Review

Principles and Materials Aspects of Direct Alkaline Alcohol Fuel Cells

Eileen Hao Yu [1], Ulrike Krewer [2,3,]* and Keith Scott [1]

[1] School of Chemical Engineering and Advanced Materials, Merz Court, Newcastle University, Newcastle upon Tyne, NE1 7RU, UK; E-Mails: eileen.yu@ncl.ac.uk (E.H.Y.); k.scott@ncl.ac.uk (K.S.)

[2] Max Planck Institute for Dynamics of Complex Technical Systems, Sandtorstrasse 1, 39106 Magdeburg, Germany

[3] Portable Energy Systems, Chair for Process Systems Engineering, Otto von Guericke University, Universitaetsplatz 2, 39106 Magdeburg, Germany

* Author to whom correspondence should be addressed; E-Mail: krewer@mpi-magdeburg.mpg.de; Tel.: +49-(0)391-6110-443; Fax: +49-(0)391-6110-536.

Abstract: Direct alkaline alcohol fuel cells (DAAFCs) have attracted increasing interest over the past decade because of their favourable reaction kinetics in alkaline media, higher energy densities achievable and the easy handling of the liquid fuels. In this review, principles and mechanisms of DAAFCs in alcohol oxidation and oxygen reduction are discussed. Despite the high energy densities available during the oxidation of polycarbon alcohols they are difficult to oxidise. Apart from methanol, the complete oxidation of other polycarbon alcohols to CO_2 has not been achieved with current catalysts. Different types of catalysts, from conventional precious metal catalyst of Pt and Pt alloys to other lower cost Pd, Au and Ag metal catalysts are compared. Non precious metal catalysts, and lanthanum, strontium oxides and perovskite-type oxides are also discussed. Membranes like the ones used as polymer electrolytes and developed for DAAFCs are reviewed. Unlike conventional proton exchange membrane fuel cells, anion exchange membranes are used in present DAAFCs. Fuel cell performance with DAAFCs using different alcohols, catalysts and membranes, as well as operating parameters are summarised. In order to improve the power output of the DAAFCs, further developments in catalysts, membrane materials and fuel cell systems are essential.

1. Introduction

Easy storage and handling, high energy density and wide availability are features that make alcohols attractive liquid fuels for the most promising alternative power sources for transportation, portable electronics and stationary applications. One of the first investigations of alcohol in fuel cells was conducted by Palve in 1954. He demonstrated that methanol acted as a fuel in aqueous electrolytes [1]. Since the development of perfluorinated cation exchange membranes, such as Nafion®(DuPont), proton exchange membranes (PEM) have dominated as the electrolyte for fuel cells. Ethanol [2–7], 2-propanol [8,9], ethylene glycol [10–13] and glycerol [14] have all been considered for fuel cell applications. In direct alcohol fuel cells (DAFCs), alcohol is directly oxidised at the anode in an acidic medium using a proton exchange membrane (PEM). Direct methanol fuel cells are the most advanced and studied systems since methanol, with only one carbon in its molecule and no C-C bonds, is the simplest alcohol. Electrooxidation of methanol is relatively simple compared to other alcohols. However, two major obstacles have restrained the more rapid development and applications of DAFCs, even for methanol systems:

- Alcohol crossover from the anode to the cathode
- The relatively low activity and complex reaction mechanism of most alcohols

Apart from methanol, it is particularly difficult to break the C-C bond in alcohols during electrochemical oxidation. In addition to these two major issues, the high costs of proton exchange membranes and precious metal catalysts (Pt and Pt/Ru based catalysts), and CO poisoning of Pt catalysts at lower temperature in acidic media have further hampered development of DAFCs.

It is known that for many reactions, electrocatalysts perform better in alkaline electrolytes. In fact, one of the first direct methanol fuel cells (DMFCs) developed in 1955 by Justi and Winsel were operated in alkaline media and used porous nickel for the anode and porous nickel-silver for the cathode [1]. A problem with alkaline fuel cells is the carbonation of the solution due to CO_2 production of the fuel oxidation and from air:

$$2OH^- + CO_2 \rightarrow CO_3^{2-} + H_2O \tag{1}$$

This can cause solid precipitation of carbonate salts on the porous electrode and a pH decrease in the alkaline electrolyte solution [15]. Consequently, it leads to a reduction in reactivity for fuel oxidation in the system [16]. The application of anion exchange membranes (AEMs) as the solid polymer electrolyte can reduce formation of carbonate from carbon dioxide, compared to aqueous electrolyte. It was also discovered that the electro-oxidation of methanol in alkaline electrolytes is structure insensitive [17], which opens up the opportunity for use of non-precious metals, such as Pd, Ag, Ni and perovskite-type oxides [18–20], which are significantly cheaper than Pt based catalysts, in alkaline fuel cells. Furthermore, the ionic current in the alkaline fuel cell is due to conduction of
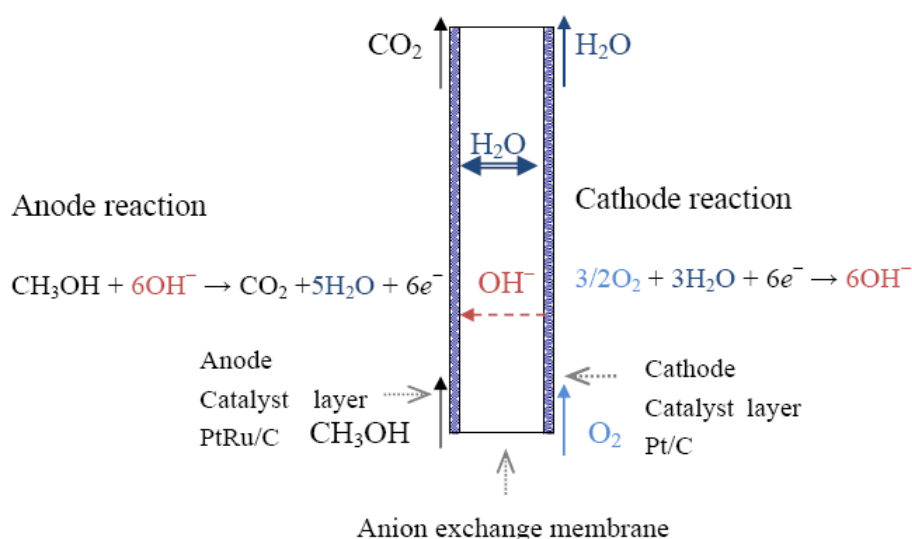
hydroxide ions. This ionic flow is in the reverse direction to that in proton conducting systems. As such, the direction of the electro-osmotic drag is reversed, reducing alcohol crossover [21].

In this study, we review recent developments in the field of direct alkaline alcohol fuel cells. We discuss progress in understanding the reaction mechanisms of fuel oxidation and oxygen reduction in alkaline media, and the recent catalyst development for alcohol oxidation and oxygen reduction. Moreover, the development of anion exchange membranes for alkaline fuel cell applications is presented. Finally, fuel cell performance using different alcohols is compared.

2. Principles and Mechanisms of a Direct Alkaline Alcohol Fuel Cell (DAAFC)

Compared to the use of hydrogen in fuel cells, liquid alcohol fuels are easy to store and transport. The direct oxidation of alcohol will also eliminate a heavy reformer needed to produce hydrogen from liquid or gaseous carbonaceous fuels. Figure 1 shows a schematic principle of a direct methanol alkaline fuel cell with a mixture of methanol, water and sodium hydroxide circulating in the anode, and oxygen in the cathode.

Figure 1. Schematic diagram of direct methanol alkaline fuel cell.
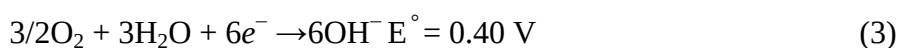
On the anode, methanol is oxidised to carbon dioxide and electrons are produced, while on the cathode side, oxygen accepts electrons and is reduced to produce hydroxide ions. Hydroxide ions then transfer through the electrolyte to the anode. The reactions and thermodynamic potentials [*vs.* standard hydrogen electrode (SHE)] on each electrode are shown below:

Anode oxidation:

$$CH_3OH + 6OH^- \rightarrow 6e^- + CO_2 + 5H_2O \qquad E^\circ = -0.81 \text{ V} \qquad (2)$$

Cathode reduction:

$$3/2O_2 + 3H_2O + 6e^- \rightarrow 6OH^- \quad E^\circ = 0.40 \text{ V} \qquad (3)$$

Overall reaction:

$$CH_3OH + 3/2O_2 \rightarrow CO_2 + 2H_2O \qquad E^\circ = 1.21 \text{ V} \qquad (4)$$
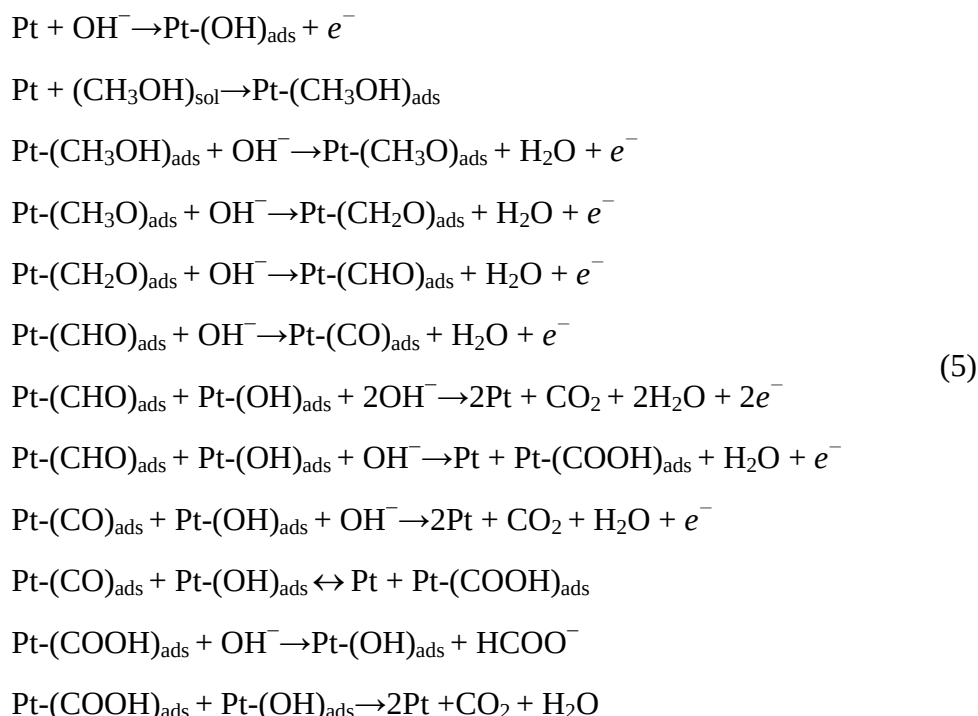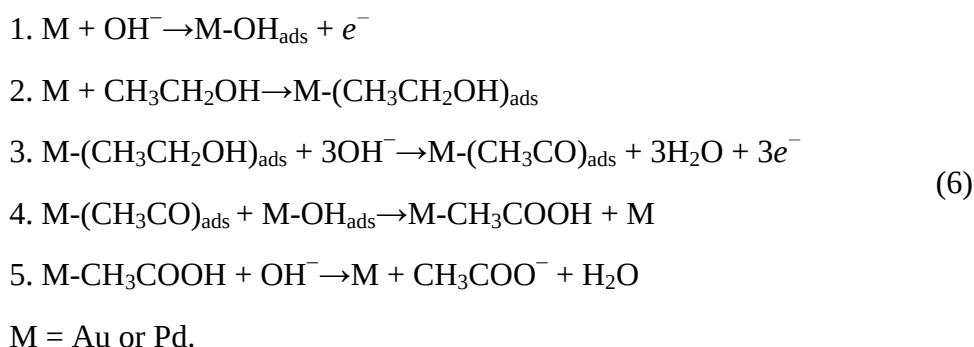
2.1. Alcohol Oxidation

The mechanism of electrochemical oxidation of methanol on platinum in alkaline systems involves formation of adsorbed methanolic species and OH on the Pt surface. The oxidation takes place through a series of reaction steps involving successive electron transfer, *i.e.* partial oxidation, to form adsorbed species. These react with adsorbed OH to potentially form carbon dioxide. The reaction mechanism has been written as follows [22]:

$$Pt + OH^- \rightarrow Pt\text{-}(OH)_{ads} + e^-$$

$$Pt + (CH_3OH)_{sol} \rightarrow Pt\text{-}(CH_3OH)_{ads}$$

$$Pt\text{-}(CH_3OH)_{ads} + OH^- \rightarrow Pt\text{-}(CH_3O)_{ads} + H_2O + e^-$$

$$Pt\text{-}(CH_3O)_{ads} + OH^- \rightarrow Pt\text{-}(CH_2O)_{ads} + H_2O + e^-$$

$$Pt\text{-}(CH_2O)_{ads} + OH^- \rightarrow Pt\text{-}(CHO)_{ads} + H_2O + e^-$$

$$Pt\text{-}(CHO)_{ads} + OH^- \rightarrow Pt\text{-}(CO)_{ads} + H_2O + e^-$$

$$Pt\text{-}(CHO)_{ads} + Pt\text{-}(OH)_{ads} + 2OH^- \rightarrow 2Pt + CO_2 + 2H_2O + 2e^-$$

$$Pt\text{-}(CHO)_{ads} + Pt\text{-}(OH)_{ads} + OH^- \rightarrow Pt + Pt\text{-}(COOH)_{ads} + H_2O + e^-$$

$$Pt\text{-}(CO)_{ads} + Pt\text{-}(OH)_{ads} + OH^- \rightarrow 2Pt + CO_2 + H_2O + e^-$$

$$Pt\text{-}(CO)_{ads} + Pt\text{-}(OH)_{ads} \leftrightarrow Pt + Pt\text{-}(COOH)_{ads}$$

$$Pt\text{-}(COOH)_{ads} + OH^- \rightarrow Pt\text{-}(OH)_{ads} + HCOO^-$$

$$Pt\text{-}(COOH)_{ads} + Pt\text{-}(OH)_{ads} \rightarrow 2Pt + CO_2 + H_2O$$

$$(5)$$

The rate-determining step is most likely the reaction with the oxidation of the active intermediate—CHO [23–29]. For other alcohols, the higher energy density and lower toxicity of polyhydric alcohols still attract lots of interest in applying these alcohols in fuel cells, but the electrochemical oxidation is more difficult and the reaction mechanism is more complicated, since it involves breaking C-C bond(s). The reaction at low temperature leads to a low Faradic efficiency. The mechanism and kinetics of oxidation of different alcohols using Pt-based and non-Pt based metal catalysts have been investigated.

Tremiliosi-Filho *et al.* [30] and de Lima and Varela [31] investigated ethanol oxidation on polycrystalline gold electrodes. Liang *et al.* [32] and Nguyen *et al.* [33] have both studied ethanol oxidation on palladium catalysts. For ethanol oxidation in alkaline media, the formation of acetaldehyde or acetic acid was identified [34]. The steps involved can be presented as:

$$1.\ M + OH^- \rightarrow M\text{-}OH_{ads} + e^-$$

$$2.\ M + CH_3CH_2OH \rightarrow M\text{-}(CH_3CH_2OH)_{ads}$$

$$3.\ M\text{-}(CH_3CH_2OH)_{ads} + 3OH^- \rightarrow M\text{-}(CH_3CO)_{ads} + 3H_2O + 3e^-$$

$$4.\ M\text{-}(CH_3CO)_{ads} + M\text{-}OH_{ads} \rightarrow M\text{-}CH_3COOH + M$$

$$5.\ M\text{-}CH_3COOH + OH^- \rightarrow M + CH_3COO^- + H_2O$$

$$(6)$$

$$M = Au\ or\ Pd.$$
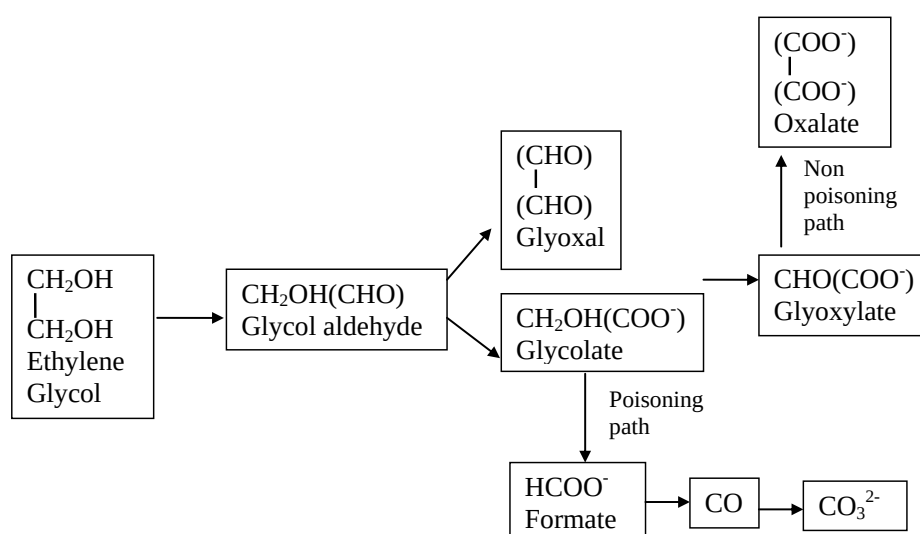
The rate-determining step is step 4, in which the adsorbed ethoxy intermediate is removed by adsorbed hydroxyl ions to form acetate. Fang *et al.* studied the mechanism of ethanol electrooxidation on a palladium electrode in alkaline solution with various concentrations of NaOH (0.01 to 5 M) [35]. Cyclic voltammetry and *in situ* Fourier Transform Infrared (FTIR) spectroelectrochemistry were used to investigate oxidation products at different pH values. They found that the ethanol oxidation activity on Pd was largely affected by pH. The highest activity was obtained in 1 M NaOH. This was supported by their previous study [36], which was attributed to OH_{ads} species on Pd. The density functional theory (DFT) calculations show that in acidic media continued dehydrogenation of ethanol is difficult due to the lack of OH species to instantly remove hydrogen, while in alkaline media, ethanol and sufficient OH can be adsorbed on Pd leading to continuous oxidation. The main oxidation product was sodium acetate with NaOH concentrations higher than 0.5 M. No CO formation was detected by FTIR suggesting low poisoning effect with ethanol oxidation on Pd in alkaline media.

The mechanism for electrochemical oxidation of ethylene glycol in alkaline media was proposed by Matsuoka *et al.* [37]. They stated that ethylene glycol can be oxidised to oxalate (COO^--COO^-) via a non-poisoning path, and to formate via a poisoning path (Figure 2). Further oxidation of formate will produce CO poisoning species, while oxalate is very stable in alkaline medium and cannot be further oxidised, and as a result, no CO poisoning species are produced. In this case, the poisoning effect on the platinum is less significant compared to methanol.

Glycerol has attracted interest in its use as fuel for DAFCs recently. It is produced in large quantities as a byproduct of biodiesel production. DAFCs provide the possibility of generating energy from the waste. The mechanism of electrochemical oxidation of glycerol in alkaline solution was investigated by Roquet *et al.* and Schell *et al.* [38,39]. Glyceraldehyde was found to be the main reaction product, but formic, glycolic, tartronic and glyceric acids were also detected [38].

Figure 2. Reaction pathways of ethylene glycol electrochemical oxidation in alkaline media [37].
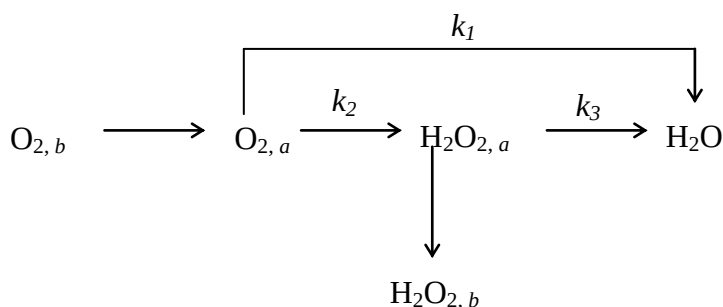

In Table 1, the electrochemical oxidation of various alcohols studied in alkaline media has been summarised.

Table 1. Electrochemical oxidation of various alcohols in alkaline medium.

Fuel	Anode Reactions	E° (V/SHE)	Energy density (Wh/kg)
Methanol CH_3OH	$CH_3OH + 6OH^- \rightarrow CO_2 + 5H_2O + 6e^-$	-0.81	6100
Ethanol CH_3CH_2OH	$CH_3CH_2OH + 2OH^- \rightarrow CH_3CHO + 2H_2O + 2e^-$ $CH_3CH_2OH + 4OH^- \rightarrow CH_3COOH + 3H_2O + 4e^-$ $CH_3CH_2OH + 12OH^- \rightarrow 2CO_2 + 9H2O + 12e^-$	-0.77	8030
iso-Propanol $CH_3CHOHCH_3$	$CH_3CHOHCH_3 + 2OH^- \rightarrow CH_3COCH_3 + 2H_2O + 2e^-$ $CH_3COCH_3 + 16OH^- \rightarrow 3CO_2 + 11H_2O + 16e^-$	-0.67	8600
Ethylene glycol $(CH_2OH)_2$	$(CH_2OH)_2 + 14OH^- \rightarrow 2CO_3^{2-} + 10H_2O + 10e^-$ or $(CH_2OH)_2 + 10OH^- \rightarrow (CO_2)_2^{2-} + 8H_2O + 8e^-$	-0.72	5200
Glycerol $HOCH_2CHOHCH_2OH$	$HOCH_2CHOHCH_2OH + 20OH^- \rightarrow 3CO_3^{2-} + 14H_2O + 14e^-$ or $HOCH_2CHOHCH_2OH + 12OH^- \rightarrow (COO^- - COH\text{-}COO^-) + 10H_2O + 10e^-$	-0.69	5000

2.2. Oxygen Reduction

The oxygen reduction reaction (ORR) has been studied extensively. Effects of different pH, electrolytes, temperature and pre-conditioning of electrodes on ORR have been investigated. The most accepted mechanism of ORR was first proposed by Damjanovic *et al.* [40,41]. They suggested that the ORR proceeds along two parallel reaction paths with comparable rates. One is the direct four-electron transfer reduction from oxygen to water; the other is the formation of hydrogen peroxide as an intermediate in a two-electron transfer reaction. The reaction scheme is shown as follows [42]:
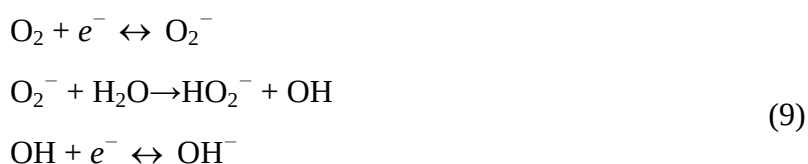
where *a* indicates an adsorbed state and *b* is the bulk solution.

The reactions in alkaline media can be presented as:

$$O_2 + 2H_2O + 4e^- \rightarrow 4OH^- \tag{8}$$

and the path involving hydrogen peroxide suggested in [38] is:

$$O_2 + e^- \leftrightarrow O_2^-$$

$$O_2^- + H_2O \rightarrow HO_2^- + OH \tag{9}$$

$$OH + e^- \leftrightarrow OH^-$$

In the low current density region, the Tafel slope is -60 mV dec^{-1} and the reaction order is 0.5 with respect to pH in alkaline solutions. The fractional reaction order was interpreted in terms of the first

electrochemical step as rate determining under a Temkin isotherm, *i.e.* the adsorption of reaction intermediates O_{ads}, OH_{ads} and HO_{2ads} [43].

The rate expression under Temkin conditions of adsorption is:

$$j = k[O_2][H^+]^{\frac{1}{2}}\exp\left(-\frac{\eta F}{RT}\right) = 3.74k[O_2][OH^-]^{-\frac{1}{2}}\exp\left(-\frac{\eta F}{RT}\right) \tag{10}$$

where k is the rate constant, η is the overpotential.

In the high current density region, the Tafel slope is -120 mV dec^{-1} and the reaction order is 0 with respect to pH in alkaline solutions, with H_2O as a reacting species. The adsorption of intermediate species changes to a Langmuir isotherm and Temkin conditions no longer hold. The rate expression under Langmuir conditions is:

$$j = k[O_2]\exp\left(-\beta\frac{\eta F}{RT}\right) \tag{11}$$

where β is the symmetry factor.

The reaction is first order with respect to O_2 in solutions. It was found that the amount of H_2O_2 formed is greater in alkaline than in acid media [40,44]. In alkaline solutions, about 80% of the reduction current is via the direct reduction and the remainder of the current goes to the formation of H_2O_2, which suggests a more complicated mechanism.

3. Catalysts for DAAFCs

As in proton exchange membrane fuel cells, platinum and other precious metals are still the most common catalysts used in DAAFCs. Low cost platinum-free and non-precious metal catalysts have been investigated for use in alkaline environment.

3.1. Alcohol Oxidation Catalysts

For alcohol oxidation under alkaline solutions, the reaction current densities obtained during alcohol oxidation at certain potentials are at least an order of magnitude greater than in acidic electrolytes. The application of alkali electrolytes could lead to a reduction in catalyst loadings, as well as allowing less expensive, non-precious metal catalysts. In this case, the cost of electrocatalysts and thus fuel cells may be reduced. Methanol oxidation in alkaline media on platinum single crystal and polycrystalline electrodes has been investigated by several research groups [27–29,45]. Unlike in acid, the electrode does not suffer severely from poisoning in alkali because bonding of the chemisorbed intermediates on platinum is weak and the amount of the suggested poisoning species CO_{ads}, is smaller than in an acidic medium [22].

3.1.1. Precious Metal Catalysts

Uniform platinum nanotubes have been synthesised by directly mixing Ag nanowires and H_2PtCl_6 in saturated NaI solutions. The Pt nanotubes were tested for methanol oxidation in alkaline. They demonstrated high active areas and higher activity compared to conventional Pt/C catalysts [46]. In acid solution, Pt/Ru is the most effective bimetallic catalyst used for methanol oxidation. It has been applied for more than 30 years and no significantly better system has yet been found. Ru dissolved in a

Pt matrix reduces the degree of anode poisoning. The Ru-containing catalysts shifted the onset potential for methanol oxidation to more negative values [47]. The study of Tripkovic *et al*. [48] investigated methanol oxidation on a Pt/C and a Pt_2Ru_3/C electrode and showed that in alkaline solutions the difference in activity between the catalysts was smaller than in acid solutions. This proved the above study that the poisoning effect from fuel oxidation to catalyst is less severe.

Matsuoka *et al.* [13] used an OH-form anion exchange membrane and polyhydric alcohols in DAAFCs with Pt-Ru/C as the anode catalysts and Pt/C and Ag for the cathode catalysts. The fuel cells showed good performance with the maximum power densities obtained in the order of ethylene glycol > glycerol > methanol > erythritol > xylitol.

For alcohol oxidation, the combination of (alloying) elements such as Ru, Mo, Sn, Re, Os, Rh, Pb and Bi with platinum give tolerance to the poisoning species compared to platinum alone.

Verma *et al.* [49] studied three different catalysts: Pt-black, Pt-Ru (40 wt%:20 wt%)/C and Pt/C (40 wt%), with varying loads at the anode against a MnO_2 cathode for alkaline fuel cells using methanol, ethanol or sodium borohydride as fuel. Liquid KOH solution was used as the electrolyte. The Pt-Ru/C produces the best cell performance for all fuels. Ethanol produced a single peak at 0.03 V (*vs.* NHE) and no characteristics of C-C bond breaking were observed. Chemical analysis confirmed production of acetaldehyde and acetic acid. For methanol, a broad plateau was produced from –0.4 to 0.6 V and indicated that Pt black was more active for ethanol oxidation than for methanol oxidation.

Electrooxidation of ethanol on Pt-ZrO_2/C catalyst was studied by cyclic voltammetry (CV) and electrochemical impedance spectroscopy (EIS) in alkaline solution. Pt-ZrO_2/C showed higher catalytic activity than Pt/C (20 wt% E-TEK). The optimum ratio for Pt:ZrO_2 was 1:4 [50].

Multi-metallic Pt based catalysts were studied on the electrooxidation of ethylene glycol (EG) in alkaline medium [51]. The addition of Bi to platinum caused a positive shift of the onset potential for EG oxidation by 70 mV but an increase of current density. The ternary catalyst PtPdBi/C did not change the EG oxidation onset potential, and a higher current density was obtained compared to PtBi/C. The performance of these catalysts was evaluated with an alkaline membrane fuel cell. OCV and power density are summarised in Table 2.

Table 2. Fuel cell performance using ethylene glycol in alkaline medium at multi-metallic Pt based catalysts [51].

Catalyst	OCV/V	Power density/mWcm^{-2}
Pt/C	0.66	19
PtBi/C	0.83	22
PtPdBi/C	0.81	28

Improved OCV and power density were obtained from binary and ternary catalysts. The catalysts containing Bi seem to activate the oxidation of EG in oxalate compared to Pt. It was proposed that in binary and ternary catalysts with Bi and Pd, Bi mainly favours the adsorption of OH but affects the product distribution by changing the composition of chemisorbed species; Pd can reduce the poisoning on Pt sites by changing the composition of chemisorbed species.

Palladium is a very good electrocatalyst for organic fuel electro-oxidation and is a potential alternative to platinum when alloyed with non-noble metals for use in DAFCs. Although Pd does not

show comparable activity to Pt on methanol oxidation, it demonstrated good activity in several studies on 1-propanol, 2-propanol, ethanol, ethylene glycol and glycerol oxidation [32,52–55].

Pd binary catalysts with addition of Ag, Au or Ru showed improved activity compared to Pd catalyst alone. Pd/C promoted by Au, with the optimum ratio of Pd:Au = 4:1, demonstrated a significant increase of catalytic activity and stability for 2-propanol oxidation [56]. Bunazawa and Yamazaki also prepared PdAu/C catalyst for methanol fuel cells using ultrasonic synthesis and found that EG was the optimum solvent resulting in highly dispersed nanoparticles on carbon support [57]. Lamy *et al.* [58] also used carbon supported Au/Pd for a fuel cell with anion exchange membrane and glycerol as the fuel. The performance with Au/Pd was lower than using Au or Pd alone, and the highest power output was obtained with Pd/C catalysts. An enhancement was also observed from Pd-Ag/C catalyst towards ethanol electrooxidation in alkaline media [33]. The catalyst was prepared by co-reduction method and Pd-Ag alloy nanoparticles were formed. The Pd-Ag/C catalyst exhibited high activity, enhanced adsorbed CO tolerance and stability for ethanol oxidation. Addition of Ru has the same enhancement on Pd catalyst for ethanol oxidation [18]. With Pd-Ru catalyst, the ethanol oxidation current density was four times of that from Pt-Ru within the potential 0.3–0.4V (RHE). An *et al*. used Pd-Ni as the anode catalyst for a direct EG fuel cell with Tokuyama AEM and a non-Pt cathode catalyst [59]. A power density of 67 mWcm^{-2} was achieved, which is the highest reported for EG fuel cells.

Ternary and quaternary Pt catalysts were studied for ethanol oxidation in alkaline by Bambagioni *et al.* [60]. Pd was spontaneously deposited on Vulcan XC-72 supported Ni-Zn and Ni-Zn-P alloys using Pd^{IV} salts. The Pd-(Ni-Zn)/C and Pd-(Ni-Zn-P)/C catalysts exhibited promising activity for ethanol oxidation. The onset potential was −0.6 V *vs.* Ag/AgCl/KCl$_{sat}$, *i.e.* −0.4 V *vs.* NHE, and a specific current of 3600 A (g Pd)$^{-1}$ was obtained on both catalysts. Higher activity and stability of the catalysts were due to interaction with oxygen atoms from Ni-O moieties.

Multi-walled carbon nanotubes (MWCNT) were used as the substrate for Pd and Pt-Ru catalysts in fuel cells with anion exchange membranes (AEM) using various alcohols as the fuel. The catalysts were very active for the oxidation of all alcohols [52,61]. The effect of a small addition of MWCNT (1–5%) and Ni (1%) into Pd catalyst was studied for methanol oxidation in 1M KOH [62]. Addition of 1% MWCNT in Pd catalyst led to a 5–8 fold increase of catalytic activity; while further addition of 1% Ni into Pd-MWCNT further increased activity by 1.4–1.7 fold. The increase of activity can be ascribed to improved geometrical and electronic properties of the catalyst.

Metal oxide promoted Pd/C catalysts were also investigated by Xu *et al.* for alcohol oxidation in alkaline media [63]. The addition of oxides like CeO_2, NiO, Co_3O_4 and Mn_3O_4 significantly promoted the activity and stability of Pd/C catalysts. Pd-Co_3O_4 showed the highest activity for methanol, EG and glycerol oxidation; Pd-NiO was the most active for ethanol oxidation, and Pd-Mn_3O_4/C improved stability of catalysts.

Another important precious metal for alcohol oxidation in alkaline media is Au. It has been studied for methanol oxidation [64,65]. The mechanism and kinetic studies of ethanol oxidation on gold in alkaline media have been carried out by different groups [30,31]. Au was also used in methanol, ethanol and EG oxidation. Au:Ru (1:1) exhibited higher activity than Au [18].

3.1.2. Non-Precious Metal Catalysts

One of the most attractive advantages of alkaline fuel cells is the possibility of using non-precious metal catalysts. Nickel has been used as an electro-catalyst for both anodic and cathodic reactions in organic synthesis and water electrolysis. It has been studied for the electro-oxidation of alcohols for decades [66]. Van Effen and Evans [67] studied the oxidation of ethanol in KOH solution on nickel. They discovered that the reaction involved the formation of a higher valence nickel oxide, which acted as a chemical oxidizing agent. This fact was confirmed [68] by cyclic voltammetry, which proved the presence of a mediation process involving the higher oxides and the organic molecules, and by alternating current impedance measurements.

Taraszewska and Roslonek [19] found that a glassy carbon/Ni(OH)$_2$ modified electrode was an effective catalyst for the oxidation of methanol. The use of Ni as a catalyst for the electro-oxidation of methanol in alkaline medium was studied using cyclic voltammetry by Abdel Rahim *et al.* [69]. Ni dispersed on graphite showed catalytic activity towards methanol oxidation but massive Ni did not. Ni was dispersed on graphite by the electro-deposition from acidic Ni$_2$SO$_4$ solution. The catalytic activity of the C/Ni electrodes towards methanol oxidation was found to vary with the amount of electro-deposited Ni. Methanol oxidation starts as Ni-oxide is formed on the electrode surface and indicates that the electro-oxidation of methanol is activation controlled, proceeding by direct chemical reaction with NiO(OH) for thin nickel oxides and by charge transfer with the electrode for thick oxides. The accumulation of NiO(OH) had an inhibiting effect on activity which can be counteracted by a period of re-activation in the hydrogen evolution potential region.

A Ni zeolite has been reported with a superior methanol oxidation activity to Ni and Pt supported on graphite [70]. This performance was assigned to a lower blocking of active sites than Pt due to repeated utilization.

Synthesis and characterisation of electrodeposited Ni–Pd alloy electrodes for methanol oxidation in alkaline electrolyte was studied by Kumar *et al.* [71]. Structural characterisation of the electrocatalysts showed that the Ni–Pd catalysts formed a complete solid solution in the alloy. The percentage shift in the d-spacing, calculated from X-ray diffraction, was in good agreement with the palladium percentages in the alloy. The catalysts were active for methanol oxidation in alkaline medium.

A Co-W alloy prepared by electroplating was evaluated by Shobba *et al.* for methanol oxidation in alkaline media [72]. Heat treatment was shown to improve oxidation performance with open circuit potentials of 0.918 V obtained.

P-M-C complex materials were prepared by polymer template coordination with metal-ions loaded with a carbon-reduction method. P stands for polymer; M = Fe, Co and Ni; C is carbon. The catalyst showed very high electrocatalytic activity and stability for ethanol oxidation in alkaline media [73].

Lanthanum, strontium oxides have been studied by several research groups: Raghuveer and Vishwanathan [74] investigated the electro-oxidation of methanol on bulk and nano crystalline La$_{1.8}$Sr$_{0.2}$CuO$_4$ in 1 M KOH. Raghuveer *et al.* [75] investigated methanol oxidation on La$_{1.8}$Sr$_{0.2}$CuO$_4$, La$_{1.6}$Sr$_{0.4}$CuO$_4$ and La$_{1.9}$Sr$_{0.1}$Cu$_{0.9}$Sb$_{0.1}$O$_4$ in 3.0 M KOH. Yu *et al.* [76] studied La$_{0.75}$Sr$_{0.25}$CuO$_3^{-\delta}$ and La$_{0.75}$Sr$_{0.25}$CoO$_3^{-\delta}$ in 1 M NaOH and 1 M CH$_3$OH. All oxides gave reasonable oxidation currents in potential ranges appropriate to fuel cell operation.

Perovskite-type oxides have been investigated for methanol and EG alkaline fuel cells. Perovskite-type ternary oxides with molecular formulae of $La_{2-x}Sr_xNiO_4$ ($0 \leq x \leq 1$) were prepared by a modified citric acid sol-gel route for a direct methanol alkaline fuel cell (DMAFC). There was no poisoning of the catalyst detected by the methanol oxidation [77].

Platinum free nanosize RuM (M = Ni, Co and Fe) catalysts for glycerol oxidation in alkaline media were prepared on Vulcan XC72 from $Ru(OH)_3Cl_3$ and metal sulfates in a hydrogen atmosphere at 400 °C. Glycerol oxidation was tested in 8M KOH and 4M glycerol at 60 °C. With a catalyst loading of 30–40 mg cm^{-2}, good activity for glycerol oxidation was observed [78].

3.2. Catalysts for Oxygen Reduction

For fuel cell performance, oxygen reduction is a kinetically limiting factor, particularly with hydrogen fuel cells. In direct alcohol fuel cells, fuel crossover to the cathode causes a mixed potential on the cathode and further decreases the oxygen reduction performance.

3.2.1. Precious Metal ORR Catalysts

Platinum, silver and palladium compounds have been used as ORR catalysts in DAAFCs. Platinum and Pt/Ru catalysts were used as the cathode catalysts for direct methanol fuel cells by Yu and Scott [79]. It was found that ORR activity was lower on Pt/Ru than on Pt due to the low activity of Ru in alkaline solution. The methanol tolerance of the Pt/C electrode with a Pt loading of 1.2 mg cm^{-2} was 0.2 M methanol in 1 M NaOH suggesting crossover may have less significant effect in alkaline.

A Ag/C catalyst was prepared by simple thermal decomposition of $AgNO_3$ in argon at 700 °C by Gamburzev *et al.* [80] to use in AFCs. Kostowskyj *et al.* [81] produced Ag nanowires by coating Ag on carbon nanotubes. The electrochemical test results showed that the electrode activity increased with increasing Ag concentration when mixed with CNTs.

Highly selective Ag-W_2C/C and W_2C/C electrocatalysts for oxygen reduction were developed for potential application in mixed-reactant alcohol fuel cells by Meng *et al.* [82]. The catalysts were prepared by an intermittent microwave heating (IMH) method. Both the W_2C/C and Ag-W_2C/C showed activity for ORR in alkaline media. The introduction of W_2C into the Ag/C enhanced its activity. The Ag-W_2C/C catalyst was highly selective for oxygen reduction in the presence of alcohol.

Pd was also studied as cathode catalyst for DAAFC [57,83]. Although the activity of Pd is lower than Pt, the Pd/C catalyst is less sensitive to alcohol contamination as compared to Pt/C, indicating better alcohol tolerance. Kim *et al.* [84] used Pd-Sn/C as a cathode catalyst on DMAFC; this cathode exhibited higher performance than commercial Pt/C catalyst in high methanol concentration. It suggested good methanol tolerance with Pd-Sn/C catalyst indicating promising application on DAAFCs.

3.2.2. Non-Precious ORR Catalysts

One of the major advantages of using alkaline media for fuel cells is the potential of applying low cost non noble metals as the catalysts. A wide range of non-noble metal catalysts have been employed in DAAFCs.

Manganese oxides have attracted increasing interest as oxygen reduction catalysts in alkaline media in recent years. The activity of MnOx depends upon the type of oxide and the carbon support. The most active were the MnO_2, Mn_2O_3 and MnOOH (manganese oxy-hydroxy) oxides [85–87]. The ORR mechanism on these catalysts involves the formation of the HO_2^- intermediate via the transfer of two electrons followed by a dismutation reaction of this species into OH^- and O_2.

Metal macrocyles have been used as oxygen reduction catalysts since the 1960's. They have shown high activity towards the ORR in alkaline media. Cobalt and iron phthalocyanine and porphyrins are of the most interest. Co phthalocyanine has exhibited similar kinetics on ORR as Pt [88]. Electrodes made of Cobalt/iron tetraphenylporphyrin (CoTPP, FeTPP) demonstrated good performance, even better than Ag catalyst. Heat treatment of carbon supports can result in structural changes and increase the surface area, resulting in enhanced catalytic activity [89,90]. However, the stability of the catalyst was poor due to loss of Co [91]. It has been reported that iron phthalocyanine (FePc) has the ability to promote the direct $4e^-$ oxygen reduction to water, while CoPc promotes O_2 reduction to H_2O_2 by a $2e^-$ pathway [92–95]. This $4e^-$ pathway is more desirable as it avoids the production of hydrogen peroxide which can damage the electrode structure. One important advantage from MnOx and metal macrocycles to Pt is their insensitivity to fuel and tolerance to alcohol crossover.

Carbon supported $La_{1-x}Sr_xMnO_3$ (LSM/C) was prepared for oxygen reduction with the presence of EG [20]. LSM/C exhibited high activity for O_2 reduction regardless of EG. This indicates LSM is a good cathode catalyst in DAAFC with no crossover problem. A Fe-Co nanoparticle based ORR catalyst, Hypermec ^{TM} K14 developed by Acta S.P.A, Cascina (Pisa), Italy, was reportedly applied by few groups as the cathode for their alkaline alcohol fuel cells [59,96–98]. Power densities ranging from 55–170 mW cm^{-2} with different fuel cell configurations and fuels were achieved indicating a very promising catalyst for DAAFCs.

4. Electrolyte and Membrane Electrolyte for DAAFC
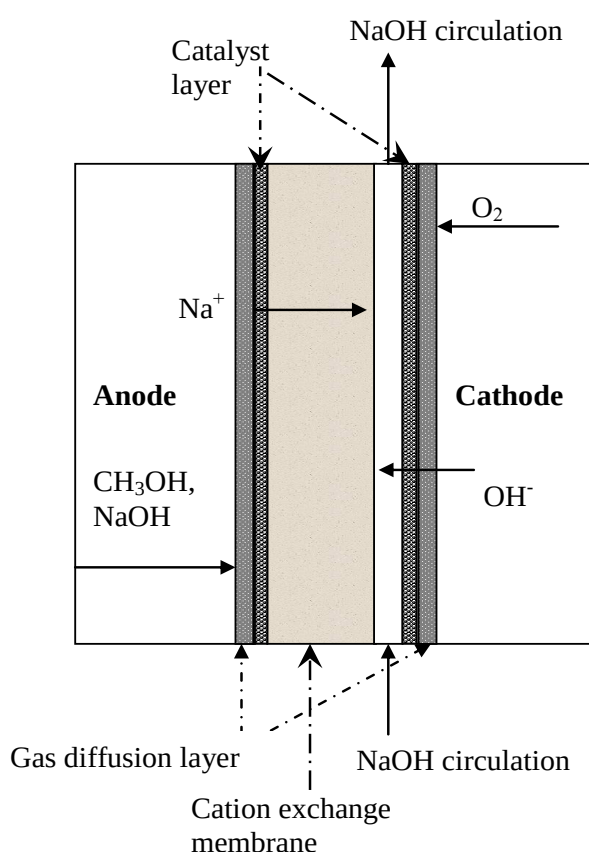
Most studies of direct alcohol fuel cells have used aqueous alkaline electrolyte or added alkaline in the fuel solutions, as an anolyte [21,49,99,100]. To date the performance of these fuel cells has not matched that achieved with the fuel cells using proton exchange membranes (PEMs) in acidic environment.

4.1. Cation Exchange Membranes

Polymer electrolyte materials such as Nafion® are used commercially both for proton transfer and for sodium ion transfer. An example is the electrolysis of sodium chloride to produce chlorine and sodium hydroxide. The conduction process in this system is realised by the transport of Na^+ ions from anode to cathode. A practical consequence of DMAFCs operating in such a manner is that hydroxide ions produced by oxygen reduction react rapidly with Na^+ ions leading to the formation of sodium hydroxide in the cathode side of the cell. In addition, water is transported across the cell to the cathode. This being the case, it is necessary to recycle this component to the anode to maintain an overall sodium ion balance in the system. A schematic diagram of the electrochemical reactions and transport processes in such a system is shown in Figure 3. The performance of a Na^+ conducting Nafion based DMFC has been studied [101]. Although the open circuit voltage obtained was favourable (*ca.* 0.8 V), in comparison to DMFCs operating in acidic media, the polarisation of the DMAFC was greater [102].

An attraction of these solid polymer electrolytes (SPEs) is that the Na^+ ion form of Nafion offers much greater stability than currently available OH^- ion (anion) conducting membranes. However, the disadvantage of the Na^+ ion form of Nafion is that the ionic conductivity is much lower than that of the H^+ ion form of Nafion, and anion conducting membranes for OH^-. This is determined by mobility of ions. The mobility of Na^+ in water solution is seven times lower than that of H^+ and four times lower than that of OH^-. The internal resistance of the cell as measured by high frequency AC impedance was 0.47 Ω [101]. This value is much higher than that with H^+ form Nafion, whose value is around or lower than 0.05 Ω [100]. Thus there will be a compromise between ionic conductivity and electrocatalyst activity at both anode and cathode. These factors affect the membrane, membrane-catalyst layer interface and the bounded electrocatalyst layers.

Figure 3. Schematic diagram of DMAFC with cation exchange membrane and incorporating an electrolyte circulating layer in the cathode compartment [101].

4.2. Anion Exchange Membranes (AEM)

Use of OH^- conducting membranes or anion exchange membranes (AEM) can improve ionic conductivity and the fuel cell performance compared to use of CEMs. AEMs are solid polymer electrolyte membranes that contain positive ionic groups (e.g., quaternary ammonium (QA) functional groups such as poly—N^+Me_3) and mobile negatively charged anions (e.g., usually OH^-).

Some commercially available AEMs have been used for DAAFC applications. MORGANE®-ADP membranes from Solvay, S.A. were used as the solid polymer electrolyte for DMAFCs in several studies, which were normally used for salt electrodialysis [21,99,100,103]. Encouraging fuel cell

performances were obtained, with the highest power density of 20 mW cm^{-2}. The basic properties of the MORGANE$^{®}$-ADP membrane at 25 ℃ are shown in Table 3 [99]. Methanol diffusion coefficients were measured by monitoring the transfer of methanol from pure methanol solution across the membrane into a NaOH solution. The methanol diffusion coefficient for Nafion is about 2.8 times higher than that for the ADP membrane. This indicates that the methanol crossover rate for ADP membrane will be potentially lower than Nafion, which may improve fuel cell performance. However, the ADP membrane is not stable in strong alkaline media. The suggested working pH is up to a value of pH 11. In fact, discolouring of the ADP membrane in 1 M NaOH was observed. This could affect the stability and the lifetime of a fuel cell with an ADP membrane.

Table 3. Basic properties of the MORGANE$^{®}$-ADP membrane [21].

Membrane	MORGANE$^{®}$-ADP
Material	Cross-linked fluorinated polymer
Exchange group	Quaternary ammonium
Thickness/μm fully humidified	150–160
Resistance (in 0.6 M NaCl)/$\Omega.cm^2$	1.5–4.5
Resistance (in 1 M NaOH)/Ω	0.5
Maximum operational temperature/ ℃	55
Working pH	0-10

Researches on using few ammonium-type AEM membranes from Tokuyama Co. Japan have been reported. A201 (developing code A-006) and A901 were used for alkaline fuel cells with ethanol [34,96,104] and AHA were used for DAAFC using other alcohols [13]. Basic properties of these membranes are given in Table 4. With A201 at 80 ℃, the power density of 55 mW cm^{-2} supplied by a passive system and 170 mW cm^{-2} obtained from an active system were reported [96]. The maximum power density of 9 mW cm^{-2} was obtained from fuel cells using 1 M EG in 1M KOH at 25 ℃ and AHA [13]. Fumatech has also developed AEMs, but studies on applying these membranes are still undergoing and no report on these studies has been published.

Research on developing anion exchange membranes with high ionic conductivity and good chemical stability in alkaline media as well as low alcohol permeability have been carried out by several groups. Polyvinylidene fluoride (PVDF, $-[CH_2CF_2]_n-$) and polytetrafluoroetheneco-hexafluoropropylene (FEP, $-[CF_2CF_2]_n[CF(CF_3)CF_2]_m-$) films grafted with vinylbenzyl chloride using radiation-grafting are compared [105,106]. The FEP membrane showed good properties suitable for the fuel cell application, and it is possible to use these new materials in DAAFC development. However, the cost of FEP is relatively high.

A number of other membrane materials have been reported for application in DMAFCs, such as polysiloxane containing quaternary ammonium groups [107], aminated poly(oxyethylene) methacrylates [108], quaternised polyethersulfone Cardo [109], and quaternised poly(phthalazinon ether sulfone ketone) [110]. The poor stability of these materials in hydroxide electrolytes limited their further application in DMAFC.

Table 4. Basic properties of Tokuyama membranes [13,34,97,98].

Membrane	AHA	A201	A901
Type	Strong basic anion permeable		
Electric Resistance (0.5 N NaCl)/Ω.cm^2	4.1	0.30	
Burst strength/MPa	$\geq$0.90	0.4	0.2
Exchange group	Tetraalkyl ammonium groups with polyolefin backbone chain	Quaternary ammonium	Quaternary ammonium
Thickness/ μm	240	28	10
Ion exchange capacity/mmol g^{-1}	1.15–1.25	1.7	1.7
OH- conductivity/mS cm^{-2}		29	11.4

Poly(2,6-dimethyl-1,4-phenylene oxide) (PPO) is a unique material with strong hydrophobicity, a high glass transition temperature (T_g = 212 ℃) and hydrolytic stability [111]. PPO based membranes were studied for DMAFC applications. Chloroacetylated poly(2,6-dimethyl-1,4-phenylene oxide) (CPPO) with bromomethylated poly(2,6-dimethyl-1,4-phenylene oxide) (BPPO) blend membranes were characterised [112]. Substituted materials have good miscibility since they all have PPO backbones. A blend membrane with 30–40 wt% CPPO was recommended. The membranes exhibited a high hydroxyl conductivity (up to 0.032 S/cm at 25 ℃) and extremely low methanol permeability ($1.26–1.04 \times 10^{-7}$ cm^{2}s^{-1}), which is suitable for application in low temperature DMAFCs [113].

Quaternized polyethersulfone Cardo anion exchange membranes have been prepared [114]. Polyethersulfone Cardo was chloromethylated with the complex solution of chloromethylether and zinc chloride. Subsequent reaction with trimethylamine and ion exchange with sodium hydroxide yielded the alkaline anion exchange membrane. Ionic conductivities of QPES-C membrane in 1 M NaOH solution were 4.1×10^{-2} S cm^{-1} to 9.2×10^{-2} S cm^{-1} and methanol permeability was from 5.72×10^{-8} to 1.23×10^{-7} cm^2 s^{-1} over the temperature range 25–70 ℃ indicating potential applications in DMAFC.

An alternative approach to the production of AEMs is the use of suitable doping/reaction of polymer films with KOH. Polybenzimidazole (PBI) membranes have attracted interests in recent years for high temperature PEMFC applications. An alternative approach to the production of AEMs is the use of suitable doping/reaction of polymer films with KOH. An alkali-doped PBI membrane showed higher conductivity than H$_2$SO$_4$-doped PBI and H$_3$PO$_4$-doped PBI at 25 degrees C [115].

Hou *et al.* used KOH-doped PBI as membrane for DAAFCs to be able to work at higher temperatures, *i.e.* at improved reaction kinetics. The PBI-based MEA yielded power densities of *ca.* 30 mW cm^{-2} for methanol [116] and 60 mW cm^{-2} for ethanol [117]. They also reported that methanol and ethanol diffusivity through the PBI membrane was significantly below that of Nafion. Modestov *et al.* reported a direct ethanol fuel cell using alkali doped PBI-membrane with Pt-free catalysts, namely 5,10,15,20-tetrakis(4-methoxyphenyl)-21H,23H-porphine cobalt(II) supported on Vulcan XC72 carbon for the cathode and RuV alloy supported on Vulcan XC72 for the anode. They achieved a maximum power density of 125 mW cm^{-2} [118]. These reports suggest a possibility to develop high temperature DAAFC which could significantly improve the reaction activity on alcohol oxidation.

Non perfluorinated membranes have attracted interests because of their low cost. Yang *et al*. studied polyvinyl alcohol (PVA) based membranes for use in alkaline alcohol fuel cells. PVA crosslinked with sulfosuccinic acid (SSA) [119], PVA/hydroxyapatite (HAP) composite membrane [120] and PVA/TiO

composite membrane [121] were used in methanol, ethanol, isopropanol and borohydride fuel cells with the presence of alkaline (from 2 M KOH up to 8 M KOH) in fuel solutions. The membranes showed good electrochemical performance. A quaternised poly(vinyl alcohol)/alumina (QPVA/Al$_2$O$_3$) nanocomposite polymer membrane was prepared by a solution casting method by Yang *et al.* [122]. In an alkaline DMFC with the PVA/Al$_2$O$_3$ composite membrane, a peak power density of 36.2 mW cm^{-2} was achieved at room temperature with ambient air.

5. Performance of DAAFC
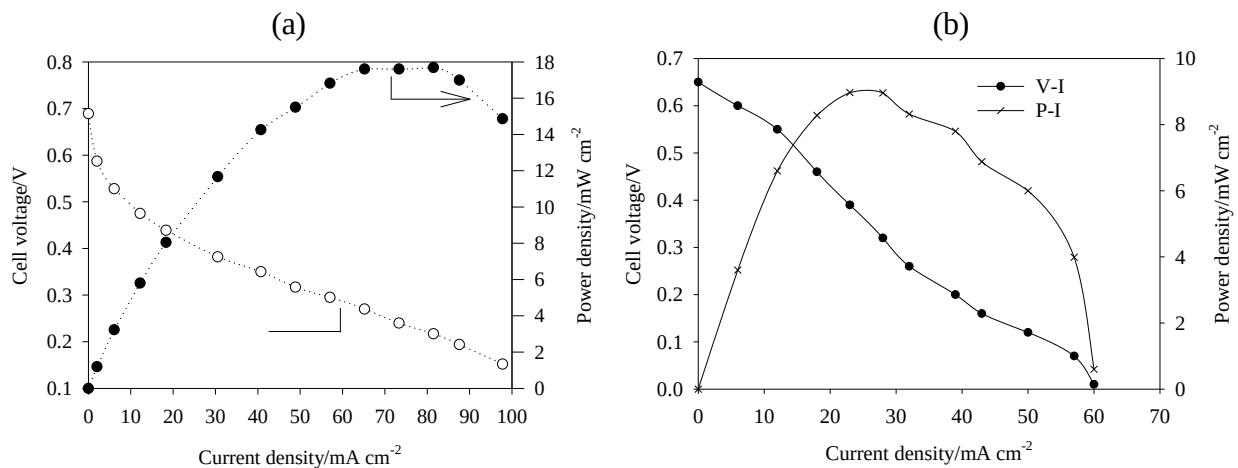
The performance of one of the first alkaline alcohol fuel cells was reported by Cairns and Bartosik in 1964 [123]. They operated the cell with vapourised methanol with an invariant alkaline electrolyte operated at 115–130 °C. The conversion of the fuel to electricity in one pass through the cell was 75 to 85%. Power densities of 40–45 mW cm^{-2} were achieved. However, there was a gap on further research on alkaline alcohol fuel cells until this decade.

Most DAAFC performances reported earlier were lower than those of the corresponding the PEM counterpart. The power density of current DMAFCs is typically less than 20% of that obtained from PEM DMFC. The DAAFC studies focused on PtRu and Pt as catalysts; the highest performance reported with such materials was 58 mW cm^{-2} [34]. This has been changed with new advances in AEM and catalyst development in the past few years. Power density of 160 mW cm^{-2} was achieved at 80 °C by Bianchini *et al.* [96] from an alkaline fuel cell using ethanol. This is comparable to what is achieved from PEM DMFCs. Even with a passive cathode, power density of 55 mW cm^{-2} was obtained using ethanol. Bianchini and coworkers also tested the system with various fuels (methanol, ethanol, glycerol). The wide range of materials used in DAAFC suggest the potential of using low cost materials in DAAFCs. Alkaline alcohol fuel cell performances reported for different alcohol, catalysts, AEMs and operating parameters are summarized in Table 5.

In most studies, alkaline liquid electrolyte was still added to the fuel despite use of AEMs. Only very few studies used liquid fuel without adding alkaline electrolyte. Varcoe and Slade [124] developed a novel quaternary-ammonium-functionalised radiation-grafted ETFE alkaline anion-exchange membrane (AAEM) and applied M$^+$OH$^-$ free methanol in a methanol/O$_2$ fuel cell. A maximum power density of 8.5 mW cm^{-2} was obtained at 80 °C. Coutanceau *et al.* also investigated AFCs using Ag/C catalyst for ORR and Pt-Pd anode catalyst with methanol and EG [125]. It was clear that fuel cell performance improved significantly with the addition of NaOH in EG.

Figure 4 compares the DMAFC performance with and without additional alkali in the fuel. With similar catalyst loading and the same type of membrane (ADP), the cell with 1.0 M NaOH in the fuel gave higher current and power density [21,23,96,103]. Without 1 M NaOH, the maximum current density was only around 60 mA cm^{-2}, while with alkali, the maximum current density increased to 100 mA cm^{-2}; the peak power density also improved from 9 mW cm^{-2} to 18 mW cm^{-2}. The OCV without NaOH was about 50 mV (0.65 V) lower than with NaOH in the fuel (0.70 V).
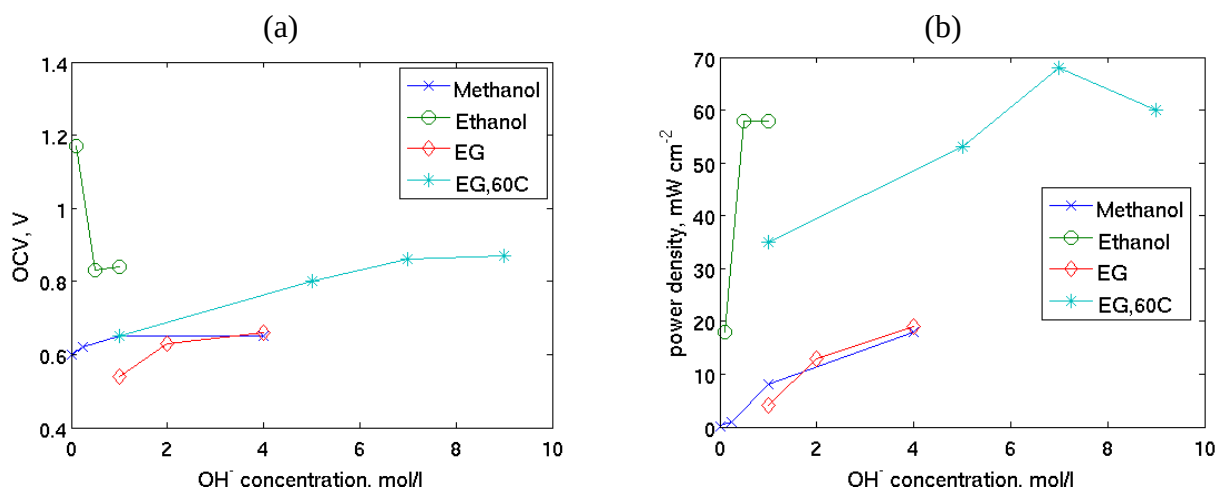
Figure 4. Fuel cell polarisation curves and power density curves for the DMAFC using air at 60 ℃, air pressure 1 bar: (a) 1 M methanol with 1 M NaOH [21]; (b) 1 M methanol [103].


Although additional liquid electrolyte increases the power density of DAAFCs, the use of alkaline electrolyte in the fuel solution is not favoured from the fuel cell system point of view. The presence of free cations such as K^+ and Na^+ allows for the unwanted precipitation of salts such as carbonates. This could limit the life time of an alkaline fuel cell. It should be also mentioned that the removal of non-gaseous products such as salts and oxygenates is not trivial in fuel cell systems.

Figure 5 depicts the relationships between reported OCVs and maximum power densities of DAAFCs to alkaline concentration. It can be observed that OCV and power density both increased with alkaline concentration until maximum values were reached. OCV and power density were not affected by further increase in alkaline concentration beyond that indicating a limited effect of high alkaline concentration on fuel cell performance.

Figure 5. (a) OCV and (b) maximum power density of DAAFCs as a function of alkaline concentration for various fuels. Methanol [126], ethanol [34], EG [51] at room temperature, and EG at 60 ℃ [59].

DAAFCs with a self-breathing or passive cathode have been investigated by several groups because of its practicality and convenience [96,126,127]. For ethanol, a power density of 55 mW cm^{-2} was reported [96]; for methanol, a maximum power density of 12.8 mW cm^{-2} was obtained with 7 M methanol at 25 °C with KOH in the fuel [126].

Other fuel cell configurations, such as laminar flow fuel cells [128] and mixed reactant fuel cells [129,130] have also been applied to DAAFCs. Choban *et al.* developed a laminar flow-based single microfluidic channel fuel cell, where an acidic anolyte containing methanol and an alkaline catholyte containing dissolved oxygen were merged in a microfluidic channel which contained electrodes at it's walls. The streams were fed in such a way that the anolyte was in contact only with the anode and catholyte with the cathode [105]. Both streams mixed only slowly due to operation in the laminar regime and at high Peclet numbers. A novel micro fabrication method, multistream laminar flow, was used. The maximum power density of 12 mW cm^{-2} was achieved with a mixed media: 1N KOH in anode and 1N H$_2$SO$_4$ in cathode. Sung *et al.* [107] developed a micro fuel cell using non-noble metal catalysts in alkaline media. The fuel cell was designed with both electrodes not facing each other, but being in-plane. Nickel hydroxide and silver oxide was the catalyst for anode and cathode respectively. The fuel (methanol) and the oxidant (H$_2$O$_2$) were both mixed into the same electrolyte, 1M KOH. Although the maximum power density obtained was only 28 μWcm^{-2}, this new technology enables high design flexibility and easy integration of the microscale fuel cell into microfluidic systems and portable devices. A more conventional approach for mixed reactant DAAFC resembling that of early studies [129] was evaluated by Zeng *et al.* [131]: a porous separator for NiMH cells was assembled with a Pt and a Pt/Ru gas diffusion electrode, and a mixed flow of ethanol, air and KOH were supplied to the fuel cell. The maximum power density was 35 mW cm^{-2} and the selectivity of the electrodes was tuned by adjusting hydrophobicity of the catalyst layers.

Table 5. Summary of DAAFC performance.

Fuel/oxidant	Catalysts		Electrolyte/ membrane	T/ °C	OCV/V	I$_{max}$/ mA cm^{-2}	P$_{max}$/ mW cm^{-2}	Ref.
	Anode	Cathode						
DMAFC w/o alkaline								
2 M methanol/O$_2$	Pt	Pt	Quaternised					
no backpressure	4 mg cm^{-2}	4 mg cm^{-2}	radiation-grafted	50	0.46	22	1.5	[123]
no backpressure			ETFE AAEM	60	0.52	34	2.4	
2.5 bar back pressure				60	0.58	34	4.2	
2.5 bar back pressure				80	0.63	68	8.5	
1 M methanol/O$_2$	Pt/Ru	Pt/C	Tokuyama	80	0.57	34	2.6	[57]
	1 mg cm^{-2}	Pd/C	A201		0.64	34	2.6	
		.						
		0.5 mg cm^{-2}						
2 M methanol/air	Pt/Ru	Pt	ADP	30	0.6	32	5.9	[102]
	1 mg cm^{-2}	1 mg cm^{-2}		40	0.62	43	6.9	
				50	0.65	57	7.6	
				60	0.65	60	9.0	
16% methanol in N$_2$/air	PtRu	Pt	PVA+10M	40	0.9	80	22	[135]
			KOH					
			PVA+10M			100	35	
			KOH/Ni-LDH					

Table 5. *Cont.*

Fuel/oxidant	Catalysts		Electrolyte/ membrane	T/°C	OCV/V	I_{max}/ mA cm^{-2}	P_{max}/ mW cm^{-2}	Ref.
DMAFC w/alkaline								
1 M methanol/O$_2$	Pt/C	Pt/C	ADP	Room T				[125]
no NaOH	2 mg cm^{-2}	2 mg cm^{-2}			0.48	3	0.2	
0.25 M NaOH					0.52	10	1	
1 M NaOH					0.6	52	8	
4 M NaOH (2 M methanol)					0.6	110	18	
2 M methanol, 1 M NaOH/air	Pt/C 2 mg cm^{-2}	Pt/C 2 mg cm^{-2}	ADP	60	0.7	100	18	[21]
2 M methanol, 1 M NaOH/ air	Pt/C 2 mg cm^{-2}	Pt/C 2 mg cm^{-2}	Nafion	60	0.80	23	4.5	[101]
7 M methanol, 1 M KOH/ air (passive)	PtRu 4 mg cm^{-2}	Pt/C 1 mg cm^{-2}	Tokuyama	Room T	0.71	58	12.8	[126]
2 M methanol, 2 M KOH/ O$_2$	PtRu/C 2 mg cm^{-2}	Pt/C 1 mg cm^{-2}	PBI/KOH	90	1.0	105	30	[116]
2 M methanol, 2 M KOH/ O$_2$	PtRu/C 2 mg cm^{-2}	Pt/C 1 mg cm^{-2}	PBI/KOH	75 90	0.92 0.98	150 190	49 61	[117]
1 M methanol, 1 M KOH/saturated O$_2$ in 1 N H$_2$SO$_4$	PtRu 2 mg cm^{-2}	Pt 2 mg cm^{-2}	laminar flow-based micro fuel cells	Room T	1.4	50	12	[125]
4 M methanol, 4 M KOH/ air	Pt/Ru 4 mg cm^{-2}	MnO$_2$/C 4 mg cm^{-2}	QPVA/Al$_2$O$_3$	Room T	0.88	153	36	[122]
DAAFC w/ alkaline								
1 M KOH /humidified O$_2$	Pt/C 1 mg cm^{-2}	Ag/C 1 mg cm^{-2} or PtRu/C 4 mg cm^{-2}	AHA	50	0.80			[13]
methanol						46	6.0	
ethylene glycol						65	9.0	
glycerol						55	6.8	
erythritol						42	5.5	
xylitol						29	4.0	
1 M ethanol, KOH/ humidified O$_2$	PtRu 3 mg cm^{-2}	Pt 3 mg cm^{-2}	AHA	Room T				[34]
0.1 M KOH					1.17	100	18	
0.5 M KOH					0.83	350	58	
1.0 M KOH					0.84	400	58	
4 M KOH/air	Pt/Ru 3.6 mg cm^{-2}	MnO$_2$/C	PVA/TiO$_2$ composite membrane	Room T	0.80			[121]
2 M methanol						33.6	9.3	
2 M ethanol						35.7	8.0	
2 M isopropanol						21.5	5.5	
2 M glycerol, 4 M NaOH/ O$_2$	Pt/C Pd/C Au/C AuPd/C	Pt/C 2 mg cm^{-2}	ADP	Room T	0.68 0.59 0.60 0.49	20 16 7.5 3.2	4.2 2.4 1.0 0.3	[58]
2 M EG, 4 M NaOH/ O$_2$	Pt PtBi PtPdBi 2 mg cm^{-2}	Pt 2 mg cm^{-2}	ADP	20	0.66 0.83 0.81	132 132 120	19 22 28	[51]
2 M EG, NaOH/O$_2$	Pt 2 mg cm^{-2}	Pt 2 mg cm^{-2}	ADP	20				[51]
1 M NaOH					0.54	42	4	
2 M NaOH					0.63	102	13	
4 M NaOH					0.66	132	19	

Table 5. *Cont.*

Fuel/oxidant	Catalysts		Electrolyte/ membrane	T/ °C	OCV/V	$I_{max}/$ mA cm^{-2}	$P_{max}/$ mW cm^{-2}	Ref.
2 M EG, 4 M NaOH /O$_2$	Pt/C 2 mg cm^{-2}	Pt/C 2 mg cm^{-2}	ADP	Room T	0.65	130	18	[125]
0.5 M ethanol, air, 2 M KOH	PtRu/C 1.8 mg cm^{-2}	Pt/C 2 mg cm^{-2}	Porous separator	Room T	1.0	110	30	[128]
DAAFC with non Pt catalyst, with alkaline								
2 M KOH/ O$_2$ 10 wt% methanol 10 wt% ethanol 5 wt% glycerol	Pd/MWCNT 1 mg cm^{-2}	Fe-Co Hypermec^{TM} K-14	Tokuyama A-210	80	0.89 0.87 0.87	530 350 550	95 74 79	[61]
2 M KOH/O$_2$ 10 wt% methanol 10 wt% ethanol 5 wt% glycerol	PdNiZn/C 1 mg cm^{-2}	Fe-Co Hypermec^{TM} K-14	Tokuyama A-210	80	0.76 0.88 0.81	610 800 540	120 165 119	[61]
2 M methanol, 0.05 M H$_2$O$_2$, 0.2M KOH	Ni(OH)$_2$	Ag$_2$O	-	Room T	0.11	1	0.03	[127]
10 wt% ethanol, 2 M KOH / O$_2$	PdNiZn/C 1 mg cm^{-2}	Fe-Co Hypermec^{TM} K-14	Tokuyama A-210	25 40 60 80	0.65 0.68 0.74 0.82	400 440 550 590	65 80 120 160	[61]
1 M ethanol, 1 M KOH/O$_2$	Hypermec^{TM}2 mg cm^{-2}	Hypermec^{TM} 1 mg cm^{-2}	Tokuyama	30 40 50 60	0.66 0.72 0.76 0.91	170 200 230 270	12 17 22 30	[98]
2 M ethanol, 3 M KOH/air	RuV/C 4.5 mg cm^{-2}	TMPhP/C 9mg cm^{-2}	PBI/KOH	80	0.93	278	125	[118]
1 M EG, KOH /O$_2$ 1 M KOH 5 M KOH 7 M KOH 9 M KOH	PdNi 2 mg cm^{-2}	Hypermec^{TM} 1 mg cm^{-2}	Tokuyama	60	0.65 0.8 0.86 0.87	320 350 390 370	35 53 67 60	[59]

6. Summary and Outlook

Liquid alcohols have significantly higher energy densities than hydrogen, and they are easier to handle. These features make direct alcohol fuel cells a promising alternative low-cost power supply for portable electronics. Direct alkaline alcohol fuel cells can benefit from the more active reaction in alkaline media. Unlike conventional proton exchange membrane fuel cells, anion exchange membranes are used in present DAAFCs to transfer OH$^-$ within the membrane electrolyte. This will also reduce the carbonation process which shortens the fuel cell life time due to the reaction between CO$_2$ and alkaline electrolyte, particularly with liquid electrolyte.

Although the power output of DAAFCs is still lower than that of direct methanol fuel cells using proton exchange membranes, the performance of DAAFCs has improved significantly in the past decade. The developments on catalysts and anion exchange membranes provide a solid base for the further development of DAAFCs.

Various alcohol fuels have been investigated for DAAFC applications. Alkaline media has particular advantages for poly carbon alcohols over acidic media because of higher reaction activity in

alkali. Apart from methanol, ethanol, isopropanol, ethylene glycol and glycerol have also shown encouraging fuel cell performances. These alcohols have higher energy density than methanol, and are not toxic, which make them potential candidates as power sources for portable electronic devices. However, due to the higher energy to break C-C bonds during the oxidation, no complete oxidation to CO_2 from polycarbon alcohols was achieved with current catalysts. Research on developing more active catalysts is a significant challenge. Besides most used precious metal Pt and Pt alloys, other lower cost metal catalysts, such as Pd and Ni and metal alloys have exhibited potential to be used as alternatives for Pt catalysts. Lanthanum, strontium oxides and perovskite-type oxides have also been investigated for alcohol oxidation.

Fuel crossover from the anode to cathode is a factor that limits fuel cell performance because of the mixed potential caused by fuel oxidation on the cathode. This effect causes a significant loss in fuel cell performance. However fuel crossover is significantly less in DAAFCs due to the direction of electric osmotic drag from cathode to anode. At present, Pt is still the most popular cathode catalyst for a direct alcohol fuel cell although Pt is highly sensitive to alcohols. Several catalysts have been developed and exhibited less sensitivity on alcohol oxidation. Examples are Pd- or Ag-based catalysts, as well as non-precious metal catalysts based on Mn-oxides.

Rather than electrolytes such as KOH and NaOH, solid electrolyte membranes have been used more and more in DAAFCs. Various types of anion exchange membranes, e.g. polytetrafluoroetheneco-hexafluoropropylene or poly(2,6-dimethyl-1,4-phenylene oxide), have been developed and investigated in alkaline fuel cells.

Direct alcohol anion exchange membrane fuel cells are still at early stages of development. In order to improve the power output from DAAFCs, and produce viable alkaline fuel cell systems as portable power sources, further research and development efforts need to be focused on novel catalysts and anion exchange membrane development:

(1) Metal oxides as the promoter for catalysts.

Some metal oxides, in particular CeO_2, Mn_3O_4 and SnO_2, have multiple oxidation states and can store and release oxygen [132]. These metal oxides can be used as promoters to improve catalyst activity and fuel cell performance.

(2) Transition metal macrocycle based oxygen reduction catalysts with improved activity and selectivity.

These catalysts have shown highly selective catalytic activity for oxygen reduction in the presence of methanol and CO in direct methanol fuel cells (DMFC) and hydrogen fuel cells [133,134]. Metal macrocyclic catalysts are stable in neutral and alkaline media. This suggests their application will be more feasible for DAAFCs.

(3) Novel anion exchange membranes with improved stability and ionic conductivity.

One of the key issues in the development of DAAFCs is the membrane electrolyte. There is still no AEM equivalent to Nafion for solid polymer electrolyte alkaline fuel cells, even though significant progress has been made in the last decade. Further investigation on poly(2,6-dimethyl-1,4-phenylene oxide) (PPO) based membranes, alkaline doped AEMs and composite AEMs might be possible to produce a novel AEM with improved properties suitable for DAAFC applications.

Direct alkaline alcohol fuel cell technology is a promising technology as a clean energy sources for portable electronic devices. New material developments on catalysts and membranes will further improve the power output and make DAAFCs viable power sources in the near future.

Acknowledgement

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