Alkaline Anion Exchange Membranes for Fuel Cells- a Patent

Review

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Abstract: Recently, Alkaline Polymer Electrolyte Membrane Fuel Cells (APEMFCs) have been attracting worldwide attention mainly due to the prospect of using non-platinum-group metal catalysts. In addition, there is growing evidence that these fuel cells can operate with the presence of carbonate. This mini review will introduce the state-of-the-art in understanding of alkaline anion-exchange membranes (AAEMs) in solid alkaline fuel cells. Ionomers for membrane electrode assembly (MEA) fabrication and the chemistry of the carbonate and bicarbonate forms of the AAEMs are also discussed. Key references to the latest scientific literature and reviews are included, along with a brief overview of directly relevant patents.

Keywords: Alkaline polymer electrolyte membrane fuel cell, alkaline anion exchange membrane, alkaline ionomer, hybrid membrane fuel cell, carbonate and bicarbonate.

1. INTRODUCTION

Fuel cells are recognized as a key technology in the delivery of clean energy for a future sustainable society. Many advanced materials and technologies have been developed over the past few decades. Despite fuel cell engine cars being demonstrated worldwide, widespread commercialization of fuel cell technology suffers from continuous delays. There is a current lack of hydrogen infrastructure resulting in higher costs when using hydrogen, while Proton Exchange Membrane Fuel Cells (PEMFC) themselves are still very expensive compared to internal combustion engines; the cost is primarily because PEMFCs are highly dependent on Pt-based catalyst (due to the presence of an acidic, low pH, environment) although the cost of other key components such as the bipolar plate and the proton

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exchange membranes are also significant (these are anticipated to be reduced with the onset of the mass manufacture). A major benefit of Alkaline Fuel Cell (AFC) technologies is the ability to use cheaper, more abundant, non-platinum catalysts. The hydroxide (OH^-) anions, however, will convert to mixtures of carbonate (CO_3^{2-}) and bicarbonate (HCO_3^-) anions when air (containing carbon dioxide) is used as the oxidant; the main issue with this is the solubility of carbonate and bicarbonate salts, which are low, and this leads to the risk of precipitation in the electrode pores and therefore fuel cell failure [1]. This highlights the importance of developing alkaline polymer electrolytes where the polymer-bound cationic groups, such as quaternary ammonium, ($\text{R}'\text{-NR}_3^+$) groups, prevent carbonate/bicarbonate salt precipitation (the polymer electrolytes are, and operate, in the solid state) [2]. There is also growing evidence of their ability to operate in the presence of carbonate anions [3-5]. Recently, the successful application of non-platinum catalysts in both the cathode and the anode of an alkaline polymer electrolyte membrane fuel cells (APEMFC) have been reported [6]. Investigations into the use of non-hydrogen fuels, such as methanol and the “higher” alcohols (e.g. ethanol, isopropanol and ethylene glycol) [7], glucose [8], hydrazine (H_2NNH_2) [9], ammonia [10], urea (urine) [11] and borohydride (BH_4^-) [12] have been studied in APEMFCs. The potential of APEMFCs has spurred on the worldwide search for, and development of, mechanically, chemically and thermally stable alkaline anion exchange membranes (AAEM). Anion-exchange membranes have even been evaluated in biological fuel cell systems containing enzymes [13] and microbes (Microbial Fuel Cells) [14-15].

AAEMs (and alkaline ionomers – see later) are key materials required for the successful implementation of APEMFCs. Anion-exchange membranes (that are not always alkali stable) have, for a long time, been used as separation membranes for seawater desalination, the recovery of metal ions from wastewaters, electrodialysis and bio-separation processes. There are many inventions [*e.g.* 16-26] that use anion-exchange membranes for desalination and electrodialysis. These membranes however may be not stable or conductive enough to be applied in APEMFCs. AAEMs used in early APEMFC studies were reviewed in 2005 [27] and included polybenzimidazole (PBI) doped with KOH, epichlorohydrine polymer quaternized with 1,4-diazabicyclo[2,2,2]octane (DABCO) or quaternized with a 1:1 ratio of DABCO and triethylamine, and commercial membranes such as AHA (Tokuyama Co, Japan), Morgane ADP (Solvey S.A.), and Tosflex® SF-17 (Tosoh) and 2259-60 (Pall RAI). Most

of these fuel cells containing AAEMs were being operated with the presence of aqueous alkaline solutions (NaOH or KOH).

In our group, we have successfully developed several kinds of quaternary-ammonium-containing radiation-grafted AAEMs based on poly(vinylidene fluoride) PVDF [28-32], poly(tetrafluoroethylene-co-hexafluoropropylene) FEP [28,29,33] and poly(ethylene-co-tetrafluoroethylene) ETFE [34-35] with good ion exchange capacities (IEC) and ionic conductivities and with sufficient stabilities to test the proof of concept of using AAEMs in fuel cells. We found that ETFE base films produced the best AAEMs for testing in APEMFCs. Note that these AAEMs were not developed with commercialization in mind: the materials cost for making the ETFE based AAEMs are $< \$150/\text{m}^2$ when purchase chemicals on the lab scale. The radiation-grafted methodology allowed for the production of AAEMs of different thicknesses, ion-exchange capacity, physical / mechanical properties, and chemistries that facilitated fundamental investigations. To partially solve the membrane-electrode interface problem (*i.e.* the lack of available alkaline analogues to the Nafion[®] dispersions used in PEMFCs) we developed a water insoluble alkaline ionomer that used *N,N,N',N'*-tetramethylhexane-1,6-diamine as the joint amination and cross-linking agent and we reported on the performance of metal-cation-free all-solid-state alkaline fuel cells with medium-term performance stability [34,36]. Many other groups have developed new conductive and chemically and thermally stable AAEMs (and alkaline ionomers). This review will focus on the state-of-the-art development on AAEMs, including patents and the primary scientific literature, and will highlight the important issues regarding the use of AAEMs in APEMFCs.

2. PREPARATION OF ALKALINE ANION-EXCHANGE MEMBRANES (AAEM)

A good AAEM will have a high ion-exchange capacity, high ion conductivity and thermochemical stability but will exhibit low degrees of swelling (especially in water and alcohols). There are several general synthetic methodologies for the preparation of AAEMs [37-38]. The easiest is using inert polymers doped with concentrated aqueous KOH: Polybenzimidazole (PBI) [39-43], poly(vinyl alcohol) (PVA) [44], composite polymers such as PVA/hydroxyapatite (PVA/HAP) [45], quaternized-PVA/alumina (QPVA/ Al_2O_3) [46], PVA/titanium oxide (PVA/ TiO_2) [47-48], chitosan and cross-linked chitosan [49-51], copolymers of epichlorohydrin and ethylene oxide [52], and cross-linked PVA/sulfosuccinic acid (10 wt.% SSA) [53] have all been doped with KOH and used as AAEMs. The invention US5569559 [54] describes the use of polar polymers (most preferred being polyethylene

oxide) doped with alkaline metal hydroxides (such as KOH), alkaline–earth metal hydroxides or ammonium hydroxides such as tetrabutylammonium hydroxide. PBI doped with KOH showed the highest conductivity which was comparable to Nafion® (a well known acidic polymer electrolyte membrane / proton–exchange membrane).

The preparation of applicable AAEMs normally involves a compromise between the properties of the membrane, such as the chemical and thermal stability, ion exchange capacity (IEC), ion conductivity, mechanical properties, water uptake and dimensional stability. Key details on the preparation of fuel cell relevant AAEMs except by the doping method is summarized in Table 1 (delineated by polymer backbone and/or active (exchange) functional group chemistry). In general, alkaline anion exchange polymer electrolytes can be polymerized directly from functionalized monomers, polymerized from monomers with subsequent functionalization or by functionalizing a commercially available polymer. The backbone of the polymer is usually selected for its good chemical and thermal stability and, therefore, typically includes aromatic rings and/or a degree of fluorination: Typical polymers classes include polysulfones and polyetherketone (and derivatives thereof), polyimides, poly(phenylene), poly(phthalazinon ether sulfone ketone), polyepichlorhydrin homopolymer, polybenzimidazole (PBI), poly(phenyleneoxide), radiation–grafted copolymers, inorganic–organic hybrids, and even perfluorinated membranes such as Nafion®. The active functional groups are commonly quaternary ammonium type ($-\text{NR}_3^+$) with a clear preference for trimethylammonium ($-\text{N}(\text{CH}_3)_3^+$) groups (NMe_3 , $\text{pK}_a(\text{H}_2\text{O}) = 9.8$).

As described in US20040023110 [55], it is easy to produce cross–linked poly(vinylbenzyltrimethylammonium hydroxide) (PVBMAOH) from the functional monomer such as vinylbenzyltrimethylammonium chloride (VBTMACl) by adding a cross–linking agent such as $\text{N,N}'$ –bismethyleneacrylamide (BMAAm) and using an azo free radical initiator such as 2,2'–azobis(2–methylpropionamide) dihydrochloride. This cross–linked PVBMAOH, which is insoluble in water, can be used as AAEM in APEMFCs. Using 4-vinylpyridine as start monomer, a 4-vinylpyridine–based alkaline anion exchange membrane polymerized by plasma polymerization has also been reported [56].

Tokuyama is one of the leading companies on the commercial front of alkaline anion exchange membranes (*e.g.* their AHA membrane). Their thin (10 μm) “fuel cell grade” AAEMs (A010, A201 – formally A006, and A901) [57–61] and dispersible alkaline ionomers (A3ver.2 and AS–4) [62–64] have

been tested by different research groups. They deserved a few words to show their alkaline electrolyte direct polymerized from different monomers.

In GB1401997 [16], Tokuyama Soda Kabushiki Kaisha (probably Tokuyama) claimed anion exchange membranes which contained cation exchange groups (sulphonic acid) on the surface of membrane to reduce contamination by organic matter (biofouling) during the desalination of water. An example membrane was synthesized by coating a paste onto a cloth of poly(vinyl chloride) (PVC) and both coated surfaces were bonded to a film of PVA; the paste consisted of divinylbenzene, styrene, PVC powder, dioctylphthalate and benzoyl peroxide. The assembly was heated for 4 hours at 120°C to form a base membrane. The base membrane was sulphonated by sulphuric acid followed by chloromethylation (treated with chloromethyl ether) and quaternization/amination (treated with trimethylamine) to form an alkaline membrane. More recently, Tokuyama have applied for a series of patents [65-72] regarding the production of solid alkaline anion exchange polymer electrolytes, membranes and alkaline electrodes for fuel cells. More specifically, WO2009148051 [70] claimed an anion conductive resin, containing a quaternary onium [*sic*] salt with at least part of counter ions of being CO_3^{2-} and/or HCO_3^- , which was used as a binder in the electrocatalyst layer of the electrodes. WO2010041641 [71] claimed an anion exchange membranes with either quaternary ammonium or quaternary phosphonium groups. A membrane for direct liquid fuel cells, described in US20100104920 [72], consisted of a porous film with the pores filled with a cross-linked hydrocarbon based anion exchange resin; the preferred porous film was a polyolefin. A polymerizing monomer with a halogen alkyl group (e.g. chloromethylstyrene), a cross-linking polymerizable monomer, an epoxy group-containing compound, and an effective amount of polymerization initiator was contacted with the porous films having a thickness of 5 to 60 μm for the pore filling process; the formulations were then polymerized in situ and cured. The halogen alkyl group possessed by the resin obtained post-curing was finally converted into a quaternary ammonium functional group. An example of the polymerizing composition is as follows: *p*-chloromethylstyrene (100%mass), divinylbenzene (5%mass), tert-butyl peroxyethylhexanoate (5%mass), and an epoxy compound (Epolite 40E: ethylene glycol diglycidyl ether, 5%mass).

A widespread strategy for the synthesis of AAEMs is to introduce halogenalkyl groups onto the backbone or side chains of the polymer via chloroalkylation, fluorination, bromination or chlorination (depending on the base polymer or the desired polymer structure) followed by amination/quaternization

and finally ion exchange. One strategy is to use a monomer that is already functionalized with halogenalkyl group or tertiary amine groups. Highly carcinogenic chloromethylethers have traditionally been used as the chloroalkylation agent, as chloromethylation of polymers is commonly observed for AAEM synthesis, but safer strategies have been introduced, *e.g.* the chloromethylation agent is generated in situ of the reaction with the polymer *e.g.* [74-76]. Wang *et al.* [77] studied the effect of parameters such as the reaction temperature, reaction time, concentration of the chloromethylation agent, polymer concentration, and amount of the catalyst for the chloromethylation of a poly(ether imide). They found that the concentration of chloromethylation agent, such as chloromethylether (CME), played an important role. This poly(ether imide)-based AAEMs showed good chemical stability in aqueous KOH (1 mol dm⁻³), however, the conductivity was too low for application (*ca.* 3 mS cm⁻¹) [78]. An alternative strategy is for the introduction of tertiary amine groups onto the polymer first, instead of chloroalkylation, followed by quaternization to produce quaternary ammonium anion exchange groups; the quaternizing agent used include methyl chloride, methyl iodide, methyl bromide, ethyl chloride, ethyl iodide, ethyl bromide, propyl chloride, propyl iodide, propyl bromide or CF₃SO₃CH₃, with toxic methyl iodide being the most preferred option. To lower the usage of toxic organic reagents like the chloromethylation agent, many researchers use the monomers that already contain chloromethyl or tertiary amine groups for AAEM synthesis. An exemplar synthesis of an AAEM based on polysulfone, one of the aromatic ring polymers (polyaromatics / polyarylenes), is highlighted in Scheme 1 [79].

The amine/ammonium groups are often connected to the backbone of the polymer via alkyl or aryl bridges. However, there is a class of AAEMs containing tertiary aliphatic diamines, polyamines or other cationic species that are coupled to a support/base polymer via –SO₂– linkages [80-83]. The –SO₂– groups are introduced using sulphonation reactions with reagents such as sulphonic acid or acidic halides (a thionyl halide, preferably thionyl chloride). Monomers containing amine groups can then react with the sulfonated polymer, to form the links, and then there is a final quaternization process. The AAEMs with these sulphoamide linked sidegroups containing quaternary ammoniums, such as *N,N,N',N'*-tetramethyl-1,3-propanediamine-modified sulfonated ETFE-g-poly(styrene) membrane, often show better stability in aqueous alkali solutions (such as NaOH) and better ionic conductivity than AAEMs with the cationic functional groups coupled to the polymer via alkyl links, such as trimethylamine-quaternized ETFE-g-VBC membranes [80-81]. A Nafion precursor polymer, which

contains $-\text{SO}_2\text{F}$ groups, has also been used to prepare a new AAEM by chemically attaching proazaphosphatranium/phosphatranium cations under microwave treatment to the sulfonic groups of Nafion-F [82].

Anion-exchange polymers that contain methacrylate, ester, amide or other carbonyl ($\text{C}=\text{O}$ double bond) containing groups (some examples in Table 1) will show low stabilities in alkali as these functional groups are highly reactive to nucleophiles such as OH^- . Recent research and modeling studies also suggest that the stability of the base polymer is not enough to obtain stable AAEMs. There are several chemical degradation mechanisms for ammonium-based anion-exchange groups in the presence of hydroxide[27]: The Hoffmann elimination reactions (when β -hydrogen atoms are present), direct nucleophilic displacements, degradation involving ylide intermediates (evidence provided from deuterium exchange experiments) and ylide-induced rearrangement reactions such as Stevens and Sommelet-Hauser rearrangements (for polymers containing benzyltrimethylammonium functional groups) [84,85]. There is also evidence from a number of independent studies that AAEMs based on alkyl pyridinium groups are a poor choice [86,87] (pyridinium group has particular low basicity – pyridine $\text{pK}_a = 5.2$); generally trimethylammonium cations are considered to be more stable than N-methylpyridinium cations. By studying the stability of model compounds such as tetramethylammonium hydroxide pentahydrate, Macomber *et al.* [84] suggest that ammonium cations may be more stable than expected but only when the functional groups are well hydrated. Vega *et al.* [88] studied four commercially available AAEMs and confirmed the Hofmann elimination and nucleophilic displacement mechanisms. DABCO ($\text{pK}_a(\text{H}_2\text{O}) = 8.8$) and quinuclidine have been researched as the use of these quaternization agents have been suggested to minimize the quaternary ammonium degradation reactions mentioned above [89] despite them containing β -hydrogen atoms; this is because the $\text{C}-\text{H}_\beta$ bonds are in the incorrect conformation to the $\text{C}-\text{N}_{\text{quat}}$ bonds for efficient Hofmann elimination (which requires anti-periplanar conformations). Similarly, *N,N,N',N'*-tetramethylhexane-1,6-diamine contains β -hydrogen atoms but quaternary ammonium groups formed from this diamine, or containing hexyloxy spacer groups, are reported to be quite stable as the electron density around the β -hydrogen atoms is not favorable for Hofmann elimination reactions [90-91]. However, highly charged (doubly charged) diamines are likely to show low chemical stabilities.

Compared to Nafion[®] proton-exchange membranes, the ion conductivity of AAEMs are generally lower. This is not surprising as the mobility of OH^- is $\frac{1}{3} - \frac{1}{2}$ of that of a H^+ (depending on the

environment and if there is an electric field present $-\mu_o \times 10^4 / \text{cm}^2 \text{ V}^{-1} \text{ s}^{-1} = 20.64$ for $\text{OH}^-(\text{aq})$ anions and 36.23 for $\text{H}^+(\text{aq})$ cations at 298 K, which translate into diffusion coefficients of $D \times 10^9 / \text{m}^2 \text{ s}^{-1} = 5.30$ and 9.31 respectively using the Nernst–Einstein equation) [1, 92]. One strategy for enhanced ionic conductivities is to increase the IEC, but this often leads to a decrease in the mechanical properties due to the excessive water uptakes. Another strategy is to synthesize tailored membranes that will exhibit hydrophilic(iononic)–hydrophobic(non–ionic) phase segregation (tethered exchange groups) and continuous ionic domains, which is hypothesized to increase ionic conductivities [76, 93]. Hickner’s work on Proton Exchange Membrane (PEM) show there is a complex interaction of polymer morphology, water motion and ion content that contribute to ion transport [94]. By independently varying the hydrophobic and hydrophilic portions of the molecules, the self-assembly of the ionic groups, ion-conduction, and mechanical support can be tuned. Hibbs and co-worker’s [73] recent work (refer to Table 1) report a functionalized copolymer DAPP-ATMPP (DAPP-TMPP is the copolymer of bCPD (bis(cyclopentadienone)) and TMbCPD, which is produced by 4,4’-dimethylbis(benzyl ketone) and 4-phenylglyoxalylbenzil, and DAPP-ATMPP is the DAPP-TMPP copolymer functionalized with quaternary ammonium groups), where the hydrophobic block DAPP was added deliberately and which exhibited improved ion conductivity and mechanical properties than the homopolymer ATMPP. It has suggested that the use of ionic and nonionic blocks would drive the formation of hydrophilic and hydrophobic domains within the membrane and contribute to better ion conductivity. Hibbs *et al.* [73] also claimed that the irregularities in linearity of poly(phenylene) backbone and bulky side groups, which prevent efficient packing of the polymer, facilitate the ion conductivity. Tertiary aliphatic diamines or polyamines [80-81,95-96] are often used to increase the concentration of ion exchange groups with concomitant cross-linking to maintain the mechanical properties of the membrane. Park *et al.* [96] found that AAEM synthesized using tertiary aliphatic diamines with longer alkyl chains (*i.e.* 6 carbon alkyl chains) shows better ion conductivities and thermal stabilities (as mentioned above). Tanaka *et al.* [97] investigated high molecular weight aromatic polymers with rigid and bulky fluorenyl groups to introduce more ionic groups and to achieve higher IECs ($> 2.5 \text{ meq g}^{-1}$); ion conductivities were promising at 50 mS cm^{-1} at room temperature with reasonable water uptakes. Other researchers have focused on monomers containing groups with high basicity, from reactions with pentamethylguanidine [98-99] ($\text{pKa}(\text{H}_2\text{O}) \sim 14$), 1,1,3,3-tetramethylguanidine (TMG) [100], and tertiary phosphine [101-102] ($\text{pKa}(\text{H}_2\text{O}) \sim 8.0$); the ion conductivity of the resulting AAEM with

quaternary guanadinium groups was 67 mS cm^{-1} at 20°C ($\text{IEC} = 2.15 \text{ meq g}^{-1}$). Kong *et al.* [82] studied proazaphosphatranium cation, attached to the Nafion[®] via a S-P bond, which exhibit reduced charge densities due to the different resonance structures that distribute the positive charge, and diminish ionic interactions, and which should facilitate hydroxide ion mobility; however no IEC and ion conductivity data were reported. Imidazolium-type ionic liquids, such as 1-allyl-3-methylimidazolium chloride [103], have also been used to introduce anion exchange group into polymers. Such membranes show good ion conductivities of up to 33 mS cm^{-1} at 30°C .

Fluorine-containing polymers generally show higher thermal stabilities than hydrocarbon polymers. Wang and coworkers [104] developed a soluble partial fluorinated polysulfone anion exchange polymer which showed a remarkable ion conductivity in excess of 60 mS cm^{-1} alongside a low swelling ratio of 33% at 20°C ; however, the swelling ratio was too high (123%) at 60°C . AAEMs based on a poly(arylene ether sulfone) containing fluorine groups showed high ion conductivities (63 mS cm^{-1} in CO_3^{2-} form at 70°C – this is an amazing result as CO_3^{2-} anions have dilute solution mobilities that are less than 33% of OH^- anions and it is rare to see CO_3^{2-} conductivities above 30 mS cm^{-1}) [105]. These last two results suggest that fluorine atoms on polyarylene backbones benefit ion conductivity. A note of caution on a conflict in nomenclature: References [97] and [105] both mention *fluorenyl* groups but which relate to totally different chemistries (one containing CF_3 groups and one containing non-fluorinated aromatic ring systems).

Organic–inorganic composite membranes synthesized using the sol–gel process is an alternative class of AAEM being actively investigated. The cross–links and the inorganic component, such as $-\text{O}-\text{Si}-\text{O}-$, are hypothesized to increase the thermal stability of the resulting AAEMs. Tripathi *et al.* [106] and Xu and coworkers [107–112], Liu and coworkers [113–114], and Suzuki *et al.* [115] have all focused on organic–inorganic composite anion exchange membranes. Commonly encountered amines containing inorganic monomers, such as aminoethylaminopropylmethyldimethoxysilane [115], alkylated triethoxysilylpropylamine (TESPA (+)) [110] and an anion exchange precursor labelled AESP [106] (see Table 1), clearly highlight the preference for resultant silicon containing inorganic–organic hybrids. A PPO–based composite membrane quaternized with triethylamine (TEA) [107–108] showed good ion conductivity (11 mS cm^{-1}) and produced a power density of 32 mW cm^{-2} (geometric) when tested in a H_2 / O_2 fuel cell (gases supplied at ambient pressure).

Coates and co-workers [93,116] developed a ring-opening metathesis polymerization synthetic route for the preparation of AAEMs. The cross-linked membrane (containing unsaturated C=C bonds in the polymer backbone) showed record OH⁻ conductivities ($> 150 \text{ mS cm}^{-1}$ at 90°C as measured using 4-probe impedance techniques) with low swelling ratios; the membrane polymerized using cyclooctene (COE) and tetraalkylammonium-functionalized cross-linkers [93] exhibit almost the same ion conductivity as Nafion112 between 20°C – 90°C in OH⁻ anion form. These recent results suggest strongly that the ion conductivities of OH⁻ form AAEMs have been previously underestimated. However, the stability of polymers containing unsaturated C=C bonds is a concern. Coates and co-workers have now reported a tetraalkylammonium-functionalized polyethylene of where the C=C bonds have been removed by hydrogenation using Crabtree's catalyst ([COD]Ir(Py)(PCy₃)]PF₆) and hydrogen gas [117]. The resulting polymer can be cast to form an AAEM and can be dissolved in aqueous n-propanol for use as an ionomer.

Irradiation of polymer films (and powders *etc.*) using γ -rays, x-rays and electron beams is a flexible way to introduce various functional groups on the polymer backbones. As irradiation produces a copious number of active sites in the polymer, it is a versatile way to functionalize (or cross-link) polymers. Detailed information on irradiation-induced copolymerization of polar and functional monomer onto non-polar polymeric films can be found in the comprehensive review by Nasef and Hegazy [118]. A wide range of chemically and thermal stable polymers can be chosen as the base films for the production of AAEMs. Patents [80-81, 119-122] use γ -rays irradiation, while other work such as at the University of Surrey [28-35] also uses electron beam irradiation. Stable polymers such as ETFE and FEP have been used to produce AAEMs using this irradiation grafting methodology. Additionally, there is a wide choice of functional monomers available that can be used to introduce ion-exchange groups into the grafted polymeric chains. The radical and peroxy-type active groups on the irradiated polymer have been confirmed to be stable at low temperatures [123] (after a sharp decrease during the first day) and the IECs of ETFE-based AAEMs have been shown statistically to be invariant even after the irradiated ETFE has been stored for 160 days at -40°C before grafting [124]. An outline of, and example of, this synthetic methodology of such radiation-grafted-AAEMs is illustrated in Scheme 2 [34]. An AAEM produced from 20 μm thick ETFE was evaluated in a H₂/O₂ fuel cell and yielded beginning-of-life peak power densities of 230 mW cm⁻² (geometric) and current densities above 1300 A cm⁻² [125].

Besides the polymer membranes above, inorganic materials like layered perovskite-type oxides such as $\text{LaSr}_3\text{Fe}_3\text{O}_{10}$, NaLaTiO_4 , $\text{Sr}_4\text{Co}_{1.6}\text{Ti}_{1.4}\text{O}_8(\text{OH})_2 \cdot x\text{H}_2\text{O}$, $\text{RbLaNb}_2\text{O}_7$, LaFeO_3 [126] and NaCo_2O_4 [127-129] have been used as electrolyte in alkaline fuel cell. The study of these new inorganic electrolyte membranes is still in its infancy. The power density of 64mWcm^{-2} at 80°C for direct ethanol fuel cell was achieved using NaCo_2O_4 thin film as electrolyte, Fe-Co-Ni/C as anode catalyst and a catalyst free cathode [128]. This is a promising result and shows that inorganic membranes are promising for use in alkaline membrane fuel cells.

3. THE APPLICATION OF ALKALINE ANION-EXCHANGE MEMBRANES IN FUEL CELLS

The main interest in using an AAEM as an electrolyte in a fuel cell is the prospect for the use of non-Pt group metal (non-PGM) catalysts, cheaper fuel cell components (less corrosive environment), and alternative fuels. Alcohols and diols, sodium borohydride (NaBH_4) and hydrazine (H_2NNH_2) have all been used directly as fuels in APEMFC. Patents [149-150] introduced more fuels including hydrated hydrazine ($\text{NH}_2\text{NH}_2 \cdot \text{H}_2\text{O}$), hydrazine carbonate ($(\text{NH}_2\text{NH}_2)_2\text{CO}_2$), hydrazine sulfate ($\text{NH}_2\text{NH}_2 \cdot \text{H}_2\text{SO}_4$), monomethyl hydrazine (CH_3NHNH_2), ammonia (NH_3), heterocycles such as imidazole and 1,3,5-triazine and 3-amino-1,2,4-triazole, and hydroxylamines such as hydroxylamine (NH_2OH) and hydroxylamine sulfate ($\text{NH}_2\text{OH} \cdot \text{H}_2\text{SO}_4$); the catalysts were Co-based for the fuel side (anode) and Ag/C, Pt/C and Ni/C for the oxygen reduction side (cathode). EP 2133946 [151] disclosed the use of transition metals as catalysts in APEMFCs. There are numerous reports on the use of non-Pt catalyst, such as MnO_2 [40], Ag/C [6, 96, 125], Au/C [125], FeTPP/BPC(Black Pearl Carbon) [152], CoPPyC [153], FeCo-CNF(Carbon Nanofiber) [154], CoFeN/C-HLH [155] in APEMFC cathodes and Cr-decorated Ni/C [6], Fe-Co-Ni/C [128, 156] at APEMFC anodes. A fully non-PGM-catalyst containing, metal-cation-free alkaline membrane fuel cell has been reported [6, 128]. For further reference, Spendelow and Wieckowski [157] have recently published a detailed review on electrocatalysis of oxygen reduction and small alcohol oxidation in alkaline media and detailed analyse of alkaline alcohol fuel cells can also be found in references [7, 158]; both these studies discuss the prospects for cheap APEMFCs.

As mentioned above, recent intensive studies have led to the synthesis of AAEMs with high ion conductivities, reportedly comparable to Nafion[®]. These promising AAEMs [93, 97-98, 103-104, 106, 116, 135] are still to be evaluated in APEMFCs. The baseline properties of a selection of membrane candidates for APEMFC are summarized in Table 2. Most hydrocarbon AAEMs are soluble in various solvents, which is useful for the formulation of alkaline ionomers required for the preparation of high performance Membrane Electrode Assemblies (MEA). If the conductive properties reported can be translated into high power outputs, then APEMFC performances comparable to PEMFC can be expected in the near future.

Water is produced at anode and consumed at cathode in APEMFCs (when fuelled with hydrogen and with 4 electron reduction of oxygen at the cathode), which is fundamentally different to what occurs in PEMFCs containing acidic electrolytes; this can cause high overpotentials at APEMFC anodes, due to suspected flooding [159]. Alternative strategies for water management in developing APEMFC are therefore required. WO2009149195 [160] focuses on the water supply and suggests ways to operate APEMFC on a “water neutral” basis or with minimal supply of water from an external source. The APEMFC can also be run in dead-ended anode operation mode. The term “water neutral” means the cell or stack generates all of its water requirements internally (*i.e.* with no external supply of water). A wicking mesh was used to introduce liquid water, from either an external water source or internal water produced at the anode, to the cathode-side membrane surface. Partially hydrophilic anode back diffusion layers were used that were created from interweaving hydrophilic fibers with the wet-proofed carbon fibers so that the water produced at anode contacts the membrane directly and facilitates water back-diffusion from the anode to the cathode; this improved reactant mass transport in the anode because the electro-generated water was efficiently transported out of the anode structure. The patent reports peak power densities as high as 425 mW cm⁻² when using non-Pt cathodes and 350 mW cm⁻² for a wholly Pt-free fuel cell containing Tokuyama’s anion exchange membrane.

Consider the anode and cathode reactions with acid and alkaline electrolytes: Water is clearly produced at the acid cathode equal quantities to the water consumed at alkaline cathode. This water can be used to maintain the water balance in fuel cells.

When using methanol and O₂ as fuel and oxidant:

Using acid electrolyte

Using alkaline electrolyte

When using H_2 and O_2 as fuel and oxidant:

Using acid electrolyte

Using alkaline electrolyte

Simple arrangement of alkaline MEAs and acid MEAs would allow a more compact system that can operate without additional water supply. This is more important for direct methanol fuel cell systems as a higher concentration of methanol can be used (and this approach mitigates the severe cathode flooding that can happen in direct methanol fuel cells containing proton-exchange membranes). US20030049509 [161] and US20050069757 [162] discloses a method for combining the acid fuel cell (PEMFC) and alkaline fuel cell (APEMFC) together. One typical arrangement [162] is shown in Fig. (1).

US0235633 [163] extends this idea further. The cathode electrode was prepared using both alkaline and acidic ionomers, where the alkaline ionomer covered the catalyst and then this was carefully covered by acid ionomer. The water produced at the alkaline ionomer | acid ionomer interface would be utilized by the cathode catalyst; a key factor is the selection of solvent for both the alkaline ionomer and acid ionomer.

Based on the above concept, the water generated at the alkaline | acid polymer electrolyte interfaces is ideal for maintenance of membrane hydration, and therefore ion conductivity, even when low (zero) humidity gases supplies are used; this has the potential to significantly simplify the fuel cell stack system. Recall that mass transport-derived performance losses are frequently caused when water is

electro-generated in the electrode structures. This concept of hybrid membrane fuel cells [164-168], which contain both alkaline and acidic electrolyte membranes and electrolytes in the electrodes (a simple example is shown in Fig. (2)), was pioneered by Ünlü, Kohl and coworkers, and their results support the hypothesis that regardless of the configuration of the hybrid membrane fuel cell, the junction potentials at the AEM/PEM boundaries balance the pH-induced shifts in the electrode standard potentials and maintain the thermodynamic cell voltage of 1.23 V. Initial results show that acidic anodes and alkaline cathodes produce superior cell performances [164] and 116 mW cm^{-2} was achieved at 80°C with dry H_2 and O_2 gas supplies [165]. Unlike the situation usually encountered with traditional PEMFCs or wholly alkaline APEMFCs, the hybrid (cationic-anionic as opposed to inorganic-organic) membranes cell performance decreases as the relative humidity of the gases are increased [164-165] and when under simple test conditions. This concept of zero water supply hybrid membrane fuel cells deserves further study; operation with alkaline cathodes and acidic anodes and membranes appears to be a particular promising combination.

4. IMPORT ISSUES FOR ALKALINE MEMBRANE CONTAINING FUEL CELLS

4.1. Alkaline anion exchange ionomers for APEMFCs

The importance of alkaline ionomers (anionomers) has been discussed in references [34, 36, 169]. Valade [170] synthesized ionomers by radical copolymerization of diallyldimethylammonium chloride (DADMAC) with chlorotrifluoroethylene (CTFE) or counter-ion exchange of a poly(DADMAC) containing fluorinated anions. The ion conductivities of these two ionomers were low (maximum of 0.79 mS cm^{-1}), however their use in fuel cells still led to a significant improvement on the cell performance. The University of Surrey developed its first generation ionomer (SION1) in 2006 [34], which was used to prepare MEAs yielding cell performance of 130 mW cm^{-2} with an S80 membrane (Surrey's a radiation-grafted AAEM with $80 \pm 15 \mu\text{m}$ thickness when hydrated) and 230 mW cm^{-2} with an S20 membrane ($20 \pm 10 \mu\text{m}$ hydrated thickness) at 50°C and where the H_2 and O_2 were supplied at ambient pressure. The synthesis of SION1 is shown in Scheme 3 [34]; this ionomer is non-ideal in that it contains β -hydrogen atoms and requires deposition in organic solvents. However, it served its purpose and allowed for the evaluation of different AAEM in fuel cell tests (with peak power densities above the $1 - 2 \text{ mW cm}^{-2}$ achieved without the presence of ionomer). A second generation of ionomer is under development in our laboratory (published in a patent application [171]). The concept

is that a water soluble anion exchange polymer is deposited on an electrodes and then rendered insoluble (*e.g.* by radiation and/or heat treatment). A major advantage is that no flammable organic solvents are required to prepare the MEAs: Organic solvents mixed with finely divided fuel cell catalysts would represent a significant hazard with mass MEA production.

In US5853798 [172] and WO09912659 [173], metal catalysts were deposited directly onto the surface of the membrane by soaking the membrane in a solution containing an anionic entity (a metal salt such as chloroplatinic acid, potassium tetrachloroplatinate *etc.*) with subsequent exposure to a reducing agent, such as sodium borohydride. This methodology guaranteed good ion conductivities in the catalyst layers without the use of an ionomer as the binder; it represents a simplified MEA architecture.

In EP1965456 [65], Tokuyama introduced an alkaline ionomer which used an intermediate layer containing a polyfunctional quaternizing agent which bonded the membrane and electrocatalyst layer together via cross-linking (selected examples presented in Table 3); examples 2–1 and 2–2 show excellent performance with peak power densities of 180 mW cm^{-2} at 0.6 V. In another report, a commercially available membrane and an ionomer (designated I2) were used to prepare a MEA [57]; more than 400 mW cm^{-2} was achieved using a Pt/C catalyst while a respectable 200 mW cm^{-2} was obtained using a non-PGM catalyst (HYPERMECTM4020 by Acta SpA) when using H₂ as the fuel and a CO₂-free air supply at the cathode of the fuel cell.

Many researchers have reported that alkaline polymers with hydrocarbon backbones can be dissolved in solvents such as DMF, DMAc and DMSO [6, 96, 98,, 103, 104, 105] and this allows their use as the ionomer for the preparation of MEAs. Zhuang *et al.* [1,6] used a quaternary ammonia polysulfone (QAPS) which can be dissolved in DMF and used as the ionomer; the QAPS polymer (in OH⁻ form: IEC = 1.08 mmol g^{-1}) was also used to fabricate the membrane, while the QAPS(OH⁻ form: IEC = 1.18 meq g^{-1}) was used as the ionomer. The performance of the APEMFC was 110 mW cm^{-2} at 60°C (H₂/O₂). Gu and Yan *et al.* [174] developed an ionomer, tris(2,4,6-trimethoxyphenyl) polysulfone-methylene quaternary phosphonium hydroxide (TPQPOH: shown in Scheme 4), which is soluble in low boiling point and water soluble solvents such as methanol, ethanol, and *n*-propanol. The solubility of this kind of ionomer is ideal for use in APEMFC MEAs; 196 mW cm^{-2} was achieved at 80°C (H₂/O₂ gases supplied at 250 kPa back-pressure) using this phosphonium ionomer with a 70 µm thick FAA commercial membrane (Fuma-Tech GmbH) as the AAEM. This group has recently also

used a quaternary phosphonium polyelectrolyte as the AAEM [101]; more than 250 mW cm^{-2} was obtained in a H_2/O_2 fuel cell at 50°C with a $50 \text{ }\mu\text{m}$ AAEM and gas back-pressures of 250 kPa . The presence of methoxy groups on the aromatic rings that are connected to the phosphonium ion centers is clearly essential for adequate chemical stability.

In state-of-the-art AAEM fuel cell technology, the role of the ionomer has not been fully investigated or understood; alkaline ionomer solutions/dispersions, comparable to the Nafion[®] dispersions used in PEMFCS (note: aqueous dispersions are available to allow mass production of MEAs containing finely divided catalysts), remains highly sought after. The development of alkaline ionomers is one of the major challenges for the development of high performance alkaline membrane containing fuel cells.

4.2. Carbonate and bicarbonate containing anion exchange membranes

In traditional aqueous KOH electrolyte containing Alkaline Fuel Cells (AFC), precipitation of the carbonate and/or bicarbonate salts can cause fuel cell performance losses or failures when air (containing carbon dioxide) is used as the oxidant [1]. The use of an AAEM as a solid electrolyte in the absence of metal cations prevents precipitation of carbonate/bicarbonate salts (the electrolyte containing the cationic groups is already a solid). However, research has now been conducted on carbonate and bicarbonate forms of AAEM; such carbonated alkaline anion exchange polymers have been utilized to capture CO_2 as reported in US20100105126 [175]. The carbonation process is quick even if the AAEM has been exposed to the air for only a short time [5, 124]. The results presented in reference [135] confirm a quick decline of AAEM ionic conductivity as a function of air exposure time. These results imply that the conductivities of the AAEMs in OH^- form may have been underestimated as most studies to date have not disclosed vigorous CO_2 exclusion procedures during conductivity measurements. Indeed, it has been hypothesized that OH^- ion conductivities in AAEMs can be estimated by measuring the ionic conductivities of HCO_3^- form AAEMs and multiplying by 3.8 [135]. However, this carbonate process may not to be a serious problem due to the in situ “self-purging mechanism” as OH^- anions are continuously generated at cathode of APEMFCs [3]. Park *et al.* report reasonable APEMFC performances (30.1 mW cm^{-2} with Pt/C catalyst) when using air as the oxidant [96]. However, Piana *et al.* [57] reported a sharp drop of performance on a switch from CO_2 -free air to

atmospheric air. Although the performance of the fuel cell had deteriorated on the switch of oxidant supply, a subsequent durability test showed only a small drop in potential and power with time with operation with non-purified atmospheric air. Fuel cells operating with a “carbonate cycle” at low temperatures have also been demonstrated in [105, 176-177]. The presence of carbonate clearly does not affect the kinetics of the oxygen reduction reaction at the cathode [176, 178] and hydrogen oxidation was feasible in carbonate environments, where the reaction followed a 2-electron pathway, analogous to the reaction with hydroxide [178]. CO_2 was also involved in the oxygen reduction reaction forming carbonate anions, which were transported from the cathode to the anode [4, 105, 176, 179]. Watanabe et al. studied the carbonate contents of MEAs during APEMFC operation and found that there was no change in CO_3^{2-} ration in MEA over long time operation when using ambient air (contains CO_2) for the oxidant, i.e. continuous accumulation of CO_3^{2-} does not occur in APEMFC unlike in AFC [180]. Landon and Kitchin [181] found that oxygen and carbon dioxide gas mixtures can be selectively separated from air using an anion exchange membrane containing electrolytic cells with cell potentials below 1.23 V with transport of bicarbonate from the cathode to the anode through the anion exchange membrane. Oxygen (20%) and carbon dioxide (1%) in the air feed was concentrated to 85% and 15% in the product stream respectively. These results demonstrate the feasibility to operate the APEMFC using air as oxidant or with bicarbonate/carbonate cycles (when deliberately supplied with $\text{CO}_2/\text{O}_2(\text{air})$ mixtures). The durability of the AAEM in carbonate solution improved over more strongly alkaline OH^- solutions [88]. However, the true extent and mechanism of how CO_2 affects the performance of APEMFC remains to be fully investigated. There are numerous hypotheses for the cause of the performance losses with the use of air at the cathode of APEMFCs: Are these performance losses due to (i) pH gradient (high at cathode, lower at anode) derived thermodynamic losses, (ii) reductions in ionic conductivity of the AAEM or alkaline ionomer, (iii) $\text{CO}_3^{2-}/\text{HCO}_3^-$ anions interfering with the hydrogen oxidation electrode kinetics on the Pt catalyst at the anode (as mentioned above, the oxygen reduction reaction at the cathode appear less affected by the presence of these ions), and (iv) an effect on the water diffusion with the additional presence of nitrogen [176, 182-183]. Such investigations are an immediate research priority.

5. CONCLUSIONS

Alkaline anion-exchange membranes (AAEM) are the key material for Alkaline Polymer Electrolyte Membrane Fuel Cells (APEMFC) and are attracting significant worldwide interest; this is principally with the hope of reduced costs due to cheaper catalysts and system components (due to less corrosion issues with the use of alkaline solid electrolytes as opposed to acid conditions). Generally, AAEM synthesis is either from (i) direct polymerization (or copolymerization) of monomers where at least one of the monomers contains (cationic) anion exchange functional groups or (ii) where the anion exchange functional groups are introduced onto the polymer backbone via chloromethylation or sulphonation reactions with subsequent amination and/or quaternization. Sol-gel processes have also been used to introduce cross-links and enhance the AAEM stability (particularly with inorganic-organic hybrid membranes). The functional groups can also be introduced via irradiation grafting, typically using γ -rays and electron beams.

A large class of AAEMs are based on aromatic polymers, commonly involving polysulfones, polyetherketones and poly(phenylene oxide), and partial fluorinated, such as poly(ethylene-co-tetrafluoroethylene), or fluorinated/perfluorinated polymers. Trimethylamine is commonly used as the quaternization agent. Increasing the number of functional groups in the polymer (without an increase in swelling or water uptake) and identifying active functional group with higher basicities will yield improved performances, AAEMs with remarkable ionic conductivities have been recently obtained.; ion conductivities as high as 75 mS cm^{-1} at room temperature and 160 mS cm^{-1} at 90°C have been reported. However, ionic conductivities are more sensitive to humidity than proton-exchange membranes with rapid drops in conductivity at lower humidities. If the anion-exchange polymers can be dissolved in solvents (commonly polar solvents such as DMF, DMAc, and alcohols) they can be used for depositing ionomer solutions in the preparation of MEAs.

The promising results reported in this article suggest high performance APEMFCs will be realized in the near future. However, the anion-exchange polymer electrolyte chemical stabilities in alkaline environments have still to be adequately proven particularly in lower humidity environments (hydrated environments “protect” the anion exchange head-groups to a certain extent). The effect of carbonate and bicarbonate anions on the polymer electrolytes and on the resulting fuel cell performances remains to be fully resolved.

An interesting development is that of fuel cells fabricated with hybrid electrolytes and membranes (containing mixed proton and alkali exchange groups): the ambition is the ability to operate fuel cells without external water supply (*i.e.* with 0% relative humidity, or ambient humidity, gas supplies). This promises significantly simplified fuel cell systems.

Finally, the authors suggest (for an idea of current research trends) perusal of the abstracts from the 218th Electrochemical Society meetings in Las Vegas (Oct 2010), which contained many sessions on alkaline membrane fuel cell state-of-the-art.

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Scheme 1 The formation of AAEMs from Polysulfones via direct chloromethylation [79].

Scheme 2 The synthesis of radiation-grafted ETFE-based AAEM [34].

Scheme 3 The synthesis of SION alkaline polymer electrochemical interface (alkaline ionomer) [34].

Scheme 4 The chemical structure of the quaternary phosphonium alkaline ionomer [174].

Fig. (1) A diagram of an acid-alkaline fuel cell combination [162]

Fig. (2) A simple hybrid-membrane fuel cell configuration.

Scheme 1

Scheme 2

Scheme 3

Scheme 4

Fig. (1)

Fig. (2)

Table 1 Summary of AAEM chemistry and preparation methodologies

Polymer Class or Base	Key Chemistry	Summary of Preparation Methodology (where applicable)	References
Fluorinated, partially fluorinated and non-fluorinated base polymer such as FEP, ETFE, and LDPE	Active functional groups: $\text{benzyl-N}(\text{CH}_3)_3^+$	Radiation grafting: electron beam irradiation of polymer, grafted with vinyl benzene chloride (VBC) and subsequent quaternisation with trimethylamine.	[28-35]
Partially fluorinated base polymers such ETFE	Fluorinated monomers:	Radiation grafting: γ -ray irradiation of polymer, grafting of vinyl monomers containing desired functional groups (A/B/C), and (where required) subsequent quaternisation / amination to introduce anion-exchange groups into the grafted polymeric chains.	[119-120]
Base polymer such as ETFE, LDPE etc.	Sidegroups (post sulfonation and amination): $-\text{SO}_2-\text{NR}^1-\text{Q}^+$, preferred below (no hydrogen in beta position) Examples: Trimethylamine; N,N,2,2-tetramethyl-1,3-propanediamine; N,N-dimethyl-1,3-propanediamine; N-methylpiperazine; 2,2-dimethyl-1,3-propanediamine	Radiation grafting: grafting of styrene/divinylbenzene (DVB) mixtures followed by chlorosulfonation (to give sulfonate groups), subsequent amination using diamines or polyamines. Radiation grafting: grafting of vinylbenzylchloride (VBC) / divinylbenzene followed by amination.	[80-81]
Base polymer such as ETFE, LDPE etc.	Amination agents: Trimethylamine (TMA), triethylamine (TEA), dimethylformamide (DMF), 2-chloroacetamide (2-CA)	Radiation grafting: γ -rays irradiation of polymer, grafted with vinyl benzene chloride (VBC) or vinyl pyridine (VPy) with subsequent amination.	[121-122]
Nafion-F	Active functional groups:	Synthesized via a microwave process using Nafion-F and phosphatranium chloride.	[82]

	<p>Proazaphosphatranium A+ Phosphatranium B+</p>		
<p>Polymers made from the below:</p> <p>where E = $-\text{SO}_2-$, $-\text{C}(=\text{O})-$, $-\text{P}(=\text{O})(\text{aryl})-$ where Z = a direct bond or $-\text{C}(\text{CX}_3)_2-$ where D = halide</p> <p>Polyphosphazenes:</p> <p>where Z = NR_1R_2 or $\text{N}(=\text{PZ}_3)$</p>	<p>Active functional groups:</p> <p>Sulfonium, phosphazanium, phosphazene or guanidinium sidegroups</p>		[130-131]
<p>Polysulfone and polyimide polymers such as:</p> <p>(aryl groups are optionally substituted at one or more aromatic carbons)</p>	<p>Active functional groups:</p> <p>R is independently selected alkyl groups such as C_1-C_4 alkyl groups</p>	<p>Copolymerisation of bisphenol A (and analogs or derivatives thereof), with a second monomer followed by chloroalkylation and quaternization with agents such as trimethylamine, triethylamine, triphenylamine <i>etc.</i>.</p>	[79]
<p>Aromatic polyimides (with aromatic ether bridges)</p>	<p>Active functional groups:</p> <p>$-\text{N}(\text{CH}_3)_3^+$</p>		[77-78]
<p>Polyarylethersulfones; polystyrene; styrene copolymers; polysulfones; polyetherketones; polyetheretherketones; polyetheretherketones; polyphenylenesulfides; polyphenylenoxide; poly(4-phenoxybenzoyl-1,4-phenylene; polybenzimidazole; polybenzazoline; polybenzothiazoline; polyimide;</p>	<p>Active functional groups:</p>		[132]

polyphenylenene; polythiophenylenene; polyphenylenchinoxalinene; polyphosphazenes			
<p>Aromatic polyethersulfones and polyetherketones:</p> <p>where X and Y are $-\text{SO}_2-$ or $-\text{C}(=\text{O})-$ links</p>	<p>Active functional groups:</p> <p>$-\text{SO}_2\text{N}(\text{R}^1)-\text{G}-\text{N}^+\text{R}^2_3$</p> <p>preferably: R^1 is H or an alkyl group bearing a hydrophilic substituent [e.g. $(\text{CH}_2)_m\text{OH}$, where m is typically 2]; R^2 is methyl or an alkyl group of up to 5 carbon atoms; G is an alkylene link containing less than 4 carbon atoms.</p> <p>For example: 1-amino-3-dimethylaminopropane</p>	<p>After sulfonation, the tertiary amine group was introduced into the backbone of the polymer and then quaternization using methyl iodide.</p>	[83]
<p>Poly(phthalazinone ether ketone):</p>	<p>Active functional groups:</p> <p>$-\text{N}(\text{CH}_3)_3^+$</p>	Synthesized by the chloromethylation and quaternization of poly(phthalazinone ether ketone).	[133]
DAPP-TMPP copolymer	<p>Active functional groups:</p> <p>DAPP-ATMPP copolymer</p>		[73]
Polysulfone	<p>Active functional groups:</p> <p>$-\text{N}(\text{CH}_3)_3^+$</p>		[6, 134]
Polysulfone	<p>Quaternisation agents:</p> <p>Trimethylamine(TMA); $\text{N},\text{N},\text{N}',\text{N}'$-tetramethylmethane diamine(TMMDA); $\text{N},\text{N},\text{N}',\text{N}'$-tetramethylethylene</p>	Polysulfone was chloromethylated quaternized using trimethylamine or tertiary aliphatic diamines .	[96]

	<p>diamine(TMEDA); N,N,N',N'-tetramethyl-1,3-propan diamine(TMPDA); N,N,N',N'-tetramethyl-1,4-butane diamine(TMBDA); N,N,N',N'-tetramethyl-1,6-hexane diamine(TMHDA).</p>		
Polysulfone	<p>Active functional groups:</p> <p>Phosphonium</p>		[101]
Aromatic polyethersulfones	<p>Active functional groups:</p> <p>Guanidinium:</p>	Synthesized via chloromethylation of poly(aryleneether sulfone), followed by amination with pentamethylguanidine.	[98]
<p>Active functional groups:</p> <p>Guanidinium:</p>		[99]
Aromatic polyethersulfones	<p>Active functional groups:</p> <p>$-N(CH_3)_3^+$ with bicarbonate anions</p>	Bromination of tetramethyl bisphenol A-based poly(sulfone)s followed by amination with trimethylamine and ion exchange.	[135]
<p>Fluorenyl group containing aromatic polysulfone and polyketone copolymers:</p>	<p>Active functional groups:</p> <p>$-N(CH_3)_3^+$</p>	Poly(arylene ether sulfone ketone) bearing fluorenyl groups was synthesized by a nucleophilic substitution polymerization of 4-fluorophenyl sulfone, 4,4'-difluorophenylbenzophenone, and 9,9'-bis(4-hydroxyphenyl)-fluorene in the presence of potassium carbonate in dry N,N'-dimethylacetamide. Subsequent chloromethylation and animation.	[97]
<p>Cardo polyethersulfone:</p>	<p>Active functional groups:</p> <p>$-N(CH_3)_3^+$</p>	Cardo polyethersulfone was chloromethylated and quaternized with trimethylamine and ion exchange with sodium hydroxide.	[136]
Polyethersulfones containing monofluorinated	Active functional groups:	Fluorinated poly(arylene ether sulfone)s with pendant quaternary ammonium groups were	[104]

aromatic groups:	$-\text{N}(\text{CH}_3)_3^+$	prepared by copolymerization of 2,2'-dimethylaminemethylene-4,4'-biphenol (DABP), 4,4'-biphenol, and 3,3',4,4'-tetrafluorodiphenylsulfone, followed by quaternisation with iodomethane.	
Partially fluorinated aromatic polyethersulfones:	Active functional groups: $-\text{N}(\text{CH}_3)_3^+$	Fluoroalkane functionalized poly(arylene ether sulfone) were synthesized via polycondensation, with subsequent chloromethylation, and amination.	[105]
Sequence-type copolymers of propylene and styrene	Active functional groups: where R ₁ –R ₅ are each alkyls of 1 – 4 carbon atoms.	The copolymer was formed using cationic polymerization followed by chloromethylation (mainly on aromatic rings) and then reacted with a tertiary amines for quaternisation.	[95]
Aliphatic polymers containing ether groups in the backbone: Preferably polyepichlorhydrine	Quaternisation agents: 1,4-diazabicyclo-(2,2,2)-octane	The reactive polymer with halogen-containing functional groups were reacted with tertiary amine and mixed with inert polymers such as polysulfone, polyethersulfone, polymethacrylonitrile, polyacrylonitrile and copolymers of the respective monomer unit (preferably polyacrylonitrile).	[137-138]
Chitosan derivatives:	Active functional groups: $-\text{N}(\text{CH}_3)_3^+$	The quaternized chitosan derivatives were synthesized using glycidyltrimethylammonium chloride as the main quaternization reagent and ion-exchanged into the hydroxide form. The resultant hydroxide-form QCD gels were further cross-linked into anion-exchange membranes using ethylene glycol diglycidyl ether (EGDE).	[139]
Copolymer of vinyl alcohol and a nitrogen-containing vinyl monomer such as 4-vinylpyridine	Active functional groups:		[140]
Polystyrene-block-poly(ethylene-ran-butylene)-block-polystyrene:	Active functional groups: $-\text{N}(\text{CH}_3)_3^+$	Polystyrene-block-poly(ethylene-ran-butylene)-block-polystyrene (SEBS) were chloromethylated and quaternized.	[75]

$\left[\text{CH}_2 - \underset{\text{C}_6\text{H}_5}{\text{CH}} \right]_x \left[\text{CH}_2 - \text{CH}_2 \right]_y \left[\text{CH}_2 - \underset{\text{CH}_2}{\underset{\text{CH}_3}{\text{CH}}} \right]_y \left[\text{CH}_2 - \underset{\text{C}_6\text{H}_5}{\text{CH}} \right]_x$			
Copolymer of 4-vinylpyridine and styrene	Active functional groups:		[86]
Photochemical cross-linked polyepichlorhydrin with a polyamide support	Quaternisation agents: 1,4-diazabicyclo-[2,2,2]-octane (DABCO) 1-azabicyclo-[2,2,2]-octane (Quinuclidine)		[89]
Cross-linked quaternized-chitosan	Active functional groups: $-\text{N}(\text{CH}_3)_3^+$		[141]
Cross-Linked poly(vinyl alcohol) and poly(acrylonitrile-co-2-dimethylaminoethylmethacrylate) copolymer	Active functional groups: $-\text{N}(\text{CH}_3)_3^+$		[142]
Poly(vinyl alcohol)-silica inorganic-organic hybrid matrix	Reactive monomer:	Sol-gel reaction of quaternized poly(vinyl alcohol) with various ratios of tetraethoxysilanes (TEOS).	[113-114]
Aliphatic hydrocarbon - inorganic oxide hybrid matrix	Active functional groups: Alkyl and heterocyclic quaternary ammonium salt; a metal hydroxide salts, preferably with aluminium hydroxides $[\text{AlX}(\text{OH})_3]^-$ and $[\text{Al}_2\text{X}(\text{OH})_6]^-$.		[143]

Cross-linked polystyrene / methacrylate copolymers	<p>Active functional groups:</p>	Co-polymerisation and the use of water or alcohol-water soluble cross-linking monomer.	[144-145]
Chlorinated polypropylene	<p>Quaternisation agent:</p> <p>polyethyleneimine (PEI)</p>	Chlorinated polypropylene (CPP) was aminated with polyethyleneimine (PEI)	[146]
Poly(vinyl pyridine) copolymers	<p>Active functional groups:</p> <p>Pyridinium groups</p>	Copolymerized from monomers on a woven support membrane. Epoxide ring opening using aromatic amines used for cross-linking.	[147]
Cross-linked methacrylates containing aliphatic polymers	<p>Active functional groups:</p>	Cross-linking monomer produced by reaction of glycidyl methacrylate (GMA) and dimethylaminoethyl methacrylate (DMAEMA) in HCl. The cross-linking monomer was then homopolymerized or copolymerized with DMAEMA followed by reaction with an alkylating reagent (such as methyl chloride) to form strong base quaternary ammonium chloride group.	[148]

Polymethylimidazolium “ionic liquid polymer” copolymerized with methacrylate	Active functional groups: Imidazolium functional groups	Free radical polymerization of 1-allyl-3-methylimidazolium chloride ionic liquid either with methyl methacrylate or butyl methacrylate.	[103]
Cross-linked aliphatic polymers containing vinyl groups in the backbone	Active functional groups:	Ring opening metathesis polymerization to generate cross-linked membranes	[93]
Cross-linked cyclic aliphatic polymers containing vinyl groups in the backbone.	Highly functionalized monomer:	Ring-opening metathesis polymerization of a tetraalkylammonium-functionalized norbornene with dicyclopentadiene as a cross-linkable co-monomer.	[116]
Tetraalkylammonium-functionlized polyethylene	Highly functionalized monomer:	Ring-opening metathesis polymerization followed by hydrogenation to remove the C=C bonds to generate tetraalkylammonium-functionlized polyethylene.	[117]
Poly(phenylene oxide) – silica organic–inorganic hybrid polymers	Active functional groups: –N(CH ₃) ₃ ⁺ and –N(CH ₂ CH ₃) ₃ ⁺ groups	PPO is modified by bromination, hydroxylation and quaternization. Subsequent sol–gel reaction with monophenyl triethoxysilane (EPh) and tetraethoxysilane (TEOS) followed by heat treatment at 120–140 °C yields the hybrid membranes.	[107-109]
Polysiloxane	Active functional groups:	Sol–gel synthesis method	[110,115]

	$-\text{N}(\text{CH}_3)_3^+$		
Polyethylene oxide (PEO)–silica organic–inorganic hybrid membranes	Active functional groups: $\text{poly}-\text{N}(\text{CH}_3)_2^+-\text{poly}$ in polymer backbones	Sol–gel synthesis method	[111]
Copolymer of vinylbenzyl chloride and γ –methacryloxypropyl trimethoxy silane	Active functional groups: $-\text{N}(\text{CH}_3)_3^+$	TMA–quaternized poly(VBC–co– γ –MPS) with subsequent sol–gel process with monophenyl–triethoxysilane to form the copolymer.	[112]
Cross–linked poly(vinyl alcohol)–silica organic–inorganic hybrid membrane	Active functional groups: 	Organic–inorganic anion–exchange silica precursor (AESP) synthesized using 3–(2–aminoethylamino)propyltrimethoxysilane and glycidoxypyltrimethylammonium chloride by epoxide ring opening reaction. Hybrid AEMs were prepared with AESP and PVA by sol–gel method in aqueous media.	[106]

Table 2 Summary of base AAEM properties

IEC (meq g ⁻¹)	Ion conductivity* (mS cm ⁻¹)	Water uptake (%)	Peak power density** (mW cm ⁻²)	Methanol permeability (× 10 ⁻⁷ cm ² s ⁻¹)	References
–	68.7(20°C) 111(50°C) 158(90°C) 28(50°C in CO ₃ ²⁻)	–	–	–	[93]
2.88	84(20°C)	179(20°C)	–	–	[104]
2.62	65(20°C)–87(60°C)	86(20°C)– 253(60°C)	–	–	
1.76	75.7(30°C)	55.6	–	4.12(30% methanol) 6.66(50% methanol)	[106]
–	10(25°C, CO ₃ ²⁻) 63(70°C, CO ₃ ²⁻)		4(25°C, H ₂ / O ₂ +CO ₂)	–	[105]
–	41(RT)–92(70°C) measured in NaOH (aq, 1 mol dm ⁻³)		–	0.572–1.23	[136]
2.54	50(30°C)–78(60°C)	160	–	–	[97]
1.89	45(20°C), 74(60°C)	55(20°C), 107(60°C)	–	–	[98]
2.15	67(20°C)	88(20°C)			
0.22	33.3(30°C)–65.7 (90°C)	–	–	~10 ⁻²	[103]
	46(in OH ⁻) 12(in HCO ₃ ⁻)	–	–	–	[135]
1.2	45		225(50°C, 250kPa)		[101]
1.4–1.6	34(50°C)	–	130(50°C, Pt/C)	–	[34-35]
1.4	18(20°C) 28(50°C)	–	–	–	[116]
1.18	32(60°C)	–	~110 (60°C)	–	[134]
1.08	17(60°C)				
–	11.4(80°C)	–	7.76 μW cm ⁻² Methanol fuel No ionic interface	6.57	[133]
0.3	9.37(80°C)	–	–	2.34–4.45	[75]
–	10	–	30.1(H ₂ /Air) Pt/C anode Ag/C cathode	–	[96]
0.86	ca. 10	–	–	–	[139]
–	8(25°C)	–	1.5(45°C, 1 mol dm ⁻³ methanol/O ₂)	–	[86]
1.18	3.45(in 0.05 mol dm ⁻³ NaCl)	–		–	[142]
1.3	2.5(20°C); 13(60°C) 75(25°C, in 2.5 mol dm ⁻³ KOH)	–	>100(25°C) KOH (aq, 7 mol dm ⁻³) applied on surface of membrane)	–	[89]
0.57	3.46(30°C) 14 (60°C)	167	–	8.45-11.6(30°C)	[114]
–	7.5	–	24 (50°C, H ₂ /Air, 241kPa)	–	[141]
–	0.1(80°C, under humidified O ₂ gas flow)	–	0.76(40°C)	–	[115]
7.38– 9.33	8.9–13.6(immersed in 0.1 mol dm ⁻³ NaCl before test)	32		–	[146]

* Ion conductivity is tested in water unless specified.

** In H₂/O₂ unless otherwise indicated.

Table 3 Summary of Membrane Electrode Assemblies in Tokuyama patent EP1965456

	Membrane composition for forming a solid electrolyte membrane	Intermediate layer composition		Electrode membrane composition(parts by weight)		Quaternarizing agent
		Bifunctional quaternarizing agent	Organic solvent	Organic compound for forming an ion exchange resin	Organic solvent	
2-1	chloromethylstyrene-divinylbenzene copolymer	N,N,N',N'-tetramethyl-1,6-hexanediamine(5)	Tetrahydrofuran (15)	chloromethylstyrene-styrene copolymer(80)	Tetrahydrofuran (20)	trimethylamine
2-2	vinylpyridine-divinylbenzene copolymer	1,6-diiodohexane(5)	Tetrahydrofuran (15)	vinylpyridine-styrene copolymer(80]	Tetrahydrofuran (20)	methyl iodide