Intermediate temperature proton-conducting membrane electrolytes for fuel cells

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This review provides an overview of intermediate temperature proton-conducting membrane electrolyte materials for fuel cells. Such fuel cells operate in the approximate temperature range of 150–300°C and can capitalize on a number of technological reasons for operating H_2/air. These reasons include enhancement of electrochemical kinetics, simplified water management, efficient cooling, and useful waste heat recovery. Importantly lower quality, for example, reformed hydrogen, containing relatively large amounts of carbon dioxide, may be used as the fuel. The materials, which have been the focus of intermediate temperature proton-conducting fuel cells, include heteropolyacids, metal pyrophosphates, solid acids, and acid-imbibed high-temperature polymers such as polybenzimidazole. © 2013 John Wiley & Sons, Ltd.

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INTRODUCTION

Fuel cells are electrochemical devices that directly convert chemical energy in fuels (e.g., hydrogen and alcohol) into electrical energy. Fuel cells are often classified according to the choice of electrolytes or type of fuel, which in turn determine the electrode reactions and the type of ions that carry the current across the electrolyte. The electrolyte can conduct either positively charged (cations, e.g., H^+) or negatively charged ions (anions, e.g., OH^-). Negative-charged ions flow from cathode to anode, which is the opposite direction to positive-charged ions.

The heart of a fuel cell comprises the electrolyte, anode, and cathode, which for practical purposes are usually engineered into a membrane electrode assembly (MEA). In theory, any substance capable of chemical oxidation that can be supplied continuously can be converted 'galvanically' as fuel at the anode of a fuel cell. Similarly, the oxidant can be any fluid that can be reduced at a sufficient rate. For practical reasons, the most common oxidant is gaseous oxygen, which is readily available from air. In the vast majority of fuel cell development, hydrogen is used as fuel. At the anode of a proton-conducting fuel cell, hydrogen gas ionizes, releasing electrons and creating H^+ ion (protons), thereby releasing energy.

$$2\,H_2 \rightarrow 4H^+ + 4e^-$$

At the cathode, oxygen reacts with protons and electrons supplied from the anode to form water.

$$4H^+ + 4e^- + O_2 \rightarrow 2H_2O$$

Proton conductivity is achieved using solid electrolytes, mainly polymers, although inorganic compounds and ceramics are also possible.[1] The most well-developed proton-conducting membrane fuel cells use a polymer electrolyte membrane (PEM), which typically operate at temperatures below 100°C. The need to handle corrosive acids (or bases) is thus eliminated in this system. They are attractive for certain mobile and portable applications and especially as a prime motive power for automobiles and other forms of transport. Polymer electrolyte membrane fuel cells (PEMFCs) can generate high power densities, in excess of 1.0 W/cm^2 of cross-sectional area, and high current densities (>1 kA/cm^2) at relatively high efficiency or single cell voltage (>0.65 V).[1] The

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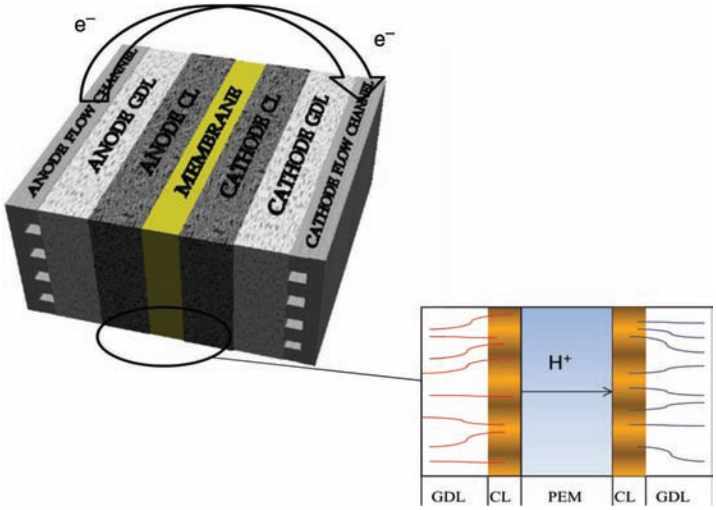


FIGURE 1 | Components of a fuel cell.

PEMFC typically operates at low temperatures, enabling faster start-up than higher temperature fuel cells. In addition, as the cell separator is a polymer film and the cell operates at low temperatures, cell sealing, assembly, and handling are less complex issues compared with most other fuel cells.

The cell components within a PEMFC, shown in Figure 1, are from the center to outward:

- An ion-exchange electrolyte. This electrolyte should be an electronic insulator, and thus only allow ion transfer and not electron transfer. Otherwise the electrons would not pass around the external circuit and thus 'short-circuit' the cell and the function of the fuel cell would be lost.
- The electrocatalyst layers (the electrodes) between a backing layer and the membrane where the cell reactions occur.
- An electrically conductive porous backing layer, which conducts electrons and allows gases to permeate to the catalyst layers.
- Bipolar plates (BP), or flow-field plates, that deliver the fuel and oxidant to the MEA, electrocatalyst reaction sites, via flow channels and electrically connect cells in the stack.
- Sealing gaskets.

The combination of the membrane, electrocatalyst layers, and porous backing layers is typically pressed together (under heat and pressure) to form the MEA. The catalytic electrodes are cast as thin films, which may be deposited onto the backing layer, then bonded to the membrane or applied directly to the membrane.

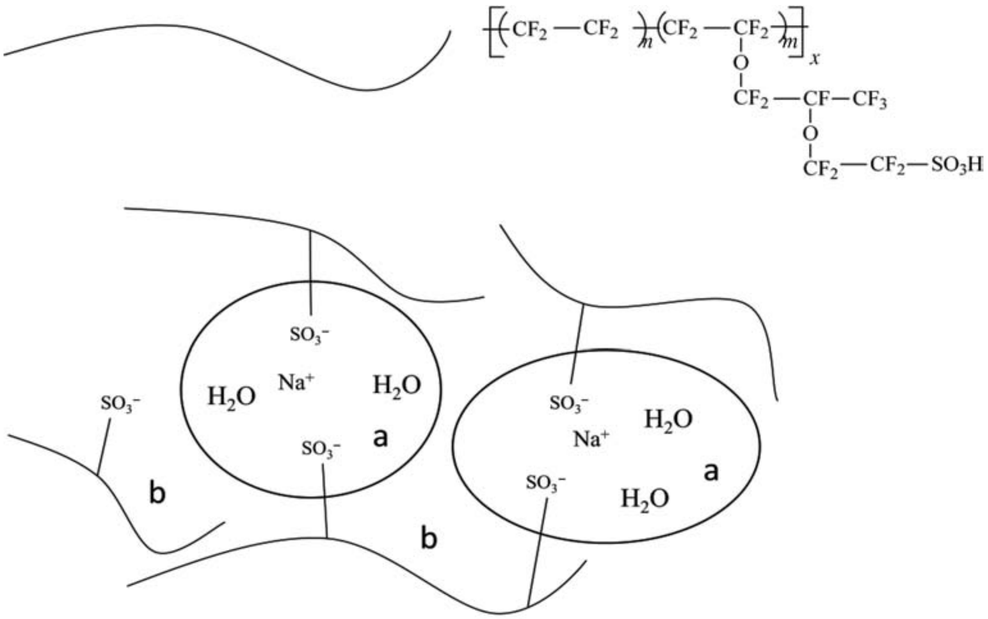
The MEA in a fuel cell must enable efficient, simultaneous transport of reactant gases, vapor, and liquid water, ions, and electrons. It must also accommodate the presence of nitrogen (from air) and any other gaseous materials (impurities) in the fuel or oxidant and any requirements for humidification and removal of heat generated within the cell. Within the MEA, the electrolyte must provide ionic conductivity between the anode and cathode as well as in the structure of both electrodes. Consequently, the electrolyte is a critical component within a fuel cell MEA.

The PEM materials used for PEM fuel cells can be classified as[2]:

- perfluorinated ionomers,
- partially fluorinated polymers,
- nonfluorinated membranes with aromatic backbone,
- nonfluorinated hydrocarbons,
- acid–base blends.

Perfluorosulfonic acid (PFSA) polymer is the most commonly used material for membranes for fuel cells. The main characteristics of PFSA membranes that are relevant to fuel cell operation are that they:

- exhibit high chemical stability—stable against strong bases, strong oxidizing, and reducing acids, Cl_2, H_2, and O_2 at temperatures up to 125°C.
- are mechanically strong and can be formed into thin nonporous films of thickness as low as 25 μm.



(a) clustered regions fo water filled sulphonic acid groups
(b) interfacial region containing some pendant side chains, some water, and sulphate groups

FIGURE 2 | Model of Nafion and ionic conductivity mechanism. The Yeager Three Phase Model: (A) fluorocarbon backbone, (B) interfacial region containing some pendant side chains, some water, and sulfate groups, and (C) clustered regions of water-filled sulfonic acid groups.

- have high conductivity (and ion-exchange capacity) when wet.
- are highly stable in operation.

The PFSA consists of three 'regions', (1) a PTFE backbone, (2) side chains of vinyl ethers (e.g., –O-CF2-CF-O-CF2-CF2-), which terminate in sulfonic acid groups in a cluster region (Figure 2). The principle reason why the ionomer membranes function well as ion-conducting materials is that the sulfonate groups form into clusters, which are very hydrophilic and attract water. When these membranes become hydrated, the protons become highly mobile in the hydrophilic regions formed by the sulfonic acid clustering. These clusters effectively form channels through which H^+ ion can move quite freely under a potential gradient. A consequence of this structure is that the membrane performance is critically dependent upon water content, as well as the transport of water through the clusters.[3]

The perfluorosulfonic acid family of membranes includes a range of alternative products from different manufacturers, using, for example, different side chains, but generally the inherent characteristics are similar. Companies who supply PFSA membranes include DuPont, Asahi Glass and Asahi Chemicals, and Solvay. Such materials are referred to as ionomers. Differences in materials are essentially in the length of the side chain and available thickness. For example, Nafion 117 has a thickness of 175 μm (the 7 in 117 refers to its thickness—seven thousandths of an inch). Now a standard for fuel cells is Nafion 112, which is 50 μm, whereas Nafion 111 is 25 μm. These thinner membranes have less mechanical strength, which has lead other companies such as W.L. Gore to develop composite membranes to reinforce Nafion. Another consequence of using thinner membranes is the resulting increase in reactant crossover, which decreases fuel utilization and causes some electrode polarization as well as potential problems for electrode and material corrosion through formation of peroxy species. Thicker membranes reduce reactant crossover but at the expense of higher resistance and hence lower power density and efficiency. Although Nafion type products have been the standard for PEM fuel cells, commercial market with different operating conditions is stimulating the research of new membranes. For example, the automobile companies would prefer operating temperatures above 100°C to reduce heat transfer requirements (i.e., the size of the radiator). However, PFSA membranes cannot maintain adequate membrane water content, and hence acceptable proton conductivity, at temperatures $>90°C$, without operating at higher pressures, which introduces higher equipment (compressor) costs and energy loss from the fuel cell itself. In addition, the glass transition temperature (T_g) of Nafion is 111°C, and thus PFSAs have limited operating temperature range as the mechanical stability is compromised at such temperatures.

One of the drawbacks of Nafion and similar materials is the relatively high cost and engineering issues related to manufacture. Hence, new alternative membranes and alternative manufacturing techniques are being developed. The membrane is characterized by its equivalent weight and the ion-exchange capacity. A typical equivalent weight range is 800–1100 mEq per dry gram of polymer. Variations in equivalent weight affect the characteristics of the membrane. Lower equivalent weight results typically in higher conductivity and tends to increase the swelling of the membrane when exposed to water or humidity. The swelling of commercial Nafion products is of the order of 25 wt%. Thus, a material such as Nafion 112, with an equivalent weight of 1100, will swell from a thickness of 50 to around 62.5 μm. Membrane swelling has implication in MEA fabrication and in operation. The proton conductivity of Nafion 112 is 0.06 S cm^{-1} at 100% relative humidity (RH) and 30°C and 0.092 in liquid water at 20°C. Thus, Nafion 112 has a cell resistance of around 0.1 Ω cm^2 equating to a voltage loss of 100 mV at 1 A cm^{-2}. However, as temperature increases, these voltage losses can increase if sufficient hydration of the membrane is not maintained. The conductivity can fall by an order of magnitude at 80°C compared with that achieved at 60°C and lower.

An advance in membrane technology was achieved by using an internal support layer to enhance the mechanical strength of the membrane film, when using very thin membrane to reduce cell voltage losses. An example is the Primea 55 and 56 series membranes manufactured by W.L. Gore.[4] Such membranes provided good mechanical stability by using an expanded microporous PTFE membrane of very high porosity into which the ionomer is introduced. This enabled the use of ionomers of equivalent weight <1000, which had high conductivity but membranes are typically 25 μm thick with conductivities up to twice that of Nafion 112 under equivalent conditions of humidity and temperature.

Asahi Glass has developed a Flemion type membrane using a PTFE fibril support to provide mechanical stability. Such membranes have resistivity values only slightly larger than the unreinforced membranes (7–8 Ω cm) but have around five times the tear strength and four times the elastic modulus at 80°C and 95% RH.[5]

Nonfluorinated membranes are made from aliphatic or aromatic polymers with benzene ring structures in the backbone or in the pendant groups attached to the membrane polymeric backbone. Hydrocarbon membranes although may not offer similar stability to PFSA types, are less expensive than PFSA membranes and their structure permits the introduction of polar sites as pendant groups to increase the water uptake.

Mehta and Cooper[6] have reviewed the area of PEM and produced a short list of 16 possible membrane materials for fuel cell applications. The use of partially sulfonated polyarylenes has been the subject of significant research because of their low cost and good stability. The aromatic rings offer the possibility of electrophilic as well as nucleophilic substitution. Materials such as polyarylene sulfone, polyarylene ether sulfone, and polyarylene ether ether ketone can be directly sulfonated using concentrated sulfuric acid or chlorosulfonic acid

Acid–base complexes considered for fuel cell membranes involve incorporation of an acid component into an alkaline polymer base to promote proton conduction. Such complexes can maintain high conductivity at elevated temperatures without suffering from dehydration effects.

INTERMEDIATE TEMPERATURE PROTON-CONDUCTING MEMBRANE ELECTROLYTES

Application of fuel cells in the intermediate temperature range of 100–400°C has attracted increasing interest over recent years.[7–9] The operating temperatures of such fuel cells are between that of solid oxide fuel cells (SOFCs) and proton-exchange membrane fuel cells (PEMFCs). Intermediate temperature fuel cells (ITFCs) are easier to use for portable power application and offer better control of the heating temperature than SOFCs.[7,8] Compared with low temperature PEMFC, the ITFC offers some significant potential advantages as follow.

1. Minimize anode catalyst poisoning caused from, for example, CO.
2. Reduce the requirement of noble metal (e.g., Pt) catalyst loading.
3. Improve the efficiency of the fuel cell.
4. Avoid fuel cell flooding by the product water.
5. Provide the possibility to use nonnoble metal catalyst.
6. Improved heat transfer characteristics of the cell.

Therefore, the development of ITFC, which has satisfactory conductivity at higher temperatures and low RH, is of great importance for fuel cell research and development.[9–13]

The use of phosphoric acid, which has a good conductivity and thermal stability, is well known in phosphoric acid fuel cells (PAFC) for intermediate temperature range (175–220°C).[9] However, the conventional PAFC has certain disadvantages such as phosphoric acid electrolyte can have limited immobilization in certain matrices. Therefore, attempts to apply the phosphoric acid to certain elements (polymer membrane), through chemical bonding, attracted much interest.[13–15] One such polymer is the generically known polybenzimidazole (PBI; see Table 1).

The phosphoric acid-loaded poly(2,21-(*m*-phenylene)-5,51-bibenzimidazole) (PBI/H_3PO_4) complex has shown a great deal of potential for medium-temperature fuel cell applications. Li et al.[12] have characterized the phosphoric acid-loaded PBI with the acid loading defined as the molar percentage of acid per repeat unit (PRU) of the polymer. Such complexes are sensitive to the acid content and temperature. At 450% loading and a temperature of 165°C, the conductivity of PBI membrane was about 4.6×10^{-2} S cm^{-1}. It was also observed that at very high levels of acid loading (around 1600%), the conductivity could reach 0.13 S cm^{-1}.

Recently, inorganic modifiers, including zirconium phosphate ($Zr\ (HPO_4)_2 \cdot nH_2O$, ZaP),[16] phosphotungstic acid ($H_3PW_{12}O_{40} \cdot nH_2O$ PWA),[17] and boron phosphate (BPO_4),[18] were combined with PBI to improve the properties of PBI/H_3PO_4 membrane. The heteropolyacids (HPAs) powders are well-known inorganic solid acids with strong acidity and have shown high proton conductivity.[19,20] However, their chemical stability are unsatisfactory because of their hygroscopicity.[20] Cesium salts of heteropolyacid (CsHPA) were insoluble in water as reported by Li et al.[21] In their work, the PBI/$Cs_{2.5}H_{0.5}PMo_{12}O_{40}$/$H_3PO_4$ composite membrane had high conductivity (>0.15 S cm^{-1}) and gave a good power density of 0.7 W cm^{-2} (atmospheric pressure, 150°C with H_2/O_2) in a fuel cell. These data indicate that CsHPA could be a good candidate to form composite membranes with PBI for ITFC applications. However, there are little data reported comparing the properties of various CsHPA/PBI/H_3PO_4 composite membranes.

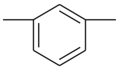
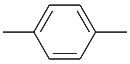
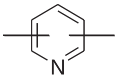
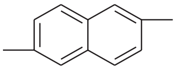
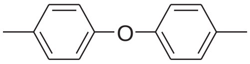
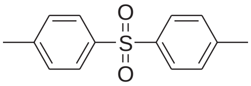
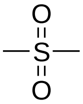
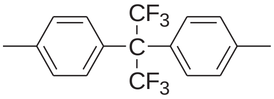
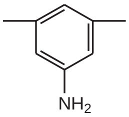
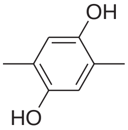
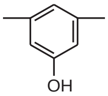
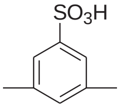
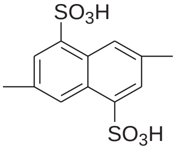
Heteropolyacids

HPAs are nanosized metal–oxygen anion clusters with a unique variety in structure and strong acidity.[22–24] HPA compounds include a metal (such as tungsten, molybdenum, or vanadium), oxygen, acidic hydrogen atoms, and a element generally from the p-block (such as silicon, phosphorus).[25,26] HPAs have different hydrated structures (Keggin and Dowson Structures), and the Keggin structure ($H_nXM_{12}O_{40}$) was a well-known structure, which consists of a central atom in a tetrahedral arrangement of oxygen atoms surrounded by 12 oxygen octahedra connected with tungsten or molybdenum because its ease of preparation and strong acidity.[22–24] HPA molecules bridge water moieties through formation of hydronium ions such as H^+, H_3O^+, $H_5O_2{}^+$, so HPAs act toward the water of hydration, which is generally loosely bound in the structure for high proton conductivity.[25] It is the reason that the conductivity of Keggin unit HPAs are related to the number of water molecules, which are determined by the RH and temperature. So HPAs are attractive as inorganic modifiers in polymer matrix to improve conductivity and thermal stability for PEMFC.

In water, all protons of HPAs are dissociated. HPAs were stronger acids than typical inorganic acids, including H_2SO_4, HBr, HCl, HNO_3, and $HClO_4$. The difference can be attributed to the larger heteropoly anions than the anions in common inorganic acids, leading to a lower strength of bonding between the proton and heteropoly anions.[27] Furthermore, greater degrees of delocalization of the charge of the anion would lower the effective negative charge on its individual basic proton accepting centers and weaken the attraction of the proton to the anion.[27] Among the HPAs, the order of acid strength was $H_3PW_{12}O_{40} > H_4SiW_{12}O_{40} > H_4GeW_{12}O_{40} > H_6P_2W_{18}O_{62} > H_5BW_{12}O_{40} > H_6CoW_{12}O_{40}$.[27] As a result, HPAs $H_{8-x}XM_{12}O_{40}$, are much stronger than $H_{8-x}XO_4$. Among the HPAs, the order of acid strength was $H_3PW_{12}O_{40} > H_4SiW_{12}O_{40} > H_4GeW_{12}O_{40} > H_6P_2W_{18}O_{62} > H_5BW_{12}O_{40} > H_6CoW_{12}O_{40}$.[27]

Heterepolyacid has been added into polymer matrices such as PBI to form composite membrane used in PEMFC. A phosphomolybdic acid ($H_3PMo_{12}O_{40}$, denoted here as PMo_{12}) and poly(2, 5-benzimidazole) (ABPBI) composite membrane had a proton conductivity of 0.03 S cm^{-1} at 185°C without humidification and was stable up to 200°C reported by Gomez-Romero et al.[28] He et al.[29] reported that phosphotungstic acid (PWA, $H_3PW_{12}O_{40} \cdot nH_2O$) and silicotungstic acid (SiWA, $H_4SiW_{12}O_{40} \cdot nH_2O$) provided good mechanical strength in a composite membrane. Staiti and Minutoli[30] reported that silicotungstic acid and silica/PBI (SiWA-SiO_2/PBI) composite membranes had high conductivity, comparable to that of the PBI membrane, and SiO_2 provided a stable structure for the HPA, avoiding its dissolution

TABLE 1 | Structures of PBI Variants

	R	X
m-PBI	 [15]	
p-PBI	 [15]	
Py-PBI	 [16]	
Naphthalin-PBI	 [17]	
O-PBI/ OO-PBI/ SO_2-O-PBI	 [18]	
SO2-PBI	 [19]	O [18]  [18]
F6-PBI	 [20]	
NH2-PBI	 [21]	
2OH-PBI	 [22]	
OH-PBI	 [23]	
Sulfonated PBI	 [19]	
Sulfonated naphthalin-PBI	 [24]	

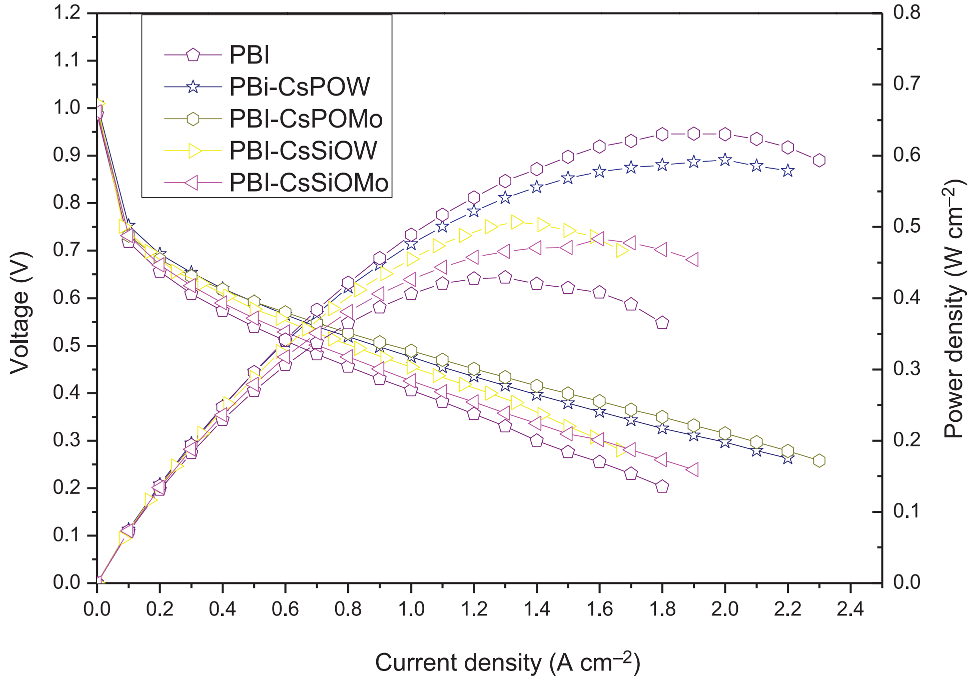


FIGURE 3 | Polarization and power density curves of a PEMFC operated at 150°C with H_2/O_2 atmospheric pressure. Pt loading: cathode 0.7 mg cm^{-2}; anode 0.7 mg cm^{-2}; anhydrous condition, H_3PO_4 loading level: 4.5, gas rate: anode: 40 dm^3 min^{-1}; cathode: 70 dm^3 min^{-1}.

in water.[30] Kim et al.[31] found that the hydrogen bonding of the bridging water molecules between the tungstic oxide and sulfonic acid was stronger than that in the pristine polymer. When the sulfonic acid group was present in the polymer, the higher degree of sulfonation created a stronger interaction between the HPA particles and polymer backbone.[32]

HPAs have a low surface area (5 m^2 g^{-1}) and are highly soluble in water.[27] So, substitution of the proton by an alkaline cation exhibits interesting effects on the surface area and solubility in water. Salts with large monovalent ions, such as Cs^+, resulted in unique changes in the surface area and hence in the amount of acidic sites on the surface and a maximum for $Cs_xH_{3-x}PW_{12}O_{40}$ compounds with $x = 2.5$. $Cs_{2.5}H_{0.5}PW_{12}O_{40}$ showed significantly higher activities than $H_3PW_{12}O_{40}$.[27] The $Cs_xH_{3-x}PW_{12}O_{40}$ compounds were synthesized by a titration method.[33] During this process, Cs_3 crystallites are initially formed followed by the epitaxial adsorption of $H_3PW_{12}O_{40}$ on the surface of Cs_3.[27] The surface area of CsHPA increased when the Cs content (x) increased from 2 to 3 and decreased when $0 < x < 2$, and a maximum number of acidic sites on the surface (surface acidity) showed at $x = 2.5$.[34]

Recently, a $Cs_{2.5}H_{0.5}PMo_{12}O_{40}$ (CsPOM)/PBI membrane, imbibed with phosphoric acid, was used in a PEMFC. The CsPOM/PBI membrane gave a much higher conductivity (even up to 0.25 S cm^{-1}) than the pristine PBI membrane. For the fuel cell performance, the peak power density with CsPOM/PBI was 0.7 W cm^{-2}, and the OCV was around 0.95 V.[21] By comparing $Cs_xH_{3-x}PMo_{12}O_{40}$ (CsPOMo), $Cs_xh_{3-x}PW_{12}O_{40}$ (CsPOW), $Cs_xH_{4-x}SiMo_{12}O_{40}$ (CsSiOMo), and $Cs_xH_{4-x}SiW_{12}O_{40}$ (CsSiOW), CsHPA/PBI composite membranes gave best conductivity and superior performance. The P form of the CsHPA provided higher conductivity, when used in composite membranes, than the CsHPA with Si atom, although the mechanical strength was inferior.[33]

The fuel cell performance results are shown in Figure 3. The open circuit voltages (OCV) of all membranes were more than 0.95 V, which can be ascribed to the low gas crossover properties of the membranes.[33] All the membranes exhibited significant activation polarization, with voltage reductions of some 0.25 V at 0.1 A cm^{-2}. The performance of the cells with the CsHPA/PBI/H_3PO_4 composite membranes was significantly better than that with the PBI membranes. Current densities of CsHPA/PBI/H_3PO_4 at 0.4 V with oxygen were over 1 A cm^{-2} at 150°C. The CsPOW and CsPOMo membranes gave better performance than those

CsHPA with Si atom. The peak power densities of H_3PO_4-loaded PBI, CsPOW/PBI, CsPOMo/PBI, CsSiOW/PBI, and CsSiOMo/PBI fuel cells were 0.429, 0.594, 0.631, 0.507, and 0.483 W cm^{-2}, respectively. The better performance was mainly attributed to the superior proton conductivity of the former and also the strong acid and water retention properties of the composite membrane.

With atmospheric air, the OCVs of membrane were more than 0.95 V. The cell voltages produced with the CsHPA composite membranes were greater than those with the PBI membrane at high-current densities. The CsPOMo gave a peak power density of 0.45 W cm^{-2} with air at 150°C. The peak power density with the PBI membrane was 0.334 W cm^{-2}.

Polybenzimidazole

PBI refers to an amorphous thermoplastic polymer with linear heterocyclic polymers containing benzimidazole nuclei as a repeat unit has a high thermal stability ($T_g = 425$–$436°C$), excellent chemical resistance, retention of stiffness, and toughness, and good membrane-forming properties.[35–40] PBI membranes can be impregnated with variable amounts of phosphoric acid to yield proton-conducting membranes that can work at temperatures up to 200°C.[40] As a speciality polymer, PBI is used as textile fibers for a wide range of high temperature applications, and refers to a commercial product under the trademark Celazole® (see Figure 4, Scheme 2-1).[41]

The PBI in the wholly aromatic form was first synthesized by Vogel and Marvel in 1961.[42] A two-stage process was developed to produce PBI with tetraaminobiphenyl (TAB) and diphenyl isophthalate (DPIP) as monomers as shown in Figure 4, Scheme 2-2.[42] Choe[43,44] developed a single-stage method to synthesize high molecular PBI through using the isophthalic acid to replace DPIP in the presence of catalysts of organo phosphorus and silicon compounds (Figure 4, Scheme 2-3).

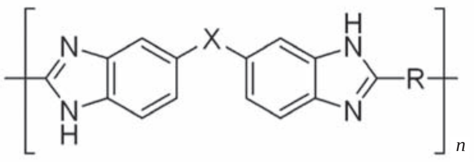
PBI can also be synthesized in homogeneous solutions with solvents such as polyphosphoric acid (PPA)[45] (Figure 4, Scheme 2-4). This method is an excellent route for preparing laboratory or small scale polymers because a moderate temperature (170–200°C) and more stable monomers (TAB stabilized by tetrahydrochloride) are used.[45] Other solvents rather than PPA were reported also been used for the homogeneous synthesis of PBI, such as molten sulfolane or diphenyl sulfone,[46] and a mixture of phosphorus pentoxide, and methanesulfonic acid.[47,48]

After poly [2, 2-p-(phenylene)-5, 5-bibenzimidazole] (pPBI; Figure 4, Scheme 2-1) was synthesized in 1961,[42] extensive work on synthetically modified PBI of varied structures, which consist of bis(3,4-tetraaminodiphenyl) containing ether, sulfone, ketone, and aliphatic groups, and various bis(phenoxycarbonyl) acid derivatives were undertaken. Some functional groups were introduced into PBIs to reduce the intermolecular forces between the polymer chains and to overcome the restricted polymer solubility as well as to improve other physicochemical properties of acid-loaded PBI electrolytes. Such groups include, ether sulfone,[49,50] fluorine,[51] N-phenyl 1,2,4-triazole group,[52] and perfluorocyclobutyl.[53] In addition, the thermal stability, oxidation resistance, and water absorption were increased. A variety of diacids or sulfonated diacids were used to prepare PBI with modified structures. Such as 4, 4-(hexafluoroisopropylidene)bis(benzoic acid),[54] (4,8-disulfonyl-2,6-naphthalenedicarboxylic acid,[55] or 5-sulfoisophthalic acid.[56] Recently, Xu et al.[57,58] synthesized a series of amine-terminated hyperbranched PBI with good mechanical properties with the help of cross-linkers. Poly(2,5-polybenzimidazole) (AB-PBI) has a simpler structure than PBI without the connecting phenyl rings and therefore a high concentration of the basic sites in the structure.

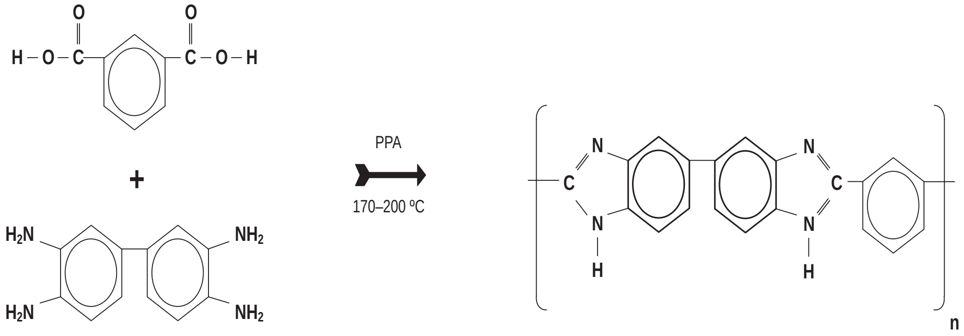
The NH groups in the imidazole rings are chemically reactive, and PBI could first react with an alkali hydride (e.g., LiH, NaH) to produce a PBI polyanion, and then react with a alkyl, aryl, or alkenyl methyl halide such as hydroxyethyl,[59] sulfoalkyl,[60–62] and cyanoethyl.[63] The N-substituted PBI may increase polymer spacing or decreased polymer packing when a group was introduced resulting in a high acid loading and therefore high proton conductivity.[44]

PBI can be dissolved in the strong acids. There are two direct casting methods used for membrane fabrication; from either phosphoric acid and trifluoroacetic acid (TFA) mixture (called TFA-cast) or from PPA (called PPA-cast).[41] PBI also dissolves in a few organic solvents, such as *N, N*-dimethylacetamide (DMAc), *N, N*-dimethylforamide (DMF), and *N*-methylpyrrilidone.[41,42] Typically, DMAc is chosen as a suitable solvent.

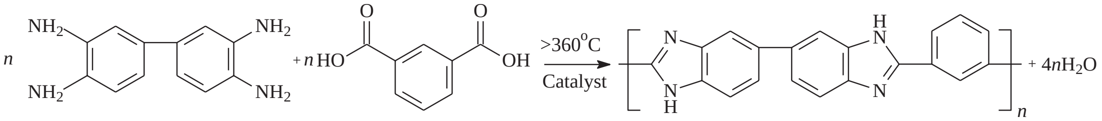
The conduction mechanisms indicate that higher conductivity will be achieved when loaded with acid. Many acids, such as H_3PO_4, H_2SO_4, $HClO_4$, HNO_3, HBr, and so on, were investigated by researches to find the most suitable acid.[41] The conductivity decreased in the order: $H_2SO_4 > H_3PO_4 > HClO_4 > HNO_3 > HCl$ for high acid loadings.[40] However, PBI is not stable in hot sulfuric acid, so phosphoric acids is better as it is amphoteric.[41,42] Generally, the higher acid loading



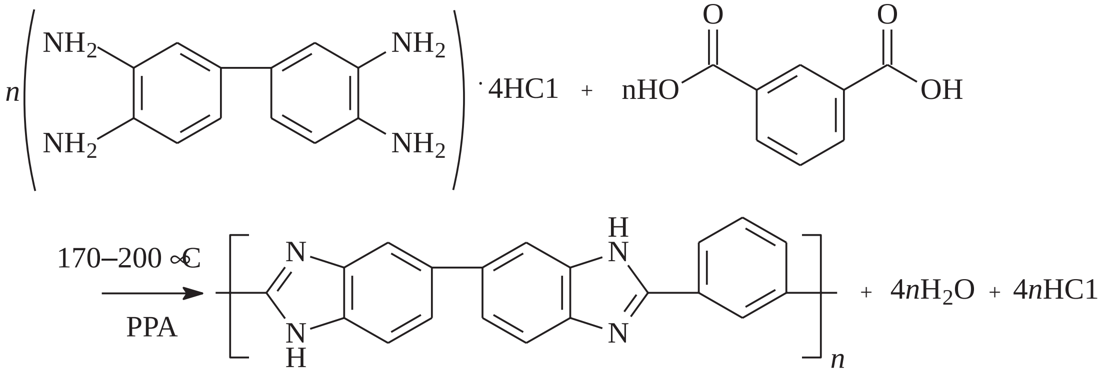
Scheme 2-1 *Poly 2,2´-m-(phenylene)-5,5´-bibenzimidazole.*



Scheme 2-2 *The two-stage process for PBI synthesis.*



Scheme 2-3 *The single stage process for PBI synthesis.*



Scheme 2-4 *The PPA process for PBI synthesis.*

FIGURE 4 | Structure of the reactants and the PBI product.

results in higher conductivity for PBI membrane, but has the opposite effect on mechanical strength, which is also influenced by the molecular weight.[42] When the PBI is loaded with acid, the selection of acid loading should take both the conductivity and mechanical properties into account. For DMAc-cast membranes, acid loadings of 5–6 PRU of molecular are considered.[42] The proton conduction mechanism for PBI has been studied by many researches and there are four possible mechanisms proposed.[48]

1. Protons directly hopping from one N site to another when it is not imbibed with; but this has a very small contribution to the conductivity.
2. At low acid loading (less than 2 PRU), proton hopping from the N–H site to a phosphoric acid anion.
3. Proton hopping along the $H_3PO_4/H_2PO_4^-$ chain at high acid loading (~6 PRU), the free acid provides the major conductivity.
4. Humidity will also increase conductivity because protons can hop via water molecules.

Kawahara et al.[63] reported the conductivity to be from 10^{-9} to 10^{-5} S cm^{-1} for PBI membranes with a PA loading of 1.9 PRU under anhydrous conditions at temperatures up to 160°C. Even under humidified conditions and at 200°C, the conductivity did not exceed 10^{-2} S cm^{-1} with low PA loading.[64] When excess PA is present in the membrane (i.e., at a PA loading of 4–6 PRU) at 200°C, the conductivity for PBI with PA loadings between 4 to 6 has been reported to be about 4–7 × 10^{-2} S cm^{-1}.[16]

The dry PBI membrane has a small elongation at break of around 1–3%, and a tensile strength of 60–70 MPa at room temperature, while saturated with water, the elongation and tensile strength increase to about 7–10% and 100–160 MPa, respectively.[65] When phosphoric acid is introduced into the polymer structure at a low acid-doping level range, there is no significant change of modulus or tensile strength of the PBI.[66] However, the strength of PBI membrane will decrease due to the free acid reducing the intermolecular forces.[66] The strength is also strongly influenced by the average molecular weight and casting method.[67]

The membrane in a PEM fuel cell is also as a separator of reactants. Hence, the gas permeability of the membrane is an important parameter to take into account. PBI membranes have low gas permeability for both hydrogen and oxygen (2×10^{-13} and 5×10^{-15} mol cm^{-1} s^{-1} bar^{-1}, respectively).[68] He et al.[69] reported a hydrogen permeability of 1.6–4.3 × 10^{-12} mol cm^{-1} s^{-1} bar^{-1} and an oxygen permeability of 5–10 × 10^{-14} mol cm^{-1} s^{-1} bar^{-1} at temperatures from 80 to 180°C.[69] The permeability of PA-loaded PBI membrane (doping level of 6) is two to three times higher than the acid-free membrane at 120–180°C, due to PA swelling the polymer matrix and thus separation of the polymer chains.[67]

Overall the conductivity of PBI can approach the target of 0.1 S cm^{-1} set for high temperature membranes. However, to achieve acceptable high ionic conductivity, the membrane must be impregnated with phosphoric acid, which is not very tightly bound to the polymer backbone. With the acid impregnated membranes, there are potential problems with acid migration, corrosion of cell components, adsorption of anions on the catalyst, and acid volatility. As a result, similar precautions as in a PAFC (avoiding liquid water, corrosion protection) are necessary. Other high temperature polymers have also been considered for fuel cells and include the use of aromatic polyethers with pyridine units (as developed by Advent TPS^R). Such membranes operate at up to 200°C and are imbibed with up to 200% phosphoric acid.

Pyrophophates

In recent years, various pyrophosphates or diphosphates of tetravalent elements (MP_2O_7 with M = Sn, Zr, Ti, and Ce) doped with small amounts of some low valency cations (e.g., In^{3+}, Al^{3+}, Mg^{2+}, Sb^{3+}, Sc^{3+}, and Ga^{3+}) exhibited remarkable proton conductivity ($>10^{-2}$ S cm^{-1}) in the temperature range 150–400°C under unhumidified conditions. These MP_2O_7 compounds have a stable cubic structure in a wide temperature range.[70] As early as 2002, Irvine proposed cubic SnP_2O_7 as a promising negative electrode material of Li-ion battery.[71] Since 2006, Hibino and coworkers[72–86] (in Nagoya University) made some major contributions to the study tin pyrophosphates as proton conductors for electrochemical devices, such as fuel cells and sensors in the intermediate temperature range (150–300°C). Several other researchers or research groups independently investigated pyrophosphates of various tetravalent cations and various doping elements for MP_2O_7.[81–99] However, the conductivity data reported by different researchers are dramatically different, even by several orders of magnitude. This may be because the pyrophosphates were prepared with different methods and thus exhibited different degrees of cation deficiency. There are some informative review articles on SnP_2O_7 recently published by Hibino.[100–102] The conductivity and temperature range of operation of these

TABLE 2 | Review of MP_2O_7 Proton Conductors

Material	Conductivity[1] (S cm^{-1})	Temperature Range (°C)	Preparation Method	Author and Reference
$In_{0.1}Sn_{0.9}P_2O_7$ powder	0.01–0.195	75–300	650°C calcination	Hibino[72,76]
$Al_{0.05}Sn_{0.95}P_2O_7$ powder	0.045–0.19	100–300	650°C calcination	Hibino[77]
$In_{0.1}Sn_{0.9}P_2O_7$ powder	0.09–0.019	130–230	650°C calcination	Wang[81]
$Y_{0.05}Zr_{0.95}P_2O_7$ film	7.4×10^{-7}–1.5×10^{-4}	200–340	Sol–gel	Li[82]
CeP_2O_7	0.001–0.018	50–200	300–400°C calcination	Sun[83]
$Sb_{0.2}Sn_{0.8}P_2O_7$ powder	0.008–0.1	100–300	650°C calcination	Scott[84]
SnP_2O_7-LaP_3O_9 composite	10^{-7}–1.7×10^{-4}	100–350	Sol–gel, 580 °C	Beck[85]
$Mg_{0.1}Sn_{0.9}P_2O_7$ powder	0.001–0.11	50–350	650°C calcination	Hibino[86]
$Sn_{0.9}Sc_{0.1}P_2O_7$ powder	2.35×10^{-6}–2.82×10^{-9}	400–900	aqueous solution method	Tao[87]
core-shell $Sn_{0.9}In_{0.1}P_2O_7$	n/a	n/a	Coprecipitation method	Song[89]
$Sn_{0.92}In_{0.08}P_2O_7$ powder	8.0×10^{-9}–6.5×10^{-6}	400–900	aqueous solution method	Tao[90]
SnP_2O_7-H_3PO_4 composite	0.001–0.035	30–300	650°C calcination	Tao[91]
protonated WP_2O_7	1.1×10^{-3}–1.7×10^{-2}	250–500	thermal decomposition	Hibino[103]
$Sn_{0.91}Ga_{0.09}P_2O_7$	0.011–0.029	50–250	600°C calcination	Ma[93]
Sc-, Y-, and La-doped ZrP_2O_7	10^{-7}–10^{-4}	500–1000	400°C calcination	Norby[94]
2% Al doped TiP_2O_7	10^{-5}–3×10^{-4}	500–1000	700°C calcination	Norby[95,96]
$Sn_{0.94}Sc_{0.06}P_2O_7$	0.015–0.0276 in wet H_2	50–250	350°C calcination	Ma[97]
CeP_2O_7 powder	0.002–0.035 with $pH_2O = 0.114$ atm	60–200	450°C calcination	Tsai[98]

[1] Unless otherwise specified, conductivity was under nonhumidified conditions.
Proton conductors for intermediate temperature fuel cells are briefly reviewed, regarding heteropolyacids, metal pyrophosphates, solid acids, and acid-imbibed high-temperature polybenzimidazole polymers.

MP_2O_7 proton conductors are listed in Table 2 in chronological order.

Hibino et al. suggested that the mechanism of proton conduction in the 'acceptor doped' pyrophosphates was related to oxygen defects and electron holes in the lattice. However, this mechanism was rarely supported by experimental results from other researchers. Norby[88] cast doubt on this semiconduction-like mechanism because in several studies, MP_2O_7 only exhibited modest proton conductivity in the temperature range 400–1200°C. Some additional phosphorus oxides, P_mO_n, which were impurities, were found to be important for the high conductivity of doped SnP_2O_7.[75] However, the P_mO_n impurities were unstable and when they were removed the conductivity of $Sn_{0.8}Sb_{0.2}P_2O_7$ declined from about 0.1 to 0.01 S cm^{-1} in dry air at about 250°C.[84] There were also some interesting investigations on proton and oxygen ion co-ion conduction of $Sn_{0.9}In_{0.1}P_2O_7$.[80] The co-ion conduction phenomenon was also seen in a study of $Sn_{0.8}Sb_{0.2}P_2O_7$, although it was suggested that the conductivity of oxygen ion in this material might be negligible compared with its proton conductivity.[104] It can be seen from Table 2 that the best preparation method to achieve high conductivity was by simply mixing metal oxides/chlorides with phosphoric acid followed by calcination at 650°C. Tao prepared a SnP_2O_7–H_3PO_4 composite electrolyte, which achieved a conductivity of 0.035 S cm^{-1} at 300°C. More recently, Hibino et al. prepared WP_2O_7, which when protonated exhibited conductivity in the range 1.1×10^{-3}–1.7×10^{-2} at 250–500°C.

However, a major challenge in applying the pyrophosphates in fuel cells is scale-up. Up to now, fuel cell results with the pyrophosphates were only obtained in laboratory cells with very small electrode area. In the study of $Sn_{0.8}Sb_{0.2}P_2O_7$, low open circuit potentials and considerable gas crossover problems were experienced when the pellet electrolyte was applied in fuel cells at 250°C.[104,105] Nevertheless, these pyrophosphates exhibited some beneficial effects for organic/inorganic composite membranes at relatively lower temperatures.[76,78,104–108] When incorporated in PBI-H_3PO_4 membranes, the pyrophosphates may enhance membrane stability, conductivity, and power density performance.[105,108] Recently, an experimental fuel cell peak power density greater than 0.67 W cm^{-2} at 175°C was reported using the PBI-$Sn_{0.8}Sb_{0.2}P_2O_7$-H_3PO_4 membrane.[105]

Solid Acids

Solid acids present chemical properties, which lie between a normal acid and a salt, and consist usually of an alkali metal (or NH_4) and tetrahedral oxyanions chains linked together by hydrogen bonds. The overall formula is presented below:

$$M_xH_y(AO_4)_z \; (M = K, Rb, Cs, NH_4; A = S, Se, P, As)$$

These materials exhibit low proton conductivity at ambient temperature but when they reach certain higher temperatures, proton conduction is enhanced by several orders of magnitude. Baranov et al.[109] and Haile et al.[110] attribute this conductivity enhancement to a phase change in the bulk of the material. Following this theory, at temperatures above 130°C (depending on the material), the material undergoes a structural change to a high temperature stable superprotonic phase. A disorder in the hydrogen bonding of the oxyanions chain takes place enabling oxyanions-free rotation. In this way, a proton has available locations on each oxyanion, which rotates to let the proton move from one to another. This provides good proton conduction for the material in the absence of water and the conduction mechanism is known as 'Grotthuss mechanism'.

However, these materials have limitations in chemical and mechanical properties in the temperature range of interest fuel cell applications. Solid acids are based usually on sulfate, selenate, phosphate, or arseniate oxyanions hydrogen-bonded chains linked through an alkali metal-based crystal structure. This structure, when they reach the superprotonic phase transition temperature, tends to acquire ductile mechanical properties, which makes it difficult to fabricate a thin mechanically strong membrane. It is also important to note that these materials are water soluble, and in a fuel cell application therefore, this factor has to be considered. Nevertheless, compared with traditional polymer membrane materials, they show proton conduction in the absence of water, which allows higher working temperature, and are impermeable to hydrogen and oxygen gases, which lead potentially to high OCV.

Alkali hydrosulfates and hydroselenates were studied early because of their ferroelectric and ferroelastic properties. There were found to undergo a phase transition in which proton conductivity was improved by some orders of magnitude caused by a dynamic hydrogen bonding dissorder. Sulfate and selenate oxyanions-based cesium solid acids experience a phase transition to a superprotonic phase in the temperature range 120–140°C, reaching conductivities of 10^{-3}–10^{-2} S cm^{-1}. Haile et al.[110] reported conductivity of 8×10^{-3} S cm^{-1} with $CsHSO_4$ at 160°C under water saturated conditions.

However, at intermediate temperatures and under reducing conditions in the presence of hydrogen, both sulfates and selenates react leading to dehydration and formation the cesium salt and hydrogen sulfide or selenide gases.

$$2CsHSO_4 \rightarrow Cs_2SO_4 + H_2O + SO_3 \quad (1)$$

$$2CsHSO_4 + 4H_2 \rightarrow Cs_2SO_4 + 4H_2O + H_2S \quad (2)$$

As a result of the above reduction reactions forming hydrogen sulfide, which is damaging to fuel cell catalysts, attention has focused on phosphate compounds. CsH_2PO_4 undergoes a superprotonic transition at 230°C, which allows proton conduction through the bulk of the material. The melting point of this material is around 345°C, which makes it an interesting electrolyte material for fuel cells. The conductivities rise to 2.2×10^{-2} S cm^{-1} at 240°C when the superprotonic phase is achieved. It is reported that CsH_2PO_4 is stable under oxidizing and reducing atmospheres at 240°C, even under a Pt catalyzed environment and no H_xP species are generated.[111,112] Nonetheless, it loses weight due to dehydration, which results in formation of intermediate hydrogen pyrophosphates and polyphosphates until its entire decomposition to $CsPO_3$. This can be controlled by a hydration of the feed gases.

The subject of solid acid proton conductors has recently been reviewed in which a large number of solid acids, including Rb compounds, have been identified as of potential interest as proton conductors.[113] Hiroki et al.,[114] reported a study of MH_2PO_4/SiP_2O_7 composite systems with RbH_2PO_4 as the solid acid the composite. Using CsH_2PO_4, the creation of a new phase takes place with a pyrophosphate as matrix in the composite. The proton-conducting $RbH_5(PO_4)_2$ compound is generated by the interaction of the solid acid with the pyrophosphate. This compound (as well as $CsH_5(PO_4)_2$ and $KH_5(PO_4)_2$) exhibits high proton conductivity in the bulk, of around 10^{-1} S cm^{-1} at 150–300°C, but this value decreased to 5×10^{-2} S cm^{-1} when SiP_2O_7 matrix (molar ratio: 1/4) was added as composite matrix (Figure 5).

Solid acids have been evaluated in PEMFC systems by Haile et al.[115] using a thick (1–1.5 mm) $CsHSO_4$ membrane as electrolyte and platinum black electrodes. This system operating at 160°C with water saturated gas streams and gave an open circuit potential of 1.1 V, although performed rather poorly because of the large electrolyte thickness. Uda and Haile[116] reported data at 150–300°C with a CsH_2PO_4 membrane of 25 μm thickness and Pt electrodes (loadings of 7.7 mg cm^{-2} (Pt black on the anode and C-supported Pt on the cathode). The cell operated at 250°C and the peak power density was

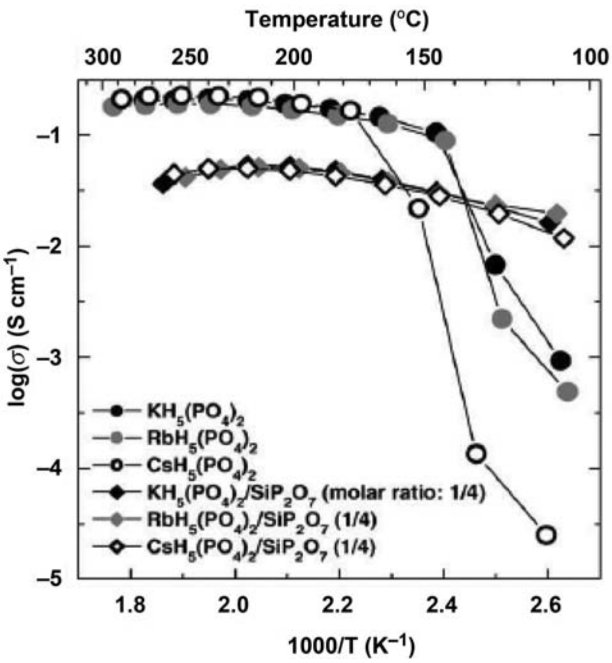


FIGURE 5 | Arrhenius plot of some solid acid/silicon pyrophosphate composites. (Reproduced from Ref 42. Copyright 1961, John Wiley & Sons Ltd.)

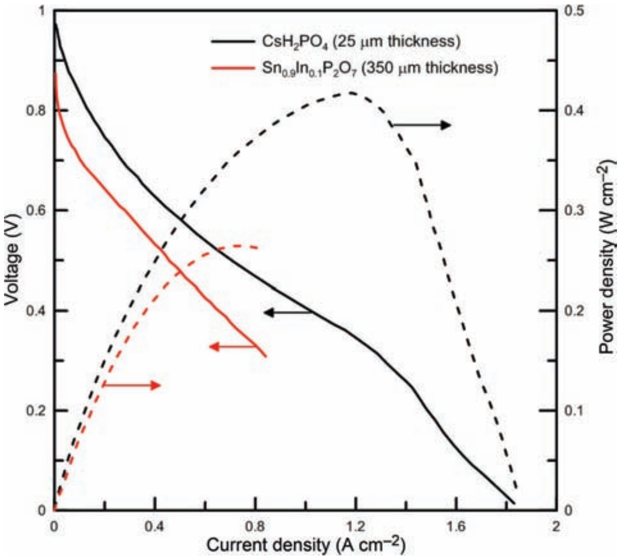


FIGURE 6 | Fuel cell performance of CsH_2PO_4[116] and $Sn_{0.9}In_{0.1}P_2O_7$[119] membranes at 250°C.

415 mW cm^{-2} (Figure 6). The high overpotential observed in the fuel cell was attributed to the slow electrocatalysis rate on the cathode side. The main obstacles that have to be overcome in the design of the fuel cell are the fabrication of a mechanically strong self-supported membrane and the control of the operating temperature and humidification to avoid dehydration or decomposition. A composite material using CsH_2PO_4 and SiO_2 particles has been used to enhance the mechanical properties of the membrane thus providing less mechanical deformation.[117] Another study in this area compared the performance using Pt and Pd-based electrocatalysts.[118] Solid acid-based materials also look promising for direct methanol fuel cells due to low fuel permeation, which would help avoid high overpotentials generated in DMFC cathodes usually seen in Nafion-based cells.

CONCLUSIONS

Significant research is being carried out in material science to find stable proton-conducting materials that operate in the range of 150–350°C. For applications in fuel cells, materials such as HPAs, acid-imbibed PBI and metal pyrophosphates have attracted some significant interest. Of these, the acid-imbibed PBI or similar polymer materials have had greatest success with scale-up and stack evaluation for transportation and CHP applications being performed. As yet, the power performance and electrical efficiencies of such fuel cells has not matched that achieved with the low temperature perfluorinated sulfonic acid fuel cells. Solid acids, because of their capacity to conduct protons in the absence of water, at temperatures in the range of 200–400°C, present a potential option, although as yet performance suitable for commercial uptake has not been achieved.

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