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Solid acid membranes for high temperature (>140 °C) proton exchange membrane fuel cells

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Abstract

Proton exchange membrane fuel cells (PEMFCs) are an exciting clean energy technology for power delivery for a range of devices from automotive applications through to portable digital equipment. Current technology for PEMFCs is limited by its inability to operate at high temperatures which is particularly desirable for automotive applications. This review summarises and discusses the key areas of research in recent years for non-polymer based high temperature membranes or so-called solid acid membranes. The review addresses: the reasons for operating at high temperatures, the proton transport mechanisms, the limitations of current polymer membranes and their modification and on the future of solid acid membranes elaborating on future pathways which may bring about tangible enhancements in this technology.
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Keywords: Solid acid membrane; Proton exchange membrane; Fuel cell; Proton conduction; Zirconium phosphate

1. Introduction

Proton exchange membrane fuel cells (PEMFC) are one of the most promising clean energy technologies under development. The major advantages include: current prototype efficiency of up to 64% [1], high energy densities (relative to batteries) and the ability to operate on clean fuels while emitting no pollutants. Despite these benefits, diffusion of PEMFC technology into the market place is being limited by cost and reliability issues [2]. Recent research has attempted to tackle these problems with moderate success. As a result, it is widely acknowledged that the goal of large scale fuel cell market penetration in areas including transport have moved from 2010 to 2015, and that there are still many technical and social issues to overcome. These challenges include: choosing the appropriate fuel source and infrastructure, industry regulation, safety and public acceptance, and in a review such as this these cannot be explored.

Research into fuel cells has grown exponentially over the last 15 years [3]. In the case of the polymer fuel cell, the major breakthroughs in technology that have allowed significant improvement in the overall performance of the PEMFC has been the modification of Nafion® by Du Pont. Nafion is the benchmark by which all new materials should be compared. A significant number of these modified derivatives of Nafion (see [4]) and other Nafion like polymers (e.g. sulfonated polyetherketones or SPEK) are appearing in a wide range of the latest fuel cell prototypes [5].

Recent reviews have suggested that the research of PEMs during the 1980's and 1990's has not advanced low temperature membrane technology very far [6]. This review seeks to demonstrate that this trend is changing and that the advancement of PEMs for medium temperature applications is building momentum. In demonstrating so, it will focus on the application of solid acid membranes for PEM fuel cells operating above 140 °C. For reviews covering the vast literature on polymer and polymer composite PEMs the reader is referred elsewhere [4,7–9].

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2. Background

2.1. Current proton conducting membrane technology (<100 °C)

Two main types of polymer membranes have dominated research efforts: sulfonated aromatic polymers (e.g. sulfonated polyetherketone, SPEEK and polyetherketone, SPEK) and perfluorosulfonic acid membranes such as Nafion which have been the industry benchmark. These membranes both exhibit phase separated domains consisting of an extremely hydrophobic backbone which gives morphological stability and extremely hydrophilic functional groups. These functional groups aggregate to form hydrophilic nanodomains which act as water reservoirs [3]. The key features of these membranes are shown in Fig. 1. A summary of the development of the polymers for these membranes has been presented by Scott et al. [10].

Sulfonated aromatic high performance polymers have generated large interest because they exhibit similar domain formation and proton conductivity as Nafion and allow direct electrophilic sulfonation and casting from organic solutions [11]. As a result they are significantly less expensive to fabricate. Unfortunately, the conductivity of the sulfonated aromatic polymers is only similar to Nafion at high levels of hydration. At low levels of hydration the diffusion coef-

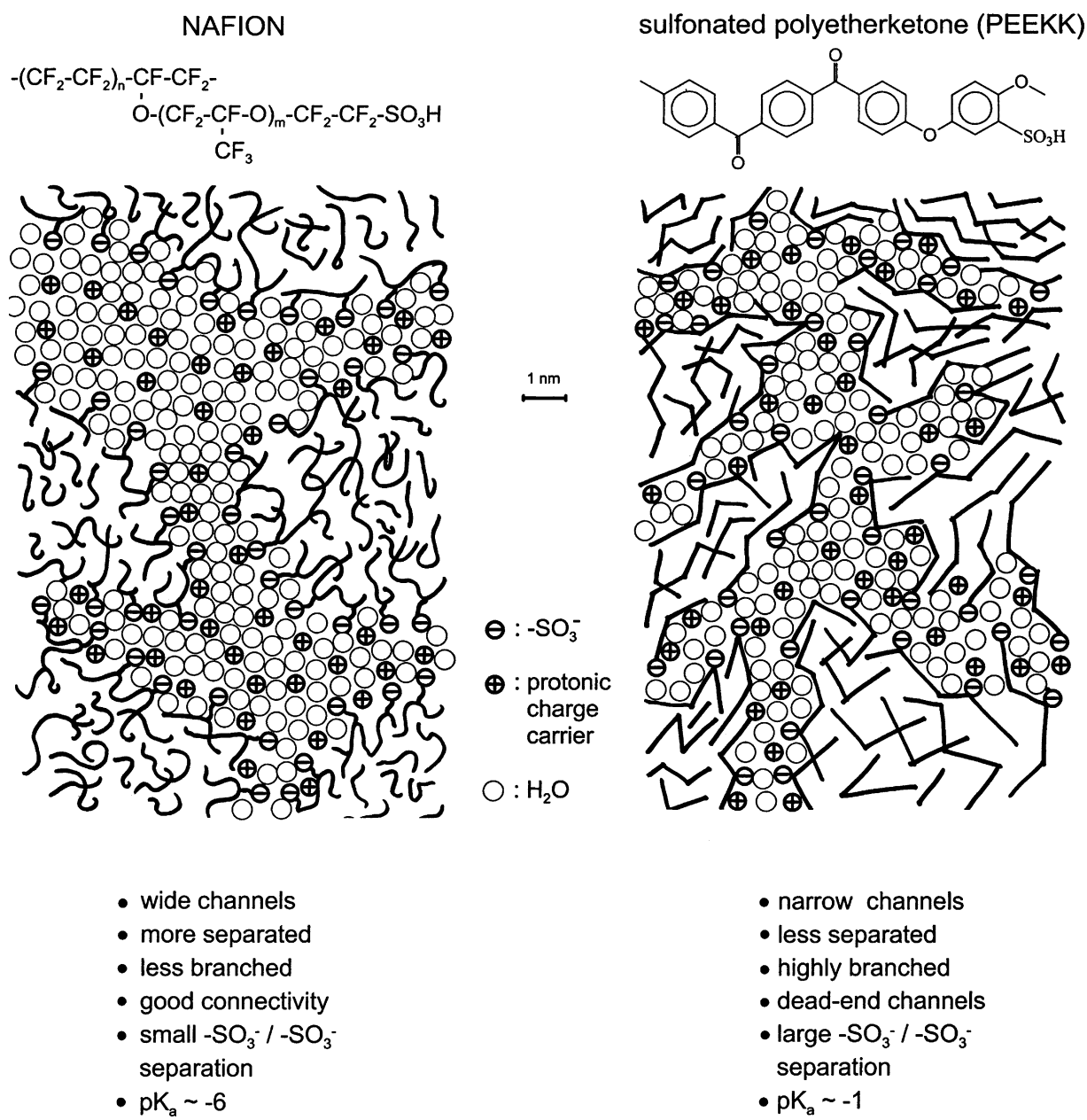

Fig. 1. Comparison of structures: Nafion and sulfonated polyetherketone (SPEEK) [12].

ficients for the sulfonated aromatic polymers are lower than Nafion and as a consequence the conductivity is significantly lower. The low diffusion coefficients are a result of increased protonic association with the $-SO_3^-$ groups and greater electrostatic potential differences due to space charges surrounding the sulfonic acid groups [11], which cause reduced phase separation (when compared to Nafion) and higher activation energies.

As a consequence of the reduced phase separation, sulfonated aromatic polymers exhibit less pronounced hydrophobic/hydrophilic separation and different morphological behaviour [3]. Correspondingly they exhibit narrower and less connected hydrophilic channels and larger phase separation between less acidic sulfonic acid functional groups (Fig. 1). This results in significantly reduced electro-osmotic drag at higher water contents reducing the effect of resistance overvoltage [12].

The conductivity of sulfonated aromatic polymers is also heavily dependant on the degree of sulfonation. At reduced levels of sulfonation the aromatic polymers have lower water contents and reduced conductivity $<10^{-2}\,S\,cm^{-1}$ which is not acceptable for use in fuel cell membranes [13]. However, if the degree of sulfonation is increased to improve conductivity, the mechanical properties of the membrane deteriorate [14]. One proposed solution is to produce nanocomposite membranes with controlled mechanical, physical and chemical properties.

Investigations by Ma et al. [15] into the behaviour of sulfonated aromatic polymers showed that the prime influence on the conductivity in SPEEK membranes was differences in the microstructure. This was demonstrated by fabricating various sulfonated hydrocarbon polymers, which when compared on an equivalent weight, had similar conductivities and quiet varied water uptake. This indicated that there existed little or no correlation between degree of sulfonation and hydration, reaffirming the concepts of Kreuer [3]. Hence, conducting ionomers should be viewed in terms of their phase formation and clustering of organic moieties [15].

2.2. High temperatures operation

The need for new PEMs, capable of operating at high temperatures (>140 °C) is a consequence of the following:

(i) CO catalyst poisoning: Carbon monoxide concentrations in excess of about 10 ppm at low temperatures (<120 °C) will poison the electro-catalyst [11]. This tolerance increases with temperature becoming negligible above about 140 °C [3,11,16]. This has further been reinforced by Yang et al. [16] who completed a theoretical thermodynamic analysis demonstrating how the CO coverage of the surface of the catalyst is reduced as a function of increasing temperature.

(ii) Heat management: Operating at high temperatures has the advantage of creating a greater driving force for more efficient cooling [17]. This is particularly important for transport applications to reduce balance of plant equipment (e.g. radiators). Furthermore, high grade exhaust heat can be intergraded into fuel processing stages.

(iii) Prohibitive technology costs: As previously discussed in Section 2.1, the cost of fabrication of current polymers is prohibitive, mainly as a result of the necessity to use fluorine. Combining manufacturing issues with the potential savings from a reduction in electro-catalyst loading forms a very strong economical driving force to develop fuel cells that operate at high temperatures [18].

(iv) Humidification and water management: The pressurisation needed to reach temperatures beyond 130 °C and maintain high humidities would likely out-weigh any efficiency gains of going beyond this temperature [19]. Membranes that are capable of operating at reduced humidities would not require pressurisation. In addition, it is less likely that they will be affected by the significant water management problems of polymer membranes.

(v) Increased rates of reaction and diffusion: As the temperature increases the reaction and interlayer diffusion rates increase. Additionally, the reduction of liquid water molecules will increase the exposed surface area of the catalysts and improve the ability of the reactants to diffuse into the reaction layer.

(vi) Other: Issues associated with catalyst, bipolar plates and design issues are discussed elsewhere [18,20].

For these reasons it is desirable to move hydrogen PEM technology toward high temperature operation for certain applications. Current polymer membranes are not capable of operating at high temperatures for two reasons: degradation at temperatures above 110–130 °C as a result of the glass transition temperature [21] and because proton conduction is dependant on the membranes being hydrated. The main solutions to this problem have been to substitute the present polymer membranes with composite polymer membranes or use solid acid membranes.

3. Proton transport mechanisms

One of the most difficult hurdles facing the development of novel proton conducting membranes is understanding the proton transport mechanism. At a molecular level the proton transport mechanism for hydrated proton conductors is usually described as either a hopping mechanism (e.g. Grotthuss transport) [22] or as a diffusion mechanism (e.g. through water solvent) [12]. This ambiguity causes a problem in the development of predictive models and new materials. There is however a series of relationships which have been elucidated regarding proton transport and a number of proposed explanations which can be used as a guide. Fig. 2 is a summary of these transport mechanisms.

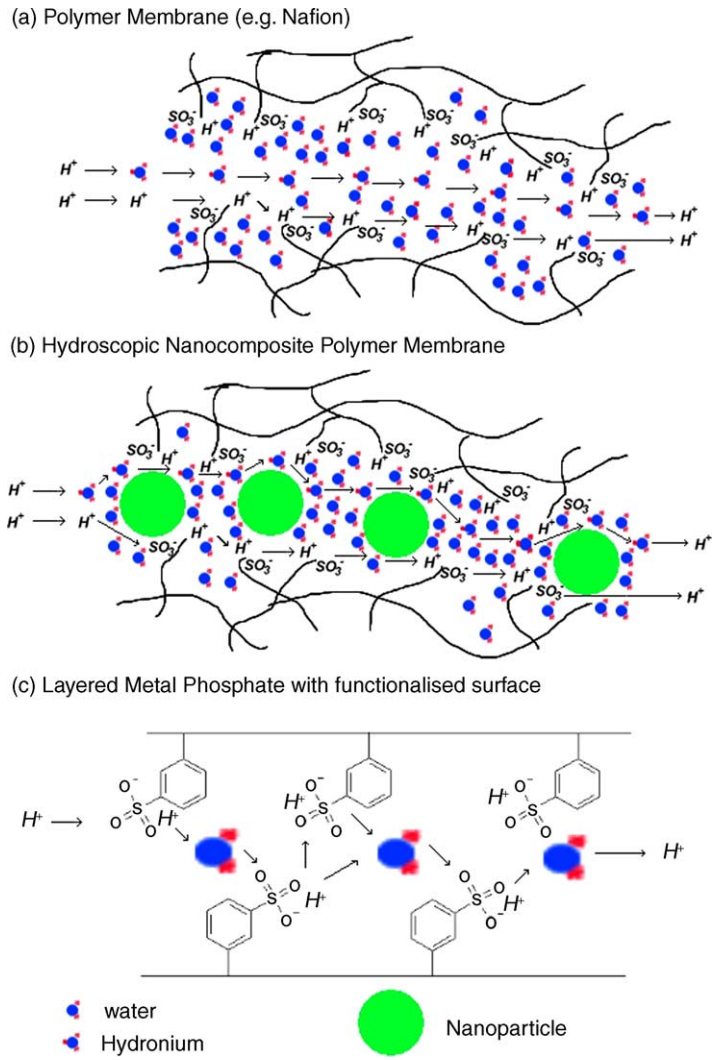

Fig. 2. Proton transport in different membrane configurations: (a) proton transport in Nafion membranes, (b) proton transport in polymer/nanoparticle composite membranes, (c) proton transport in surface functionalised solid acid membranes.

3.1. Polymer membranes

The factor that has the highest influence on conductivity of proton conducting polymers is the degree of hydration. As discussed in Section 2.1 the hydration is dependant on the phase separation of the hydrophilic and hydrophobic domains. Thus in designing new polymer materials this is one of the most important considerations. The effect of hydration in Nafion at constant temperature is significant. The conductivity of Nafion membranes quoted in literature often very widely depends on the system, pretreatment, and equilibrium parameters used. At 100% relative humidity (RH) the conductivity is generally between 0.01 and 0.1 S cm^{-1} and drops by several orders of magnitude as the humidity is decreased [8,16,19,23–25]. As a result, generally one or both of the streams for the perfluorinated sulfonic acid polymers and sulfonated aromatic polymers (e.g. Nafion and SPEK) must be hydrated to keep the membranes swollen so that the ionic inclusions are bridged. Consequently, understanding transport within PEM membranes is partly a matter of understanding the conduction through water.

Transport in water is generally a result of protonic defects and occurs through the breaking and reformation of bonds. This is caused because the protonic defect weakens the intermolecular interactions which causes large variations in bond length combined with rapid breaking and forming of bonds (Fig. 3) [3,26,27]. In a PEM, the hydrated environment, often acidic, acts as a solvent for the diffusion of the hydronium and dimer ions which are formed. This diffusion like effect is shown is Fig. 2a together with the hopping model which may also play a role, especially at reduced hydration.

With the migration of protons through the membrane comes other associated design issues. Firstly the transport of the defect pulls other water molecules through the membrane. This is known as electro-osmotic drag and is caused in part by the size of the molecule and by the molecular attractions between molecules. Secondly, another competing force to proton conduction is back diffusion from the cath-

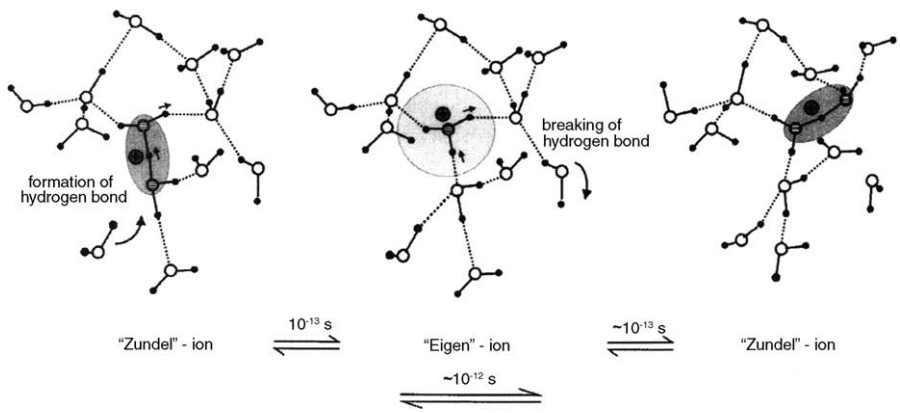

Fig. 3. Transport mechanism of a protonic defect in water [3].

ode, this occurs because of the driving forces formed as the water is removed from the anode due to the electro-osmotic drag. Integrated systems balancing these processes by using product water to maintain hydration are still underdevelopment [16,28].

The challenge when designing PEM membranes is to synthesise a microstructure capable of facilitating the aforementioned proton transport while meeting the other design hurdles. This has been achieved in part with current membrane technology however, refining the technology and understanding how the microstructure influences transport is proving more difficult.

3.2. Transport in composite membranes

Proton transport in composite membranes is the result of a complex process dominated by the surface and chemical properties of both the polymer membranes and composite. Recent results have confirmed this complexity and the difficulty in developing reliable models [24]. Despite this lack of understanding there are three general approaches to increase the proton transport through the use of nanocomposite membranes:

(i) Hygroscopic composites: In this case the introduced material (e.g. silica) is hydroscopic. This effectively increases the swelling of the membranes at lower relative humidities while at the same time increasing the resistance to fuel crossover by creating more resistance in the flow channels. This increases the proton transport through the water phase and reduces methanol permeability (e.g. Fig. 2b).

(ii) Conductive composites: Generally a second proton conducting specie is introduced into the polymer to reduce the methanol and water permeability of the membranes. The aim is to constrict the pores in the polymer matrix and hence create greater resistance to molecular migration of the unwanted species. The introduced conductive specie (e.g. α-ZrP) is assumed to make up for conduction losses due to the reduced water within the membrane.

(iii) Water substituted composites: These composites consist of the polymer matrix to which an alternative proton transporter is added (e.g. hetropolyacids and acid doped polybenzimidazole). The aim is to immobilise a highly conductive acid in the matrix so that the proton conductivity is independent of hydration and electro-osmotic drag is reduced. These membranes have had some success, however the substituted composite tends to leach from the membrane over time.

3.3. Solid acid membranes

Proton transport in solid acid membranes can be either a bulk phenomena or a surface dominated process. Cesium phosphate is a good example of a promising solid acid that has a bulk conduction mechanism [3,29–33]. At room temperature it has a monoclinic structure, however, upon heating through 141 °C it undergoes a phase change to tetragonal. This phase change is accompanied by an increase in the conductivity by 2–3 orders of magnitude and is often referred to as a "superprotonic" transition [33].

A second very promising solid acid for use in PEMFCs is zirconium phosphate [19,34–63]. Surface transport is the dominant transport mechanism for zirconium phosphate and many of its derivatives (e.g. fully hydrated α-ZrP and γ-ZrP)[37,38]. For many metal^{IV} phosphates, surface transport occurs along the exposed acid sites on the surface (inter-layers or pores) which are either involved in the interactions themselves, or responsible for water domains within the structure which promotes the transport similar to polymer membranes. It is this latter water assisted transport which is likely to be the most dominant(e.g. Fig. 2c).

To exploit the surface transport properties of zirconium phosphates, research has focused on the intercalation of Brønsted bases, and weak and strong acidic functional groups. A focused effort on more overlooked areas including synthesis routes and surface area maximisation combined with surface functionalisation (using the aforementioned groups) may lead to further improvements. Ordered mesoporous materials may be an avenue in this regard.

4. High temperature proton conducting membranes (>100 °C)

It is important to understand that high temperature operation is being prevented by three barriers: (1) loss of hydration of the PEM and coincident increase in membrane resistance [16]; (2) membrane degradation of the polymer above 120 °C; (3) lack of intermediate proton conductors in the range of 100–400 °C with a unique proton 'solvating' species supporting conduction in the regime [64]. This has had a significant bearing on the direction of high temperature PEM research which is focused on: modification of existing polymer membranes with composites to increase water retention and possibly contribute to conduction (limited by glass transition temperature); or, novel non-polymer based solid proton conductors that have reduced or no reliance on hydration (often called solid acid proton conductors). Greatest promise for solid acids has been demonstrated by zirconium, titanium and cesium phosphates.

The thermodynamic limitations of high temperature use of water dependant PEMs has been discussed by Yang et al. [16]. Yang et al. suggest that the addition of the organic phases in composite membranes which interacts strongly with the water can reduce the chemical potential of the liquid water. This in turn reduces the differential in the chemical potential between the liquid and vapour phase reducing the water loss from the membrane at a given relative humidity. Thus any modifications to the membrane that can reduce the chemical potential of the liquid phase would be advantageous (*ceteris paribus*). Unfortunately however, above 100 °C the gains realised by reducing the chemical potential by addition of an organic phase are limited as a result of the low water vapour pressure.

The use of microporous membranes also has to be considered in terms of the potential effect on the vapour–liquid equilibrium. It is well established that the thermodynamic assumptions that hold for large volumes cannot be directly applied to micro and nano-domains that are a feature of microporous membranes. Considerations must be given to such effects as capillary forces and diffusion. In this way micro and mesoporous membranes may behave markedly differently in terms of their water management at higher temperatures than polymer membranes. Ultimately the best way of testing the limitations of these membranes is to study them in prototype MEAs and fuel cells.

A further reason for fuel cell testing is that interpreting high temperature conductivity results of PEMs can be misleading. When a direct current is applied to a cell, it is accompanied by water migration from the anode to the cathode (electro-osmotic drag) thus drying the anode side of the membrane. Consequently there is a significant drop in conductivity unless there is a significant back diffusion to compensate [6,65]. There are essentially three ways of resolving this issue: reducing the electro-osmotic drag, making the membrane ultra permeable to water so that back diffusion can allow the cell to reach a steady state, or by hydrating the feed streams. Under high temperature operation, these conditions are yet to be fully understood.

There are many other significant issues that will need to be resolved before solid acid membranes are used in PEM fuel cells. These issues include standard operating considerations such as mechanical strength and durability, cyclability, synthesis and integration in addition to design issues including catalyst compatibility and scale up (or down). Finally, it is important to recognise potentially that the greatest barrier faced will be startup and shut down operation, as typically the cells low temperature and high temperature conductivity mechanisms vary greatly.

A summary of the standout high temperature proton conductors in both hydrated, semi-hydrated and anhydrous conditions are presented in Table 1.

4.1. Nafion and SPEEK at high temperatures

Recently a number of investigations have examined the use of polymeric membranes for high temperature operation [8,16,65,66]. These studies have demonstrated that both Nafion and SPEEK polymer membranes are capable of conducting in reduced humidities ($1 \times 10^{-2}\,\mathrm{S\,cm^{-1}}$ at 160 °C and 34% RH for Nafion), however, they are constrained by their glass transition temperature [8,66]. Passing through the glass transition temperature causes irreversible changes in the crystallinity of the membranes and the achieved conductivities are not repeatable after this occurs.

Alberti et al. [65] also demonstrated that under medium to high temperatures and low humidity, Nafion is superior to the SPEEK membranes due to its superior structural properties. In addition they found that the conductivity of the membranes at low humidities depends directly on the concentration of acid groups and the strength of the acids. Thus, if the goal is to reduce the dependance on humidity, it is very important to focus on acid strength while maintaining the concentration of acid sites.

To attempt to overcome the problems of low conductivity associated with high temperature operation a large number of research groups have focused on nanocomposite membranes. The reasons for this are generally associated with "trapping" more water inside the membrane as elucidated in Section 3.2. A brief summary of some of the composite membranes is presented in Table 2 and zirconium phosphate composites are also discussed in Section 4.5.

4.2. Acid doped polybenzimidazole (PBI)

Acid doped polybenzimidazole (PBI) membranes, usually containing an oxo-acid like phosphoric or sulfuric acid, have been developed as an alternative polymer to Nafion and the SPEEK derivatives for high temperature operation [4,9,67,68]. Development of these membranes has been warranted by their high glass transition temperature (above 200 °C) and the ability of the impregnated acid to act as the

Table 1
Benchmark high temperature conductors

Compound	σ (S cm^{-1})	Conditions	E (kJ mol^{-1})	Reference
Composites				
Nafion/α-ZrP	0.1	373 K,100%RH		[19]
SPEEK/α-ZrP	0.01	298 K,100%RH		[25]
STA/α-ZrP polymer compound	1.9×10^{-2}	373 K,100%RH		[54]
Imidazole/Nafion (transverse)	0.1	433 K,100%RH		[16]
Zirconium				
α-$Zr(O_3POH)_2 \cdot H_2O$	10^{-5} to 10^{-6}	293 K, 90%RH	25	[101]
α-$Zr(O_3POH)_2$	1×10^{-7}	453 K, 00%RH		[102]
pellicular α-$Zr(O_3POH)_2 \cdot nH_2O$	1×10^{-4}	293 K, 90%RH	28	[103]
α-$Zr(O_3PCH_2OH)_{1.27}(O_3PC_6H_4SO_3H)_{0.73} \cdot nH_2O$	1.6×10^{-2}	293 K, 90%RH	18	[34]
	8×10^{-3}	373 K, 60%RH		[34]
α-$Zr(O_3PCH_2OH)_{1.15}(O_3PC_6H_4SO_3H)_{0.85}$	1.2×10^{-4}	453 K, 00%RH	63	[34]
α-$Zr(O_3PC_6H_4SO_3H)_2 \cdot 3.6H_2O$	2.1×10^{-2}	378 K, 85%RH		[78]
γ-$Zr(PO_4)(H_2PO_4) \cdot 2H_2O$	2×10^{-5}	293 K, 90%RH		[38]
γ-$Zr(PO_4)(H_2PO_4)_{0.54}(HO_3PC_6H_4SO_3H)_{0.46} \cdot nH_2O$	1×10^{-2}	293 K,90%RH	21	[36]
Zirconium phosphate (sol–gel)	3×10^{-2}	293 K, 50%RH	40	[94]
Zirconium phosphate pyrophosphate	1.3×10^{-3}	293 K, 90%RH	19	[40]
	2×10^{-6}	373 K, 02%RH		[40]
Titanium				
$Ti(HPO_4)_{0.25}(O_3PC_6H_5)_{0.12}(O_3PC_6H_4SO_3H)_{1.63}$	1.3×10^{-1}	278 K, 85%RH	60	[78]
Cesium				
β-$Cs(HSO_4)_2(H_x(PS)O_4)$	3×10^{-5}	363 K, 00%RH		[19]
	1.6×10^{-2}	473 K, 00%RH		
α-$Cs(HSO_4)_2(H_2(PO)_4)$	2.5×10^{-3}	313 K, 00%RH		[19]
Other				
Fullerene	7×10^{-7}	293 K, 00%RH		[104]

Table 2
Summary of nanocomposite polymer membranes

Compound	Comments on high temperature operation compared to base case	Ref.
Nafion Composites		
Nafion/α-ZrP	Conductivity similar to Nafion, improved MEA and fuel crossover	[16,24,105,106]
Nafion/silica	Conductivity similar to Nafion, improved fuel crossover	[107]
Nafion/HPA	Good improvements in conductivity over Nafion counteracted by leaching	[3,13]
Nafion/mordenite	Very small conductivity improvements at high temperatures only	[108]
Nafion/imidazole	Very good conductivity results however imidazole poisoned Pt catalyst	[11,16,109]
SPEEK Composites		
SPEEK/α-ZrP	No appreciable improvement over SPEEK	[25,106]
SPEEK/ZrO_2	>1 Order of magnitude reduction in methanol permeability and conductivity	[25,106]
SPEEK/silica	Reduction in H_2O permeability without a significant decrease in conductivity	[106]
SPEEK/α-ZrP /ZrO_2	Large reduction in methanol permeability without a large conductivity sacrifice	[106]
SPEEK/BPO_4	Reasonable conductivity compared to Nafion composites at 100–140 °C	[14]

proton solvating species which enables them to conduct virtually independent of water.

Reported proton conductivities of acid doped PBI membranes vary markedly, due in part to the number of different synthesis techniques for these membranes. In addition it is widely acknowledged that the conductivity is also strongly dependent on the acid doping level. For membranes doped with H_3PO_4 values between 0.001 and 0.05 S cm^{-1} at 140 °C have been reported [69]. While these results do appear to be very encouraging there has been little advancement of this technology since early reports in 1996 [67,68] and very few reported MEA and fuel cell trials owing to the acid stabilisation and leaching issues.

4.3. Solid acid membranes – zirconium phosphate

Layered metal^{IV} phosphonates are good proton conductors. Organic moieties (R) which are contained in the $\alpha(M^{IV}(O_3P{-}R)_2 \cdot nH_2O)$ and γ $(M^{IV}PO_4(O_2P(OH)R)_2 \cdot nH_2O)$ structure are bridged through phosphorus atoms to an inorganic two dimensional matrix. These species act as protonic conductors when the R contains a protogenic function (e.g. $-COOH$, $-PO_3H$, $-SO_3H$, $-NH_3^+$) [38].

The most extensively studied groups of metal^{IV} phosphates in terms of proton conductivity is zirconium phosphate. Zirconium hydrogen phosphate, α-$Zr(HPO_4)_2 \cdot H_2O$ (henceforth α-ZrP), was first synthesised by Clearfield and

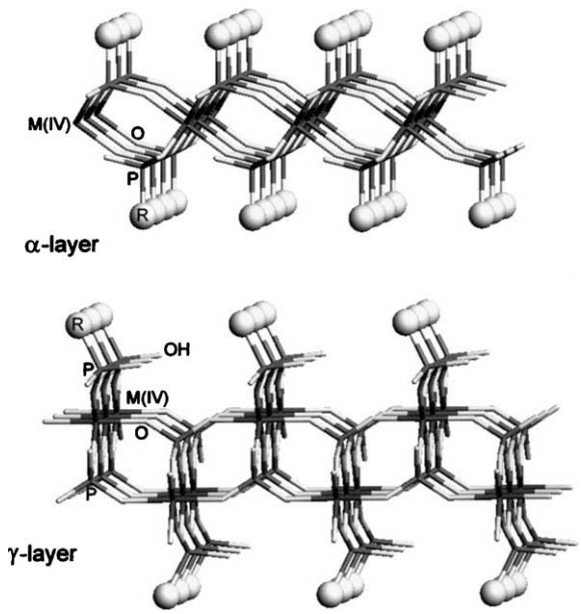

Fig. 4. Schematic representation of α- and γ-layers of meal^{IV} phosphonates [79].

Stynes in 1964 [44] by reflux, and then Alberti and Torracca [70] produced this material by complexing with hydrofluoric acid. Nonetheless, extensive investigations into its use as a proton conductor did not commence until the 1990's. For details on synthesis methods including hydrothermal synthesis, exchanged derivatives and structural properties the reader is referred to earlier papers [71–73].

There are two predominate structures of zirconium hydrogen phosphate α- and γ- as illustrated in Fig. 4. Recent investigation has led to the discovery of new structures synthesised via hydrothermal routes, designated as τ-ZrP [46] and Ψ-ZrP [74]. The structure of α-ZrP lends itself best to proton transport because it has a pendant OH group which extends into the interlayer region and forms a hydrogen bonded network with water. That said, the γ-ZrP does have the advantage of having an extra water molecule per formula unit and is more acidic than the α-ZrP [73].

The transport mechanism in α-ZrP at room temperature is dominated by surface transport; four orders of magnitude greater than the bulk transport, however the crystallinity also plays an important role [75]. Isoconductance measurements also indicate that the conductivity varies linearly with the number of surface phosphate groups [76]. In addition, conductivity in α-ZrP is highly dependant on the hydration, varying by two orders of magnitude as the relative humidity is increased form 5 to 90% [77]. Recent research has confirmed the dominance of the surface transport and demonstrated enhancements that can be made through modification of the P–OH groups [41].

Based on this understanding of α-ZrP, attempts to enhance the proton conductivity have been made in the following directions:

(i) Intercalation of functional groups.
(ii) Composites α-ZrP membranes.
(iii) External surface area maximisation (mechanical and colloidal synthesis).
(iv) Internal surface area maximisation (sol–gel synthesis and pillaring).

4.4. Intercalation of functional groups

Attempts to improve the conductivity of solid acid membranes have included the synthesis of new layered compounds, where Brønsted bases are intercalated in the interlayer region or functionalised organic radicals replace the hydroxyl of the phosphate group [73]. Significant improvement was achieved with the intercalation of strong acidic functional groups of $-SO_3H$ (there was little improvement for the weak $-COOH$) into the interlayer region. Metal^{IV} sulfophosphonates and zirconium alkyl sulfophenylphosphonates or the variety $(Zr(O_3PC_6H_4SO_3H)_{0.85}(O_3PC_2H_5)_{1.15}\cdot nH_2O)$ and $(Zr(O_3PC_6H_4SO_3H)_x\ (O_3PCH_2OH)_{2-x}\cdot nH_2O)$ have been investigated for their conductivity under different temperature and relative humidity regimes [34,78]. The best conductivity reached in the anhydrous state was by the ethylsulphophenyl phosphonate: $5 \times 10^{-6} \leq \sigma \leq 1.2 \times 10^{-5}$ S cm^{-1} at 180 °C (as compared to 10^{-6} S cm^{-1} for microcrystalline α-ZrP). This put it amongst the best fully anhydrous proton conductors [34–36]. For hydrated results at 20 °C the conductivity increased from 10^{-4} at 22% RH to 1.6×10^{-2} S cm^{-1} at 90% RH while at 100 °C and 90% RH conductivities as high as 0.05 S cm^{-1} were reported (comparable to Nafion).

Unfortunately the sulfophenylphosphonates, when compared to standard α-ZrP exhibit increased dependance on relative humidity at humidities less than 50%. They are however, still capable of conducting at 0.01 S cm^{-1} at 65% RH and 100 °C [35]. One of the other significant advantages of the sulfophenylphosphonates is that as the temperature is increased from ambient conditions up 100 °C there is no drop in conductivity, indicating that the hydroscopic nature is not affected.

More recent work [79] has shown the zirconium sulfoarylphosphonates also display high conductivity values, although it is more strongly affected by humidity. In this work, zirconium compounds were synthesised with the sulfonic function attached to a phenyl, benzyl or to a fluorinated benzyl group. The highest conductivity reported were for the sulfophenylphosphonates of up to 5×10^{-2} S cm^{-1} at 100 °C and 100% RH through to 2×10^{-2} S cm^{-1} at 150 °C and 100% RH.

Titanium phosphates are also very good at conducting protons [13,59]. Mesoporous MCM type zirconium and titanium phosphates synthesised by the sol–gel route using surfactant templates have surface areas 240–330 m^2 g^{-1} [59]. The best conductivity values were achieved for samples where the surfactant was removed by HCl extraction and for the titanium samples. All conductivities recorded were very low ($<5 \times 10^{-7}$ S cm^{-1}).

Better results have been achieved by intercalating sulfophenylphosphonate groups [80]. $Ti(HPO_4)_1$-$(O_3PC_6H_4SO_3H)_{0.85}(OH)_{0.3}\cdot nH_2O$ generally had a conductivity an order of magnitude greater than the similar zirconium derivative (0.1 S cm^{-1} at 20 °C and 90% RH and >0.1 $S\ cm^{-1}$ at 100 °C and >65% RH). For hybrid Nafion membranes slight improvements in conductivity were made together with increases in the thermal stability, however humidity dependance remained unchanged.

Other attempts to improve the transport of α-ZrP are summarised in Table 1. It is important to note when considering the fully sulfonated compounds that they are highly deliquescent and hard to recover from solution; this is circumvented by preparing mixed derivatives where the sulfonated groups are replaced by non-sulfonated groups (e.g. O_3PCH_2OH) [81]. It is also of importance to realise that sulfonated materials are likely to have a temperature limit at 200 °C where in some instances decaying of the proton conductivity has been attributed to the decomposition of the SO_3H groups [38].

4.5. Composite zirconium phosphate membranes

The glass transition limitations of perfluorinated and aromatic sulfonated membranes have been extended by composite modification. Conductivities of composite membranes now surpass most basic polymer membranes for high temperature operation. The best results reported have employed interfacial surface maximisation of dispersed colloidal zirconium phosphate derivatives through exfoliation. This affects simultaneously the conductivity, mechanical properties and fuel crossover.

Increased swelling in the polymer membranes leads to increases in proton conductivity [11]. Therefore, to improve the water retention properties of Nafion above 100 °C, Costamagna et al. [19] investigated Nafion/zirconium phosphate composite membranes at up to 130 °C and 3 bar. Commercially available Nafion was impregnated with α-ZrP by reacting $ZrOCl_2$ with H_3PO_4 at 80 °C in a similar method to that described in [82] and later replicated by others [24]. The results highlighted how MEA performance of composites can be superior to polymer membranes at high temperatures even though the conductivity is not significantly increased. Current densities in MEAs were 4–6 times better than that of pure Nafion (130 °C at 3 bar fully hydrated). Concurrently the results demonstrated that current platinum catalyst technology is compatible with this composite arrangement [16], which potentially overcomes any development challenges, and that there was a reduction in methanol crossover.

Similar experiments [82] showed that composite Nafion/ZrP membranes can be produced with a conductivity of 0.64 S cm^{-1} compared to pure Nafion 0.40 S cm^{-1} at the same conditions, while halving the methanol permeability (100% RH, conditioned in boiling water for 1 h). Furthermore, composite membranes of dispersed α-ZrP in SPEEK, have been demonstrated to show a three-fold improvement in conductivity with composites loaded with 10 wt.% α-ZrP [25]. Experiments varying the inorganic species (silica, zirconium phosphate sulfophenylphosphonate or α-ZrP) have been also been conducted [83], however only slight improvements in the conductivity were realised, falling short of pure zirconium phosphate sulfophenylphosphonate.

Conductivities of 10^{-3} and 10^{-4} S cm^{-1} achieved at 61% RH and 60 °C were reported from composite α-ZrP and poly(vinyl acetate)/glycerin gel membranes [84]. It was found that the composite performed poorly below 60 °C, however it improved over the non-composite membranes above this temperature. The composite also exhibited a Williams–Landel–Ferry relationship indicating that the ion conductivity mechanism was similar to that exhibited by liquids.

Early efforts to increase the conductivity of α-ZrP by engineering composite α-ZrP and fumed silica failed [61], however more recent efforts with colloidal dispersions of inorganic silicates were successful [37,49]. Pressed pellets with surface areas up to 500 m^2 g^{-1} achieved maximum conductivity at 100 °C and 97% RH of 3×10^{-3} S cm^{-1} for $x_{Zr} = 25\%$ [37], one order of magnitude higher than crystalline α-ZrP ($\sigma = 1.5 \times 10^{-4}$ S cm^{-1}) under the same conditions. Under anhydrous conditions the maximum conductivity was 8×10^{-8} S cm^{-1} at 200 °C. This indicates that there is no proton diffusion along the anhydrous surface and only the bulk phosphate groups are contributing to the conduction process.

Damay and Klein [24] suggested that the improved properties of composite membranes are a result of complex interactions between the structure and proton mobility. It was hypothesised that changes in the thermodynamic properties in the membrane due to the hygroscopic nature of the entrapped nanoparticles may be the cause. Recently, Benziger and coworkers [66] suggested that it was only the increases in the rigidity of the membrane which come from the addition of a composite that were responsible for the increases in conductivity. What these studies suggest is that the effect of adding a composite to a polymer membrane is a result of one, or a number of the following: (1) thermodynamic changes due to hygroscopic nature, (2) changes in capillary forces and the vapour liquid equilibrium as a result of changes in the pore properties, (3) surface charge interactions between the composite species, and (4) changes to the morphology of the membrane. This demonstrates that the exact nature of the composite interactions still requires further investigation at a fundamental level in order to understand the key relationships that can help engineer better composite membranes in a controlled manner.

4.6. External surface area maximisation

4.6.1. Ball-milling

Ball-milling α-ZrP with α-Al_2O_3 has a significant affect on conductivity [49]. A composite of 23% α-Al_2O_3 showed a conductivity increase of 5–10 times that over the standard α-ZrP when milled [49]. This was attributed to modification

of the surface character, creating local, proton rich, hydrated domains. The importance of changes in the structure and surface on the conduction mechanism was further highlighted by experiments with pure α-ZrP. Ball-milling of standard α-ZrP for 6 h caused the proton conductivity to increased from 3×10^{-6} to 6×10^{-4} S cm^{-1}, due to the reduction in crystallinity and increase in exposed surface.

4.6.2. Colloidal zirconium phosphates

Investigations into the proton conductivity of modified ZrO_2 have demonstrated the applicability of surface modification techniques to metal oxides [41,85]. Surface modification of nanometre sized zirconia (ZrO_2) particles by reaction with phosphoric acid was able to produce pseudo zirconium phosphate particles with a conductivity of 5.0×10^{-3} S cm^{-1} at 90% RH [41]. Further Carriere et al. [41] were able to exploit the *meta*-sulfophenylphosphonic acid (SPPA) grafting [34], previously only used in the layered zirconium phosphates. Despite this there were still hurdles to overcome related to an increased reliance on hydration (Section 4.3), and limits due to steric hinderance of the grafted molecules. More significant was the subsequent reaction with zirconium propoxide to yield a nanometre sized colloidal dispersion with a high concentration of sulfonate and hydroxyl surface groups. This final modification significantly reduced the dependance on humidity of the sulfonated materials. Processes of this nature give a clear example of how the surface transport mechanism can be exploited to increases surface area and develop proton conductivity. Conductivity of the modified SPPA membranes were $>2 \times 10^{-2}$ S cm^{-1} at relative humidities as low as 50% (pressed powders). It was concluded that the smaller (5 nm) particles lead to a larger number of grain contacts per unit volume, making proton transport from grain to grain easier.

4.7. Internal surface maximisation – porous zirconium phosphates

Evaporation-induced self-assembly [86,87] offers an exciting path to the modification of zirconium phosphates and porous metal oxides [88–93], for fuel cell applications. Drawing parallels, adapting synthesis techniques and applying the principles used in fields such as catalysis has the potential to enhance the proton conductivity of solid acid conductors. Similarities such as an increased performance with surface area and increased concentration of acid sites on available surface should not be overlooked. Realising the benefits of integration and cross over of techniques can increase efficiency in this important research field.

Sol–gel synthesis for PEMs has been demonstrated [94,95]. Honma et al. [95] showed the versatility of this technique, creating hybrid materials with nanosized interfaces between inorganic and organic domains. In essence this is the principle used for the majority of composite work discussed. Through the synthesis of bridged tri-alkoxysilanes, they demonstrated that controlling the sol–gel conditions for hydrolysis and condensation of monomers can change conductivity. This technique could equally be applied to the tuning of the synthesis of solid acid conductors – engineering of the nanophase. Sol–gel processing is indeed a versatile synthesis route to the tailoring of nanostructure of solid acids and one method of creating mesoporous solid acids.

Mesoporous zirconium phosphates have been analysed for proton conductivity by Jimenez-Jimenez et al. [51] and Tian et al [93]. In a novel approach Jimenez-Jimenez et al. dissolved a bromide surfactant template in orthophosphoric acid prior to reacting it with zirconium *n*-propoxide [51]. The surfactant was then removed by either extraction with HCl/ethanol or calcination to 540 °C. Of particular interest was the decrease in acidity after calcination as a result of the condensation of neighbouring hydrogen phosphate groups. This suggests that calcination at lower temperatures to preserve acidity may be an avenue of exploration to enhance proton conductivity. Surface areas of 326 and 251 m^2 g^{-1} and average pore diameters of 2.7 and 2.5 nm, for the extracted and calcined samples, respectively were reported. There was an absence of long range hexagonal ordering of the pores. Tian et al. [93] also achieved a similar result, successfully synthesising ordered mesoporous zirconium phosphate with surface areas reaching a maximum value of 212 m^2 g^{-1} and achieved conductivities of the pressed powders in the order of 7.5×10^{-7} S cm^{-1} (298 K and 76% RH).

Another recent approach to the synthesis of high surface area porous zirconium oxo-phosphate was reported by Ciesla et al. [43]. Surfactant templated synthesis with $Zr(SO_4)_2$ as a Zr source and a hexadecyltrimethylammonium bromide surfactant was used. The product was compared to MCM-41 hexagonal structured silica zeolite, however, upon calcination, the ordered pore structure collapsed. Stabilisation was achieved through treatment with phosphoric acid, however there was still a reduction in long range ordering after calcination. BET surface areas as high as 390 m^2 g^{-1} with a C_{20} surfactant were recorded.

Based on their knowledge of the proton transport mechanisms of α-ZrP (i.e. surface transport is dominant) Alberti et al. [40] investigated the conductivity of mesoporous zirconium phosphate pyrophosphate to examine the effect of increasing the surface area. Conductivity at 20 °C reduced from 1.3×10^{-3} to 4×10^{-7} S cm^{-1} as the humidity was reduced from 90 to 20%, approximately a 350-fold increase over crystalline α-ZrP. Contrary to expectation the evidence suggested that there was as increase in bulk −POH groups as the conductivity rose implying that when hydrated, the proton conductivity is a bulk property. Increases in the conductivity over α-ZrP were attributed to a reduction in the activation energy of the sample (4.6 kcal mol^{-1} at 20 °C and 90% RH). Longer term observations of the materials lead to the discovery that the interlayer phosphate groups tend to rehydrate and the mesopores disappear (the surface area had reduced to $<10\, m^2\, g^{-1}$). This is a disconcerting result as it raises questions as to the stability of this structure in near fuel cell conditions.

A method of creating micro and mesoporous zirconium for catalysis applications has been explored through the pillaring of the layers of the compound [45,57,58,72]. It works on the basis of allowing access to the interlayer region by propping (pillaring) open the layers creating pores. Reports by Clearfield [72] use a diphosphonic acid together with a suitable inorganic cation to form inorganic layers of the metal and PO_3 groups. These are then crosslinked with alkyl or aryl groups, R, which form pillars spaced with phosphate or phosphite groups. Surface areas up to 375 $m^2\,g^{-1}$ have been achieved by using this method. More recent methods extending the same approach have created very strong Brønsted acid catalysts with a high pore tailorability in the region of 1–2 nm and surface areas as high as 400 $m^2\,g^{-1}$ [45]. Potential exists for the use of such catalysis preparation techniques for proton conducting membranes.

One possible barrier to the use of these techniques may be the removal of templates. As discussed evidence suggests that calcined samples exhibit lower conductivities than their uncalcined counterparts. Novel approaches (e.g. [96]) where the organic structure directing agent is disassembled within the zeolite pore space is one solution. This would preserve the hydration of interlayer groups and structure that are responsible for the higher conductivity of the unclacined samples.

4.8. Solid acid membranes – cesium phosphate and sulfates

The structure of cesium hydrogen sulfate ($CsHSO_4$) is characterised by a disordered hydrogen bond network and is attractive for use in PEM fuel cells because of its anhydrous conduction at high temperatures and stability up to 250 °C [30–33]. At a temperature of 141 °C it undergoes a "superprotonic" phase change (from monoclinic to tetragonal structure) and the proton conduction changes to a mechanism involving proton transfer between neighbouring SO_4 tetrahedra and tetrahedra reorientation [29]. The first example of a $CsHSO_4$ fuel cell was published in 2001 [33]. This was able to operate at 150–160 °C in a H_2/O_2 configuration with an open circuit voltage of 1.1 V and a short circuit current density of 44 mA cm^{-2}. It was also stable in humid environments which had up till then been an issue. Whilst encouraging, this result is well short of the performance of equivalent composite polymer membranes operating at 130–140 °C [19].

More recently the same research group have extended the solid acid demonstration with a CsH_2PO_4 electrolyte membrane fuel cell operating on both methanol and hydrogen at 250 °C [30]. This was explored because of the reduction of the sulfate and selenate solid acids under hydrogen atmospheres [97], which could also be a problem with sulfonated zirconium phosphates at high temperatures. The cell was able to operate stably and peak power and maximum power densities of 48.9 mW cm^{-2} and 301 mA cm^{-2} (short circuit) were attained for the H_2O_2 fuel cell. This was a very positive result however the conductivity of ($CsHSO_4$) at low temperatures (<140 °C) is low (10^{-6} S cm^{-1}) and as a result, it is likely that these fuel cells will have a number of startup issues when used in cyclic applications (like automobiles). Fabrication methods also need to be streamlined as similar experiments have been unable to draw current [16].

4.9. Summary of high temperature membranes

A summary of the conductivity of membranes for high temperature applications is provided in Table 3.

5. Discussion

5.1. Engineering future solid acid membranes

To achieve success at engineering high temperature PEM membranes it is important to define goals. Steele and Heinzel [18] suggest that a combined area-specific resistivity of fuel cell components should be below 0.5 Ω cm^2 and ultimately approach 0.1 Ω cm^2, thus giving power densities of at least 1 kW dm^{-3} and 1 kW kg^{-1}. It is apparent from an analysis of the recent development of solid acid membranes that attainment of these goals under high temperature operation is likely to be achieved by a focus on:

Table 3
Conductivity summary of solid acid conductors

Compound	Comments on high temperature operation compared to base case	Ref.
Zirconium phosphate (α-ZrP)	Reasonable conductivity in all temperature ranges compared to Nafion	[34–38,94]
Sulfonated ZrP	Very significant increases in conductivity compared to α-ZrP	[34–38,94]
Milled ZrP	Small increases in proton conductivity compared to α-ZrP	[49]
Pillared ZrP	Large increase in conductivity compared to α-ZrP; stability questionable	[73]
Sulfonated TiP	Higher conductivities than comparable zirconium materials	[78]
Cesium phosphate	Good conductivity above 141 °C; requires further development	[30–33]
cesium sulfate	Good conductivity above 141 °C; questionable stability	[30–33]
Sol–gel P_2O_5–TiO_2–SiO_2	Conductivity of ca 10^{-3} S cm^{-1}; low stability	[110]
ZrO_2	Slightly improved conductivity compared to ZrP	[111]
Sulfonated ZrO_2	Conductivity of ca 0.05 S cm^{-1} from 60 to 100 °C at saturated conditions	[85,41]
Fullerenes	Promising results for dry conductivity up to 200 °C	[104,112]
Fumed silica/α-ZrP	Hydration dependant conductivities ca. one order of magnitude below Nafion	[37,49,61]

(i) Surface functionalisation: It is clear that surface functionalisation of porous solid acids via intercalation or other methods can increase the conductivity by in excess of three orders of magnitude. This is a very powerful option available. New breakthroughs in this area will come by investigating new proton solvating species with increased acid strength, concentration and thermal and chemical stability which can be attached to the surface of mechanically stable membranes. One possibility with great promise in this area is sol–gel porous metal oxides.

(ii) Surface area modification: In cases where a solid acid uses a surface transport mechanism it is clear that increases in surface area can have a direct impact of the conductivity. By integrating increases in surface area and specific surface functionalisations tailored for proton conduction, further conductivity enhancements can be made.

(iii) Structural and chemical modification: Preliminary indications are that high conductivities are not only achieved with zirconium phosphates but also titanium and cesium phosphates and other various metal oxides. A possible avenue for investigation is mixed metal oxides and metal oxides with different crystalline and pore structures. Changes to the metal and pore characteristics are not yet understood.

(iv) Cesium phosphates: Cesium phosphates are a very strong contender for high temperature proton conductors. Research focusing on both the stability of its structure and degradation in humid environments as well as modification and operating considerations including startup and cyclability will likely be the focus of research. The demonstration of the application of this class of materials will only serve to increase research efforts in this area.

(v) Composites: Solid acids may be used in composite membranes in a number of ways. For example, supporting solid acids in a mechanically stable porous matrix is one possible solution to the current mechanical shortcomings of these membranes. Other composite proton conductors may incorporate the conductive properties of organic species such as fullerene because of their stability in higher temperatures.

(vi) Tuning of synthesis: Controlling and tuning of the synthesis cannot be underrated as a method for manipulating the proton conductivity of species. It has been demonstrated that the proton conductivity of α-ZrP is highly dependant of the crystallinity. Controlling the synthesis of zirconium phosphate and other acid metal phosphates through sol–gel or other synthesis routes is a further area that warrants investigation.

While these modifications to the design of the membrane have the potential to increase the conductivity significantly, constructing an efficient MEA may require small design changes. For example, it will be important to ensure that

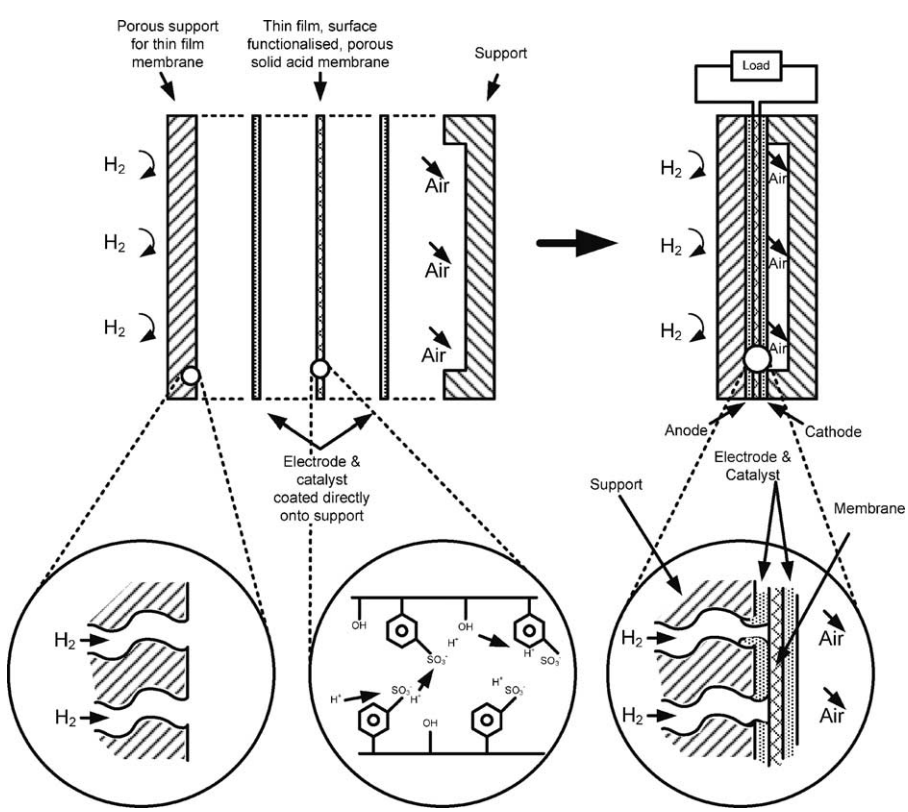

Fig. 5. Example solid acid fuel cell based on a surface functionalised, porous, thin film PEM.

the tri-phase electrode/catalyst/membrane interphase contact is optimised. Another critical considerations is the effect of variations in mechanical properties caused by changing from polymer to ceramic membranes.

These challenges are not insurmountable. For example, one possible prototype MEA model conforming to these design goals is presented in Fig. 5. It is constructed using a simple porous substrate, onto which a thin coating of catalyst and electrode are made. Onto this surface, a thin film of surface functionalised, mesoporous, metal oxide is coated, before coating the cathode electrode and catalyst directly onto the membrane. This satisfies the above design considerations and has the advantage of being able to be made extremely thin and having no issues with gas distribution at the cathode. The concepts of such a design are not far removed from those used in anode supported solid oxide fuel cells [98,99], however the low operating temperatures would remove a great deal of the complexity related to sealing issues.

5.2. Other applications of solid acids

In addition to being highly suited for use in high temperature PEMFCs, solid acid membranes also have potential applications for use as direct alcohol fuel cells. High fuel crossover is a significant problem in polymer membranes which leads to large efficiency losses (>30%) [100]. Solid acid membranes do not have this problem because of their different structure and transport mechanisms [30,34].

Methanol crossover in polymer PEMs occurs because methanol dissolves easily in the polar domains of the matrix. It is then dragged through the membrane with the water molecules by electro-osmotic drag. Solid acid membranes have the potential to overcome these problems if designed with a reduced dependance on water and without the polar domains of the polymers.

6. Conclusion

Composite polymer membranes through modification with inorganic species have demonstrated favourability for PEMFCs in the temperature range of 100–130 °C. Comparable conduction to low temperature polymer based membranes has been achieved with small improvements in fuel crossover and MEA performance, however these are ultimately limited by the glass transition temperatures of the polymer. To pass through the 140 °C barrier will require the development of new novel membranes.

Solid acids are a very strong contender in this regard. Research has demonstrated the stability and operability of acid metal phosphates above 140 °C and at reduced levels of hydration. The focus must now turn to the development of these materials by combining research paths. The ultimate challenge will be to produce a mechanically stable membrane that can operate both at high temperatures in reduced humidity environments for normal operation and at lower temperatures and varied humidities for startup and shutdown.

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