by the commercialisation of viable membrane alternatives. Rikukawa and Sanui (2000) suggest that in order to produce materials that are less expensive than Nafion®, some sacrifice in material lifetime and mechanical properties may be acceptable, provided the cost factors are commercially realistic. Hence the use of hydrocarbon polymers, even though they had been previously abandoned due to low thermal and chemical stability, has attracted renewed interest.

Other promising polymers that may be considered for porous polymeric support membranes include polysulfone, polyethersulfone, poly(ether sulfone ketone), poly(ether ethyl ketone), poly(phthalazinne ether sulfone ketone), polyacrylonitrile, polypropylene, cellulose acetate, and cellulose diacetate or cellulose triacetate. These polymer materials have high potential for developing competitive membranes with high thermal, mechanical and chemical stability.

Many promising materials for future investigation and commercialisation involve composite materials. Cheap proton conducting composite membranes offering stability up to 150 °C can allow for promising developments in upcoming commercial areas such as fuel cell technology, electrodialysis and water treatment (Savadogo, 2004). Recent patents describing solid acid polymer electrolyte membranes using carbon nanotubes have been employed for use in fuel cells (Lee et al., 2010). Further patents for similar materials are desired to promote the commercial capability of polymer membranes.

Despite increasing patents for such materials, these membranes still face some commercial limitations. These membranes are typically in the demonstration phase of the commercialization progress with these new materials needing to demonstrate performance on par with current Nafion® membranes in large scale systems. The water industry has been most successful in implementing these low cost alternative membranes in water purification and treatment systems. This is primarily due to the low profit margins of these industries, causing increased demand for novel, low cost technologies. Commercial markets in fuel cells and electrodialysis industries are further expected to develop with demonstrated results, technological advances and as economies of scale reduce costs to competitive levels.

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