

Chapter 2

Alkaline Membrane Fuel Cells

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Glossary

AEM	Alkaline (anion) exchange membrane.
AFC	Alkaline fuel cell
AMFC	Alkaline membrane fuel cell (also known as APEMFC)
DMFC	Direct methanol fuel cell
MEA	Membrane electrode assembly
OCV	Open circuit voltage
PEM	Proton-exchange membrane
PEMFC	Proton-exchange membrane fuel cell
QA	Quaternary ammonium
RG-AEM	Radiation-grafted alkaline (anion) exchange membrane

Definition

The disruptive approach of applying alkaline anion-exchange membranes (AEMs) in alkaline membrane fuel cells (AMFCs) potentially meets several of the challenges facing other approaches to low temperature fuel cells, including the otherwise high catalyst and fuel costs. Thus, the move to alkaline conditions at the electrodes opens the potential use of a range of low cost non-precious-metal catalysts, as opposed to

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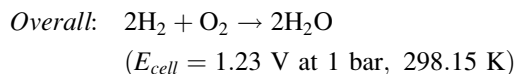
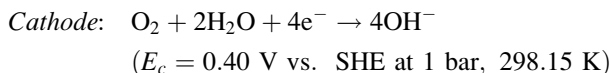
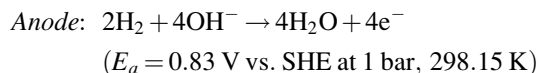
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the otherwise necessary use of platinum-group-metal (PGM) based catalysts. Further, it becomes possible to consider hydrogen fuels containing substantial amounts of impurities, whereas an acidic membrane approach (that in proton exchange membrane fuel cells, PEMFCs) requires high-purity gases and PGM catalysts.

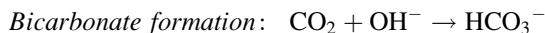
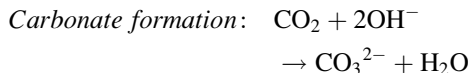
Introduction

The first entry in the AMFC area was published in 2005 [1], since when activity and interest have continued to increase steeply internationally. Zeng and Varcoe have recently reviewed the developing patent literature [2]. Some researchers have recently termed these systems HEMFCs, hydroxide exchange membrane fuel cells; that terminology is not fully appropriate in view of the complex hydroxide/hydrogen carbonate/carbonate equilibria that are present (even after handling membranes in air), inevitable in the use of air (containing $\text{CO}_2(\text{g})$) as source of oxidant and also produced in the oxidation of methanol in direct methanol fuel cells (DMFCs). Another acronym applied to these systems, APEMFCs, is also potentially confusing, the first three words of the full form then seemingly being “alkaline proton exchange” (following the very similar PEMFC acronym) but being readable alternatively as alkaline polymer electrolyte membrane fuel cells (possibly AEMFC would be clearer).

Alkaline fuel cells (AFCs, hydrogen-fuelled cells with an alkaline liquid electrolyte such as $\text{KOH}(\text{aq})$) are the best performing of all known conventional hydrogen–oxygen fuel cells operable at temperatures below 200°C . This is due to the facile kinetics at the cathode and at the anode; cheaper non-noble metal catalysts can be used (such as nickel and silver [3, 4]), reducing cost. McLean et al. gave comprehensive review of alkaline fuel cell technology [5]. The associated fuel cell reactions both for a traditional AFC and also for an AMFC are:



A major issue with traditional AFCs is that of electrolyte and electrode degradation caused by the formation of carbonate/bicarbonate ($\text{CO}_3^{2-}/\text{HCO}_3^-$) on reaction of OH^- ions with CO_2 contamination in the oxidant gas stream [5–7]:



The major cause of the degrading performance of AFCs is the consequent precipitation of metal carbonate crystals (most commonly Na_2CO_3 or K_2CO_3 , depending on the alkaline electrolyte used) in the electrolyte-filled pores of the electrodes, blocking pores and mechanically disrupting and destroying active layers.

The cost of fuel cells still retards commercialization in most markets. AFCs are promising on a cost basis mainly because cheap and relatively abundant non-platinum-group metals (non-PGM) are viable catalysts, but are hindered by degradation due to formation of precipitates as above. Catalyst electrokinetics (for fuel oxidation and oxygen reduction) are improved in alkaline, as opposed to acidic, conditions (the acid-stability criterion precludes the use of most non-PGM catalysts in PEMFCs). The replacement of the KOH(aq) electrolyte with an alkaline electrolyte membrane (AEM), to give AMFCs, retains the electrocatalytic advantages but introduces CO_2 tolerance (there being no mobile cations that could give carbonate/bicarbonate precipitates) with the additional advantage of being an all-solid-state fuel cell (as with PEMFCs – i.e., no seeping out of KOH(aq)). Additionally, thin (low electronic resistance) and easily stamped (cheap) metal mono/bipolar plates can be used, with reduced corrosion-derived problems at high pH (the cost of bipolar plates for PEMFCs can be as much as one third of the cost of the stacks themselves). A key and yet to be convincingly met requirement is, however, the development of a dispersible alkaline ionomer (sometimes termed an anionomer) to maximize ionic contact between the catalyst reaction sites and the ion-conductive membranes. As in the case of AFCs, water is produced at anode and consumed at cathode in AMFCs (when fuelled with hydrogen and with four 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 AMFC anodes, due to suspected flooding [8].

The use of an AEM as a solid electrolyte including no metal cations prevents precipitation of carbonate/bicarbonate salts. (The electrolyte containing the cationic groups is already a solid.) The carbonation process is quick even if the AEM has been exposed to the air for only a short time [9, 10]. The conductivities of the AEMs in OH^- form may have been underestimated because most studies to date have not disclosed vigorous CO_2 exclusion procedures during conductivity measurements. It has been hypothesized that OH^- ion conductivities in AEMs can be estimated by measuring the ionic conductivities of HCO_3^- from AEMs and multiplying by 3.8 [11]. This carbonation process may not to be a serious problem due to an in situ “self-purging mechanism” because OH^- anions are continuously generated at the cathode in AMFCs [12].

AEMs are solid polymer electrolyte membranes that contain positive ionic groups (typically quaternary ammonium (QA) functional groups such as poly-NMe_3^+) and mobile negatively charged anions. A widely quoted concern with

AEMs is membrane stability, especially at elevated temperatures [13, 14]. The general issues are:

1. The diffusion coefficients and mobilities of OH^- anions are less than that of H^+ in most media, and QA ionic groups are less dissociated than the typical sulfonic acid groups ($\text{p}K_a$ for sulfonic acid groups are typically -1 but for QA groups the related $\text{p}K_b$ values are around $+4$); there were concerns that AEMs would not possess adequate intrinsic ionic conductivities for application in fuel cells.
2. The OH^- anions are effective nucleophiles which potentially cause degradation via (a) a direct nucleophilic displacement and/or (b) a Hofmann elimination reaction when a β -hydrogen is present; methyl ($-\text{CH}_3$) groups may also be displaced by OH^- ions forming tertiary amines and methanol [13, 14]. If the AEMs contain good leaving groups (e.g., QA $-\text{NMe}_3^+$ groups) then the chemical stability of the AEMs might have been inadequate for use in fuel cells, particularly at elevated temperatures.
3. Precursor anion-exchange membranes are generally submerged in aqueous NaOH/KOH solutions to exchange them to the OH^- form AEM; the AEM must have the chemical stability to withstand this process. Despite this, over a decade ago, the stabilities of various benzyltrimethylammonium-based AEMs were found to be stable at up 75°C in NaOH(aq) at concentrations up to 6 mol dm^{-3} for several days [15].

A major potential application of AMFCs is, however, as power sources for at or near room temperature (as for PEMFCs), which means such degradation can be minimal.

This entry considers the current understanding and application of AEMs in hydrogen-fuelled AMFCs and other fuel cell types employing AEMs. Figure 2.1 enables comparison between hydrogen- or methanol-fuelled PEMFCs and AMFCs; the electrode reactions in a hydrogen-fuelled AMFC are discussed above. In contrast to PEMFCs, operation of an AMFC requires the presence of water as a reagent at the cathode (oxygen reduction reaction, ORR – to form OH^-) and the product water is formed by the hydrogen oxidation reaction (HOR) at the anode (as opposed to being formed at the cathode in PEMFCs). The entry begins with consideration of the main classes of AEMs.

An Overview of Alkaline Anion-Exchange Membranes (AEMs)

AEMs and alkaline ionomers (anionomers) are key to the successful implementation of AMFCs. Anion-exchange membranes 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, for example [16–26]. These membranes may, however, not be stable or conductive enough to be applied in AMFCs. AEMs used in early AMFC studies were reviewed in 2005 [1] and included polybenzimidazole (PBI) doped with KOH, epichlorohydrin polymer

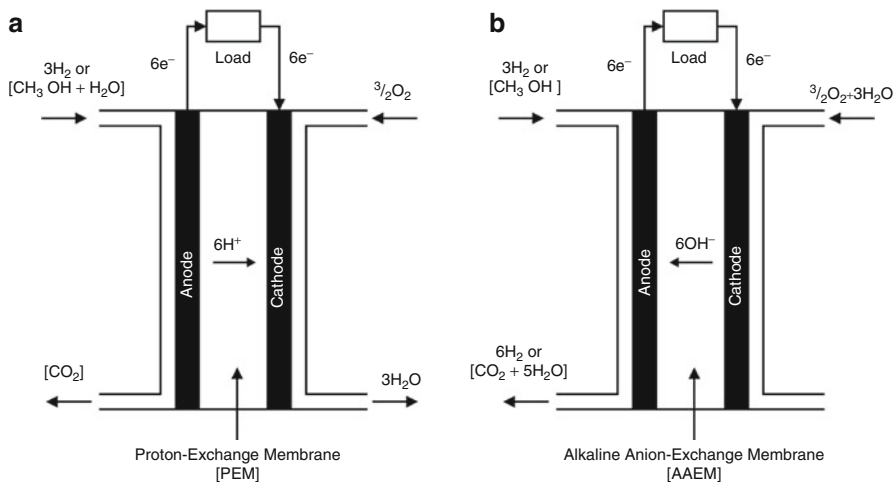


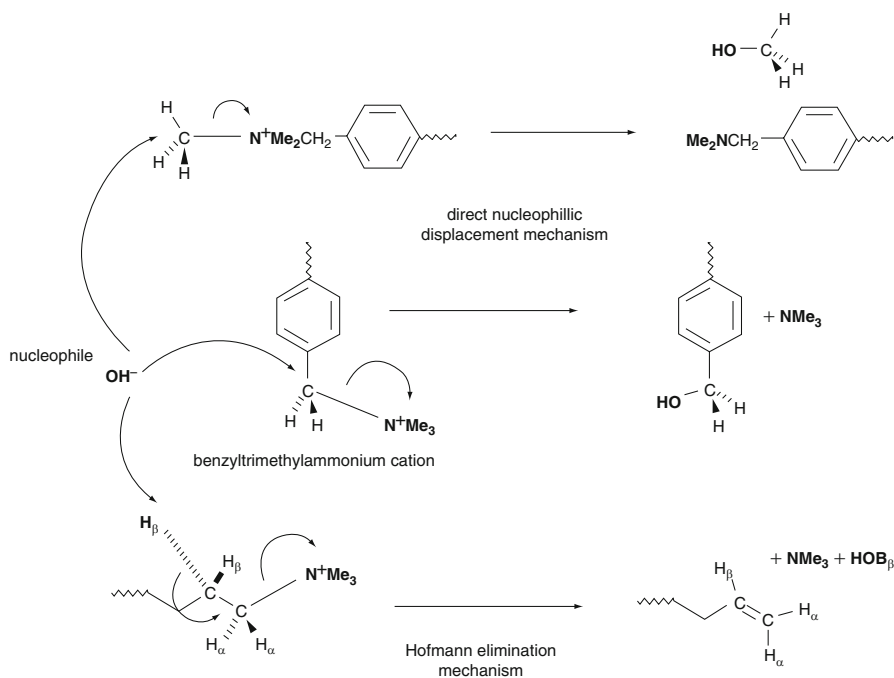
Fig. 2.1 A schematic presentation of (a) a proton-exchange membrane (PEMFC) and (b) an alkaline membrane fuel cell (AMFC), both fuelled either with H_2 gas or directly with methanol (DMFC mode). The stoichiometric ratios of reactants and products are shown in each case

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.), Tosflex® SF-17 (Tosoh) and 2259-60 (Pall RAI). Most of these fuel cells containing AEMs were, however, being operated in the presence of aqueous alkaline solutions (containing NaOH or KOH).

In the UK (at the University of Surrey), several kinds of QA-containing radiation-grafted AEMs (RG-AEMs) based on poly(vinylidene fluoride) PVDF [27–31], poly(tetrafluoroethylene-co-hexafluoropropylene) FEP [27, 28, 32] and poly(ethylene-co-tetrafluoroethylene) ETFE [32, 33], with good ion-exchange capacities (IEC) and ionic conductivities and with sufficient stabilities to test the proof of concept of using AEMs in fuel cells, have been developed. ETFE base films produce the best AEMs for testing in AMFCs. The radiation-grafted methodology (using gamma rays or electron beams for irradiation) allowed for the production of AEMs of different thicknesses, ion-exchange capacity, physical/mechanical properties, and chemistries that facilitated fundamental investigations. A water-insoluble alkaline ionomer that used N,N,N',N' -tetramethylhexane-1,6-diamine as the joint amination and cross-linking agent first enabled studies of the performance of metal-cation-free all-solid-state alkaline fuel cells with stable performance into the medium term at $50^\circ C$ [33, 34]. Many other groups have now developed new conductive and chemically and thermally stable AEMs (and candidate alkaline ionomers), as discussed below. AEMs in the hydroxide form typically become brittle if allowed to dry; hydroxide forms are typically prepared just before use, from the chloride form analogue.

Properties of AEMs

The most common class of NaOH-/KOH-free AEMs being investigated for use in fuel cells is based on QA chemistry and has reasonable stability in alkaline environments (especially those AEMs containing benzyltrimethyl ammonium exchange sites). There are three main classes of chemical degradation reaction mechanisms by which nucleophilic OH^- anions can remove QA groups. The presence of β -hydrogens allows the Hofmann elimination reaction to occur (Scheme 2.1), often in parallel to the reactions discussed below, yielding alkene (vinyl) groups; this can give rise to QA-AEMs that have low thermal and chemical (to alkali) stabilities. If, as in RG-AEMs, no β -hydrogen atoms are present, direct nucleophilic substitution reactions were traditionally thought to take place yielding alcohol and tertiary amine groups. However, recent density functional theory (DFT) calculations and deuterium exchange experiments at Los Alamos National Laboratory (USA) on model small QA-containing compounds indicate that a mechanism involving an ylide intermediate (trimethyl ammonium methylide, also known as a 1,2-dipolar ylide compound) may predominate and be more severe when the AEMs are dehydrated [35].



Scheme 2.1 Alternative mechanisms for degradation of AEMs by displacement of the trimethylammonium groups by hydroxide anions at elevated temperatures

AEMs from Tokuyama Co have good thermochemical stability. The thin (10 μm) Tokuyama “fuel cell grade” AEMs (A010, A201 – formerly A006 and A901) [9, 36–39] and their developmental dispersible alkaline ionomers (A3ver.2 and AS-4) have also been tested at up to 50°C by several research groups in direct alcohol fuel cells [40–42].

Quaternized pyridinium- or phosphonium-based AEMs were thought to have thermochemical stabilities that are not suitable for use in AEM fuel cells but there are reports of recent work on polysulfone-phosphonium-based AEMs and anionomers (see later).

Surrey’s benzyltrimethylammonium-containing S80, S50, and S20 RG-AEMs (the number designating the fully hydrated thicknesses in micrometers) are chemically stable up to 80°C in aqueous KOH [32–34] (aq, 1 mol dm^{-3}) and can exhibit ionic conductivities $> 0.03 \text{ S cm}^{-1}$ at room temperature when fully hydrated; the ex situ and in situ ionic conductivity of fully hydrated S80 is 0.06 S cm^{-1} at 60°C (cf. Nafion® acidic PEMs are typically $> 0.1 \text{ S cm}^{-1}$ at these temperatures). AEM conductivities are, however, considerably reduced at humidities $\text{RH}/\% < 100$ and drop to values between 0.01 and 0.02 S cm^{-1} after only an hour when exposed to air (especially with very thin membranes) due to the reaction of OH^- anions with CO_2 forming CO_3^{2-} and HCO_3^- within the membrane. The lower dissociation constant for $-\text{NMe}_3\text{OH}$ groups (requiring a higher number of water molecules for complete dissociation), compared to $-\text{SO}_3\text{H}$ groups in PEMs, and a very low number of water molecules directly associated with the ionic groups lead to the poor performance at low RHs (at high humidities much of the water present in AEMs is located in aggregates not directly associated with the ionic groups) [32].

The developing published and patent literature in this area has recently been reviewed by Zeng and Varcoe [2]. Further classes of AEM for fuel cells have included membranes based on quaternized poly(epichlorohydrin), polysulfone, poly(phthalalazinone ether ketone), poly(2,6-dimethyl-1,4-phenylene oxide), and poly(vinyl alcohol) grafted with (2,3-epoxypropyl)trimethylammonium chloride. Common quaternizing agents include alkyl iodides, trialkylamines, N,N,N',N' -tetramethylalkyl-1, n -diamines, polyethyleneimine, 1,4-diazabicyclo-[2.2.2]-octane (DABCO), and 1-azabicyclo-[2.2.2]-octane. The final two of these have been used extensively; they contain β -hydrogen but their structures do not permit molecular conformations favored in the Hofmann elimination mechanism. Metal-cation-containing AEMs based on doping polymer films (e.g., polybenzimidazole (PBI), poly(vinyl alcohol) and its composites, and bio-compatible chitosan) with NaOH/KOH(aq) are also being investigated, but the presence of mobile cations may introduce problems associated with precipitation of carbonate salts.

Ionic conductivities of AEMs are generally lower than those of comparable PEMs. This is not surprising as the solution mobility of OH^- is one third to one half of that of a H^+ (depending on the environment and if there $-\mu_o \times 10^4/\text{cm}^2 \text{ V}^{-1} \text{ s}^{-1} = 20.64$ for $\text{OH}^-(\text{aq})$ anions and 36.23 for $\text{H}^+(\text{aq})$ cations at 298 K) [1, 43]. One strategy for enhanced ionic conductivities is to increase the ion-exchange capacity (IEC) via synthetic methodology, but this often leads to a decrease in the mechanical strength

due to excessive water uptakes. Another strategy is to synthesize tailored membranes that will exhibit hydrophilic(ionic)–hydrophobic(nonionic) phase segregation and continuous ionic domains, which is hypothesized to increase ionic conductivities [44, 45].

Recent intensive studies have, however, been reported to lead to AEMs with high ionic conductivities, reportedly comparable to Nafion®. These promising AEMs [11, 45–51] are still to be evaluated in AMFCs. Most hydrocarbon AEMs are soluble in various solvents, which is potentially useful for the formulation of alkaline ionomers required for the preparation of high-performance membrane electrode assemblies (MEAs). If the conductive properties reported can be translated into high power outputs, then AMFC performances comparable to those of PEMFCs can be expected in the near future.

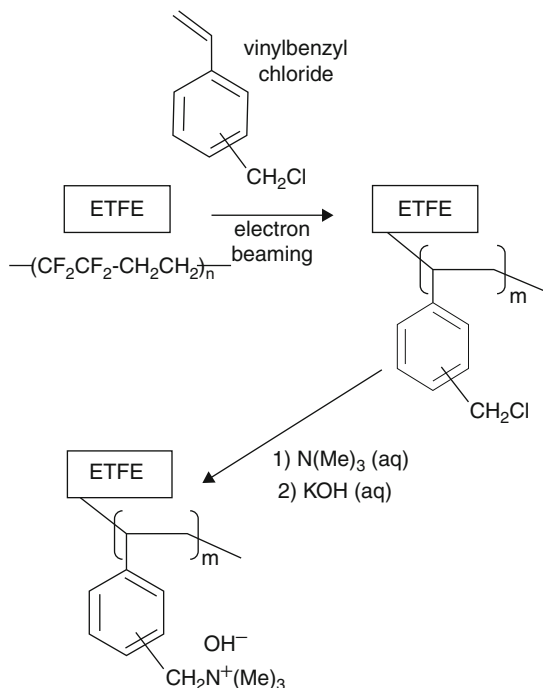
Synthetic Routes to AEMs

The preparation of applicable AEMs 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. 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 polymer classes include polysulfones and polyetherketones, polyimides, poly(phenylene), poly(phthalazinone ether sulfone ketone), polyepichlorohydrin homopolymer, polybenzimidazole (PBI), poly(phenylene oxide), radiation-grafted copolymers, inorganic–organic hybrids, and even perfluorinated membranes such as Nafion. The active functional groups are commonly quaternary ammonium type ($-NR_3^+$) with a clear preference for trimethylammonium ($-N(CH_3)_3^+$) groups ($pK_a(H_2O) = 9.8$).

A suitable AEM will have a high ion-exchange capacity, high ionic conductivity, and thermochemical stability, but will exhibit a low degree of swelling on hydration. There are several general synthetic methodologies for the preparation of AEMs [52, 53]. Fluorine-containing polymers generally show higher thermal stabilities than hydrocarbon polymers. AEMs based on a poly(arylene ether sulfone) containing fluorine atoms show high ionic conductivities (63 mS cm^{-1} in CO_3^{2-} form at 70°C) [53]; this is a key result as CO_3^{2-} anions have dilute solution mobilities that are less than 33% of that of OH^- anions. (It is rare to see CO_3^{2-} conductivities above 30 mS cm^{-1}).

Irradiation of polymer films (and powders, etc.) using X-rays, γ -rays, or electron beams (as at Surrey, see previous section) is a flexible way to introduce various functional groups on the polymer backbones (Scheme 2.2). A wide range of

Scheme 2.2 The radiation-grafting of vinylbenzyl chloride onto ETFE and subsequent amination and alkali-exchange, yielding alkaline anion-exchange membranes (RG-AEMs)



chemically and thermal stable polymers, such as ETFE and FEP, can be chosen as the base films for the production of AEMs. Additionally, there is a wide choice of functional monomers available that can be used to introduce ion-exchange groups into the grafted polymeric chains.

A common strategy in the synthesis of AEMs is to introduce halogen alkyl groups onto the backbone or side chains of the polymer via chloroalkylation, fluorination, bromination, or chlorination, followed by amination/quaternization and finally ion exchange. Highly carcinogenic chloromethylethers have traditionally been used as the chloroalkylation agent but safer strategies have been introduced, for example, the chloro methylation agent is generated in situ (e.g., [44, 55, 56]). An alternative strategy is the prior introduction of tertiary amine groups into the polymer, followed by quaternization.

The easiest synthetic route is to use inert polymers (as above) doped with concentrated $KOH(aq)$ (as above): polybenzimidazole (PBI) [57–61], poly(vinyl alcohol) (PVA) [44], composite polymers such as PVA/hydroxyapatite (PVA/HAP) [62], quaternized-PVA/alumina (QPVA/ Al_2O_3) [63], PVA/titanium oxide (PVA/ TiO_2) [64, 65], chitosan and cross-linked chitosan [66–68], copolymers of epichlorohydrin and ethylene oxide [69], and cross-linked PVA/sulfosuccinic acid (10 wt. % SSA) [70] have all been doped with KOH and used as AEMs. Patent US5569559 [71] 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 ionic conductivity, comparable to Nafion® (a standard acidic proton-exchange membrane, PEM). All of these materials could, however, lead to carbonate precipitates.

Anion-exchange polymers that contain methacrylate, ester, amide, or other carbonyl (C = O double bond) functional groups show low stabilities in alkali as these functional groups are highly reactive to nucleophiles such as OH[−].

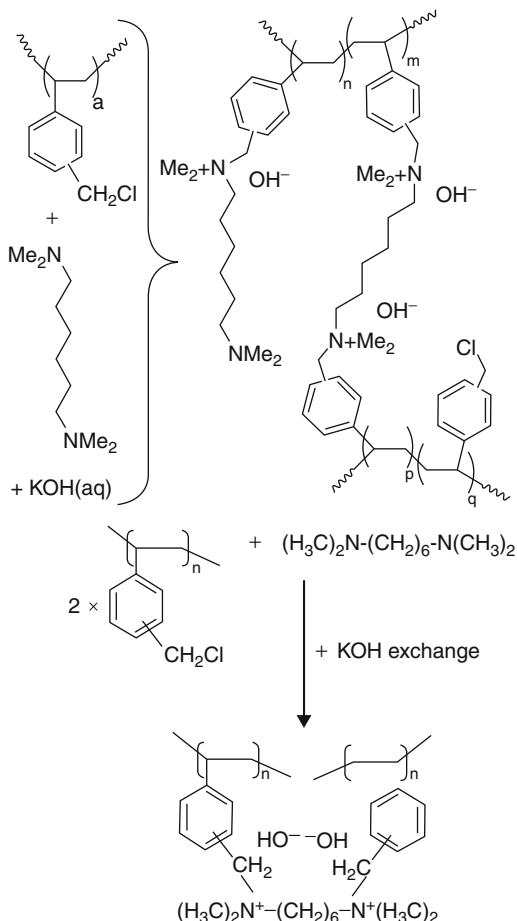
Development of Alkaline Ionomers

Alkaline analogues to the oligomeric perfluorosulfonic acid dispersions used to produce optimized ionic contact between the catalyst reaction sites and the PEM in PEMFCs have yet to be convincingly developed and this has resulted in the use of nonideal strategies for the fabrication of alkaline MEAs: the use of Nafion dispersions (acidic, cation exchanging); concepts involving adsorbed potassium hydroxide, and quaternized copolymers made from 4-vinylpyridine monomer at the electrode–AEM interface. Polysulfone-based alkaline ionomers that are compatible with polysulfone AEMs have been developed by various teams. On the commercial front, it has been reported that Fumatech have developed a ionomer concept for use with their commercial Fumasep®FAA AEMs, that uses two precursors that react to form a cross-linked polymer when mixed together, and Tokuyama's alkaline ionomers can be deposited from solution (designated A3 or AS-4) and are chemically compatible with Tokuyama's fuel cell AEMs.

Surrey developed an alkaline ionomer (SION1, [Scheme 2.3](#)) for MEA fabrication, with the objective of developing a system that would allow the testing of different AEMs and electrodes in AMFCs [\[72\]](#); without this alkaline ionomer, the performances were too low for satisfactory testing. That alkaline ionomer also allowed for the operation of fuel cells in metal-cation-free mode, in contrast to the possible use of doped polymers containing alkali metal hydroxides. An alkaline MEA that was deliberately converted to the CO₃^{2−} form operated as well as an OH[−] form MEA; even more interestingly, the CO₃^{2−} content of the carbonated MEA decreased during fuel cell operation with air (containing CO₂) at the cathode. The SION1 ionomer contains β-hydrogen atoms and, therefore, allows the Hofmann elimination degradation mechanism to operate, limiting the thermal stability to below ca. 60°C. Surrey is currently developing a next-generation β-hydrogen-free alkaline ionomers deposited from aqueous solutions (Patent GB 0814652.4).

Many researchers have reported that alkaline polymers with hydrocarbon backbones can be dissolved in solvents such as DMF, DMAc, and DMSO [\[47–49, 54, 73, 74\]](#), and this allows their use as the ionomer for the preparation of MEAs. Zhuang et al. [\[73, 75\]](#) used a quaternary ammonium 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 used to fabricate the membrane, while a QAPS film (OH[−] form: IEC = 1.18 meq g^{−1}) was used as the ionomer.

Scheme 2.3 The formation of SION1 alkaline ionomer (anionomer) by cross-linkage of poly(vinylbenzyl chloride) with tetramethylhexanediamine (TMHDA)



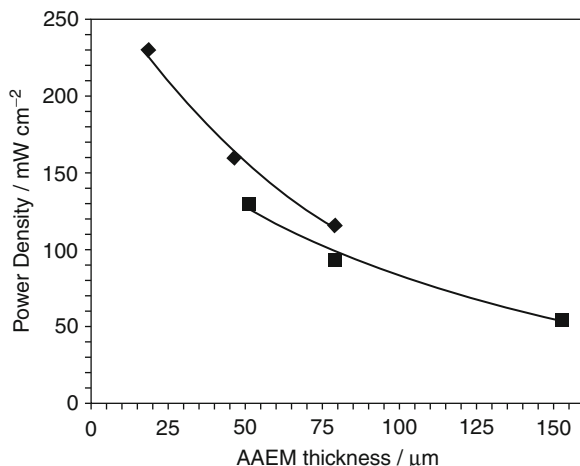
The development of alkaline ionomers is one of the major challenges for the development of high-performance alkaline membrane containing fuel cells. In state-of-the-art AMFC technology, the role of the ionomer has not been fully investigated or understood; alkaline ionomer solutions/dispersions, comparable to the Nafion dispersions used in PEMFCS, remain highly sought after.

AMFCs with H₂ as Fuel

Fundamental studies at Surrey revealed the following [31–34]:

A major source of performance loss is the mass transport of H₂O to the ORR reaction sites. S80/S50/S20 radiation-grafted RG–AEMs, Solvay’s Morgane®–ADP, and Tokuyama’s A201 were evaluated in H₂/O₂ fuel cells at Surrey using both commercial

Fig. 2.2 Variation in power density for H_2/O_2 AMFCs as a function of fully hydrated RG-AEM thickness. The cells contained ETFE-derived RG-AEMs. All electrodes were treated with SION1 ionomer and utilized E-TekPt/C (20% mass) catalyst-loaded carbon cloth (*squares*) or carbon paper (*diamonds*) supports



(prefabricated) and in-house produced electrodes containing SION1 ionomer [72]. As discussed earlier, water is required as a stoichiometric reactant for the ORR at the cathode when using AEMs (unlike in PEMFCs).

The primary source of H_2O to the cathode appears to be the back transport of the H_2O electro-generated at the anode. Even with the use of fully hydrated gas supplies, evidence for this was that enhanced back transport of H_2O from the anode, and therefore superior performances, was observed with thinner AEMs: beginning-of-life peak geometric power densities, P_{peak} , of $54 \rightarrow 94 \rightarrow 130 \text{ mW cm}^{-2}$ were recorded using $154 \rightarrow 78 \rightarrow 51 \text{ }\mu\text{m}$ thick AEMs, respectively, under identical test conditions (less than 20 mW cm^{-2} was obtained with the $230 \text{ }\mu\text{m}$ thick Tokuyama AHA AEM – not developed for use in fuel cells) (Fig. 2.2). The commercial Pt/C (20% mass – $0.5 \text{ mg}_{\text{Pt}} \text{ cm}^{-2}$ loading)-containing Type A carbon cloth prefabricated cathodes (E-Tek division of BASF) that were used contained PTFE binder (current commercially available fuel cell electrodes are optimized for use with PEMs and not for AEMs) and it was suspected that this restricted the transport of the H_2O supplied in the humidified oxygen supply to the reaction sites.

Achieving an optimal MEA is still hindered by the available anionomers. Switching to the use of Toray carbon paper commercial electrodes ($435 \text{ }\mu\text{m}$ thick containing Pt/C (20% mass) catalyst at $0.5 \text{ mg}_{\text{Pt}} \text{ cm}^{-2}$ loading and containing PTFE binder – supplied by E-Tek division of BASF) at both the anode and cathode led to an increase in obtainable power densities (Fig. 2.2). $P_{\text{peak}} = 230 \text{ mW cm}^{-2}$ and a maximum i at full discharge of 1.3 A cm^{-2} was obtained in a H_2/O_2 fuel cell at 50°C with S20 ($20 \text{ }\mu\text{m}$). A $P_{\text{peak}} = 260 \text{ mW cm}^{-2}$ was obtained at 50°C with Tokuyama A201 using SION1-treated electrodes. Fully satisfactory MEA lamination cannot, however, be achieved with SION1 alkaline ionomer and there are still considerable, variable, contact resistances.

Pt-free electrodes are viable in AMFCs (more evidence is given below). Ag/C (60% mass, $4 \text{ mg}_{\text{Ag}} \text{ cm}^{-2}$) performed well when used as a cathode catalyst (Ag/C catalyst performed poorly in the cathode of a PEMFC). Open circuit voltages (V_{OC}) were normally in the range 1.0–1.1 V with Solvay ADP and Pt/C electrodes (ca. 100 mV higher than obtained with Nafion–115 PEMFCs); a drop of 100 mV in V_{OC} was observed when Pt was replaced with Ag at the cathode.

The activity of the carbon supports needs to be evaluated for each catalyst material to be tested. An important finding was that metal-free Vulcan XC–72R (i.e., carbon black only) cathodes produced significant currents ($P_{\text{peak}} = 22 \text{ mW cm}^{-2}$ and $V_{\text{OC}} = 0.88 \text{ V}$ with Solvay ADP at 50°C). Carbons reduce O_2 primarily through a 2e^- mechanism at high pH producing hydroperoxide anions (HO_2^-), which may form highly reactive hydroxyl radical species.

Other groups have been investigating nonradiation-grafted AEMs. A fully non-PGM-catalyst-containing metal-cation-free alkaline membrane fuel cell was first reported by the team at Wuhan University [73], for an AMFC containing a QA-polysulfone AEM and an MEA that did not contain any PGM catalysts; a $P_{\text{peak}} = 52 \text{ mW cm}^{-2}$ at 60°C (open circuit voltage, OCV, $V_{\text{OC}} = 0.94 \text{ V}$) was obtained using Ni-based anode catalyst and a Ag cathode catalyst.

Polysulfone-based AEMs (see earlier) have been tested in H_2/air fuel cells at 60°C using a polysulfone alkaline ionomer (dew point of the gases was 55°C). A $P_{\text{peak}} = 28 \text{ mW cm}^{-2}$ at $V_{\text{cell}} = 0.47 \text{ V}$ was obtained with Pt/C (40% mass, Johnson Matthey) with loadings of $0.5 \text{ mg}_{\text{Pt}} \text{ cm}^{-2}$. $P_{\text{peak}} = 30 \text{ mW cm}^{-2}$ at $V_{\text{cell}} = 0.42 \text{ V}$ was obtained when the cathode contained a Ag/C catalyst (40% mass, E–Tek) at a loading of $2 \text{ mg}_{\text{Ag}} \text{ cm}^{-2}$. OCVs were 100 mV lower with Ag compared to Pt, which correlates with the results above. A $P_{\text{peak}} = 365 \text{ mW cm}^{-2}$ at 0.4 V ($V_{\text{OC}} = 1.04 \text{ V}$, $r = 0.152 \Omega \text{ cm}^2$) was reported at the 214th Meeting of the Electrochemical Society in 2008 by Wang’s team at Penn State University, using Tokuyama’s A901 (10 μm) AEM and AS-4 alkaline ionomer ($\text{IEC} = 1.3 \text{ meq g}^{-1}$) at 50°C in a H_2/O_2 AMFC with 0.4 mg cm^{-2} Pt/C catalysts; these values dropped to 212 mW cm^{-2} ($V_{\text{OC}} = 1.02 \text{ V}$, $r = 0.19 \Omega \text{ cm}^2$) when the O_2 at the cathode was replaced with purified air ($<1 \text{ ppm CO}_2$) and the P_{peak} dropped to 113 mW cm^{-2} ($r = 0.22 \Omega \text{ cm}^2$). The higher value represents the highest H_2/O_2 AMFC performance publicly reported to date.

KOH-doped membranes (see earlier) represent metal-cation-containing AEMs. A H_2/O_2 fuel cell has been tested with a KOH-doped PBI membrane ($t = 40 \mu\text{m}$) at 50°C yielding an $i = 620 \text{ mA cm}^{-2}$ at $V_{\text{cell}} = 0.60 \text{ V}$ ($P = 370 \text{ mW cm}^{-2}$) [60]. This performance was similar to that of the same apparatus with a Nafion–117 PEM and also, remarkably, with a PBI AEM doped with both KOH and K_2CO_3 . The question of the long-term stability and leaching out of the KOH (if any) remains to be fully addressed for this class of AEM, as does the issue of potential for carbonate/bicarbonate precipitation.

Gu and Yan et al. [76] developed an ionomer, tris(2,4,6-trimethoxyphenyl) polysulfone–methylene quaternary phosphonium hydroxide (TPQPOH), 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 could be ideal for use in

AMFC MEAs; 196 mW cm^{-2} was achieved at 80°C (H_2/O_2 gases supplied at 250 kPa back-pressure) using this phosphonium ionomer with a $70 \text{ }\mu\text{m}$ thick FAA commercial membrane (Fumatech GmbH) as the AEM. A maximum power of more than 250 mW cm^{-2} was obtained in a H_2/O_2 fuel cell at 50°C with a $50 \text{ }\mu\text{m}$ AEM and gas back-pressures of 250 kPa. The presence of methoxy ($-\text{OCH}_3$) groups on the aromatic rings that are connected to the phosphonium ion centers seems essential to adequate chemical stability.

The Application of AEMs in Other Fuel Cell Types

The utility of AEMs as potential electrolytes in fuel cells arises not only from the prospects for the use of non-Pt-group metal (non-PGM) catalysts and cheaper fuel cell components (less corrosive environment) but also from potential for use of alternative fuels.

Alcohols and diols, sodium borohydride (NaBH_4), and hydrazine (H_2NNH_2) have all been used directly as fuels in AMFCs. Patents [77, 78] 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). EP2133946 [79] disclosed the use of transition metals as catalysts in AMFCs. There are numerous reports on the use of non-Pt catalyst, such as MnO_2 [58], Ag/C [74, 75, 79], Au/C [80], FeTPP/BPC (Black Pearl Carbon) [81], CoPPyC [82], FeCo-CNF (Carbon Nanofiber) [83], CoFeN/C-HLH [84] in AMFC cathodes and Cr-decorated Ni/C [73], Fe-Co-Ni/C [85, 86] at anodes.

Zhuang et al. conducted a feasibility analysis of the use of AEMs in DMFCs [87]; this important study concentrated on the thermodynamic disadvantages versus kinetic advantages of such cells by considering the reactions taking place in aqueous solutions and the authors concluded that the thermodynamic voltage losses due to the pH difference across the AEM would be approximately canceled out by the kinetic voltage gains. Ogumi et al. studied direct alcohol fuel cells (methanol and ethylene glycol) with a commercial AEM (Tokoyama AHA, thickness $\approx 240 \text{ }\mu\text{m}$) [39]. Solutions of ethylene glycol and methanol were made to a concentration of 1 mol dm^{-3} dissolved in KOH (aq, 1 mol dm^{-3}), and so the system was not metal-cation-free (common with other AMFCs obtaining reasonable power levels with alcohols as fuels). Cell voltages were around 100 mV higher for ethylene glycol compared to methanol. This fuel cell is *not* quite an alkaline analogue of an acid membrane DMFC, as the authors used alkaline fuel solution. No indication was given concerning completeness of oxidation of the ethylene glycol to CO_2 and H_2O . Yu and Scott also reported the operation of a direct methanol alkaline fuel cell, with

platinized titanium mesh anodes ($1.5 \text{ mg cm}^{-2}\text{Pt/Ti}$) and a commercial alkaline anion-exchange membrane (Morgane ADP membrane from Solvay SA) [88].

It has been proposed that ammonia would make a good energy vector/carrier [6] and an indirect fuel for a hydrogen fuel cell; ammonia is environmentally benign (it is already used as a fertilizer and neutralizes acid rain), already available cheaply, contains 50% more H per dm^3 than liquid hydrogen, and is a liquid at much lower pressures (8–9 bar); it also has the advantage of a strong smell, allowing the easier location of leaks. Cracking ammonia to form hydrogen free of traces of ammonia for use in traditional PEMFCs requires temperatures of above 900°C ; PEMFCs cannot tolerate any NH_3 contamination. An advantage of AFCs is that they will tolerate low levels of NH_3 , and so cracking can be undertaken at lower temperatures; this has yet to be explored using AMFC approaches.

A Brief Overview of the Patent Literature

Zeng and Varcoe have recently reviewed in depth the patent literature concerning AEMs [89]. A small number of patents of direct interest to application of AEMs in AMFCs are considered in this section.

In the area of novel AEMs:

- Patents relating to the application of radiation-grafted ion-exchange membranes in fuel cells have been granted to Scherer et al. [89] and to Stone and Steck [90, 91]. These patents mention the functionalization of base polymers with quaternary ammonium groups to yield alkaline polymers. The use of fluorine-substituted styrenic monomers is also claimed to improve membrane chemical stability when utilized in fuel cells (removal of undesired and reactive C–H bonds).
- Fauvarque was granted a patent on aqueous alkaline solid electrolyte based around polyether polymer matrices [92].
- Yao et al. were granted related patents on alkaline polymers containing alkyl quaternary ammonium salts, nitrogen containing heterocyclic quaternary ammonium salts, and metal hydroxide salts for potential applications in alkaline batteries and fuel cells [93–95].

In the area of device architecture:

- Jaouen patented a novel cathode structure for a solid polymer fuel cell [96]; that cathode structure consisted of a solid polymer anion-exchange membrane surrounding the catalysts particles (entirely within the cathode structure), which was in contact (surrounded) with a cation-conducting polymer membrane.
- Lu and Zhuang were granted a patent on alkaline-resin-containing fuel cells with direct fuelling with liquid organic fuels [97].
- Related patents from Divisek describe the invention of a methanol fuel cell utilizing an anion-exchange membrane [98, 99].

Future Directions and Research Challenges

There are a number of research challenges that must be overcome before AEMs can be successfully applied in pre-commercial AMFCs:

1. As a priority and to complement *ex situ* stability measurements, AEMs must be evaluated in H_2/O_2 , H_2/air , and methanol/air fuel cells for several thousand hours to ensure adequate *in situ* membrane stability and assess the effect of and level of $\text{CO}_2^{2-}/\text{HCO}_3^-$ formation. The effect of adding alkali to the methanol solution must also be thoroughly investigated over long timescales.
2. AEMs must be created with higher conductivities, to ensure good fuel cell performances at high current densities. It should be noted, however, that with application of an alkaline DMFC as a power source for portable devices, an overriding priority is maximizing the energy density of the fuel and fuel efficiency (cell voltage). These DMFCs will be operated at low-to-medium current densities (higher efficiencies), where electrode overpotentials are the dominant cause of voltage losses.
3. It is essential that a solubilized form of an alkaline anion-exchange polymer be developed to improve the interface between the electrodes and the AEM electrolyte. Success in this effort will decrease MEA resistances. A water-based soluble form which can be rendered water insoluble when cast would be preferred, as there are safety concerns (primarily with industrial scale production) about using organic solvents near finely dispersed (pyrophoric) metal catalysts (unsupported or supported on carbon).
4. If AEMs are to be applied to fuel cells for other applications (such as automotive power etc.), more temperature stable AEMs must be developed. Operation of alkaline-membrane-based fuel cells at elevated temperature would reduce thermodynamic voltage losses due to pH differences across the AEM and would also improve the electrokinetics. Successful, stable over the long term, and being operational at elevated temperatures, all would allow application in fuel cells for the automotive mass market.
5. If AEMs are shown to be stable in fuel cells over thousands of hours, an in-depth investigation into effective and cheaper non-noble metal catalysts (e.g., Ni, Ag etc.) is indicated. There would also be a greater chance of finding methanol-tolerant catalysts for use in the cathodes than in related PEM-based DMFCs.
6. Finally, removal of fluorine from the polymer systems would be of interest to enhance the environmental credentials of the technology (facilitating easier disposal) and reduce costs. The substitution of fully fluorinated FEP with non-fluorinated LDPE is feasible. While oxidative radical degradation is a problem at the cathode and anode (via oxygen diffusion through the membrane) with non-fluorinated PEMs, it has been shown using electron paramagnetic resonance (EPR) studies that such degradation is prevented in highly alkaline (pH > 11.7) conditions pertinent to AEMs [100–102].

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