

## Direct oxidation alkaline fuel cells: from materials to systems

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Received 2nd September 2011, Accepted 29th November 2011

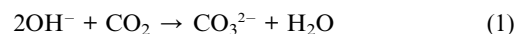
DOI: 10.1039/c2ee02552c

Direct oxidation alkaline fuel cells (DOAFCs) possess particular advantages on the possibility of employing low cost non-noble metal catalysts. A wide range of fuels can be used due to superior reaction kinetics in alkaline media. The development of DOAFCs was hindered by the carbonation of electrolyte due to the presence of CO<sub>2</sub>. The application of the anion exchange membrane (AEM) provides the possibility of reducing the effect of carbonation and fuel crossover which is an issue in the proton exchange membrane fuel cells (PEMFCs). The latest developments in alkaline fuel cells are examined in this paper, considering different types of fuels, novel catalysts and anion exchange membranes. Moreover, alkaline fuel cell systems and configurations are studied, particularly the new designs for portable or microelectronic devices. Further development of DOAFCs will rely on novel AEMs with good ionic conductivity and stability, low cost non-Pt catalysts with high activity and good stability for various fuels and oxidant. We envisage that DOAFCs will play a major role in energy research and applications in the near future.

### 1. Introduction

First fuel cells using aqueous KOH electrolyte were patented by Reid in 1902 and Noel in 1904, 63 years after Grove's acid fuel cells in 1839. Dr Francis Bacon commenced his research on alkaline fuel cells (AFCs) in 1932 and completed the construction of a 5 kW hydrogen–oxygen fuel cell power plant in 1952. One of the main reasons for Bacon to choose an alkaline electrolyte was to use non-noble metal catalysts. In his fuel cell, nickel was the catalyst for the anode and lithiated nickel oxide was for the

cathode. In NASA's Apollo missions, fuel cells using 80–85% KOH (molten KOH), operated at 250 °C and close to atmospheric pressure, were developed by the Pratt and Whitney Division of United Technologies Corporation.<sup>1</sup> These fuel cells could last for two to four weeks. Siemens and Exxon also developed highly efficient alkaline fuel cells and a current density of 420 mA cm<sup>-2</sup> at a cell potential of 0.77 V was achieved with their systems.<sup>1,2</sup> Although the alkaline fuel cell system is the most efficient of all fuel cells, the major problem is the carbonation of the solution due to CO<sub>2</sub> production of the fuel oxidation and from air:



This can cause solid precipitation of carbonate salts on the porous electrode and a decrease of pH in the alkaline electrolyte solution.<sup>1</sup> Complete removal of CO<sub>2</sub> from the anodic and cathodic gas stream is a great challenge and leads to high costs.

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### Broader context

Direct oxidation alkaline fuel cells have attracted more and more interest in recent years. There have been many reviews published on the topic. Most of them were focused on a particular topic, for example, gas diffusion electrodes, anion exchange membranes (AEMs), and alkaline alcohol fuel cells. An overview covering latest development of materials and systems on DOAFCs has not been studied. In this work, new insights into both the current state and future trends in DOAFC development are discussed. Many topics, such as the N-doped nanocarbon materials, various fuel cell configurations and systems as well as different fuel sources have rarely been discussed previously. In this perspective, not only were the challenges in the current DOAFC system analysed and the methods to tackle the challenges identified, but also the trends of future developments in low cost catalysts, AEMs and wide varieties of fuels were indicated.

Since the development of perfluorinated cation exchange membranes (CEMs), such as Nafion®, proton exchange membranes (PEMs) have dominated as the electrolyte for fuel cells. However, three major obstacles have restrained more rapid development and applications of PEM fuel cells:

- High cost of membranes and noble metal catalysts.
- The relatively low activity and complex reaction mechanism of most organic fuels.
- Fuel crossover.

Direct oxidation alkaline fuel cells (DOAFCs), which oxidise fuel directly on the anode in alkaline media, have attracted attention again in recent years because of the potential solutions to overcome the problems in the PEM fuel cells. The application of anion exchange membranes (AEMs) as the solid polymer electrolyte can reduce formation of carbonate from carbon dioxide, compared to the aqueous electrolyte. It was also discovered that the electro-oxidation of fuels, such as methanol, in alkaline electrolyte is structure insensitive<sup>3</sup> which opens up the opportunity for use of non-precious metals, such as Pd, Ag, and Ni and perovskite-type oxides in alkaline fuel cells,<sup>4-6</sup> which can significantly reduce the catalyst cost compared to Pt based catalysts. 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 fuel crossover.<sup>7</sup> Fig. 1 demonstrates a schematic diagram of a direct methanol fuel cell.

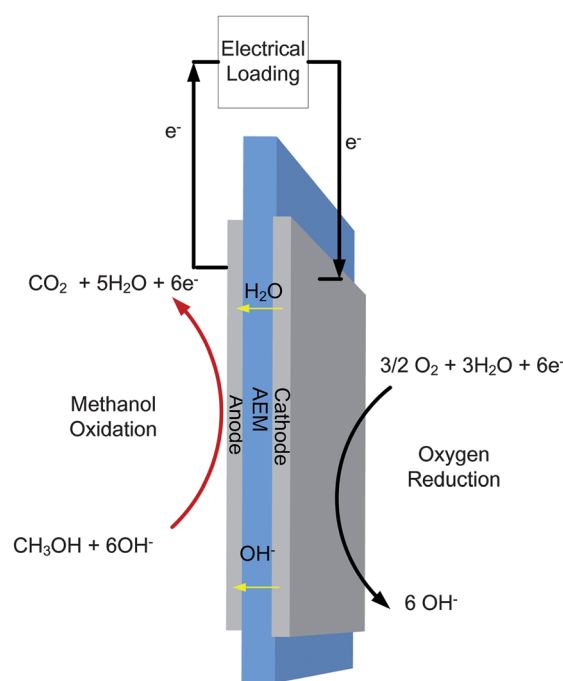


Fig. 1 Schematic diagram of the operating process in a direct methanol fuel cell.

In this work, we focused on the latest development in alkaline fuel cells on examining different types of fuels, novel catalysts and anion exchange membranes. Moreover, the alkaline fuel cell system and configuration are studied. The challenges and perspectives on future developments of DOAFCs are discussed.

## 2. Fuels used in DOAFCs

A broad range of fuels have been applied for alkaline fuel cells. Commercial fuel cell systems were developed using hydrogen<sup>2</sup>

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and hydrazine<sup>8–10</sup> in 1960s and 70s for NASA space shuttles and emergency power supply. Various organic fuels from the simplest alcohols, methanol<sup>11</sup> and ethanol<sup>12</sup> to polyhydric alcohols, ethylene glycol,<sup>13</sup> and sugars<sup>14–16</sup> have been investigated. The wide range of fuels makes DOAFCs versatile in applications. The mechanisms and dynamics of electrochemical oxidation of some carbon containing fuels can be found in our recent review.<sup>17</sup>

Direct alcohol alkaline fuel cells are the most common alkaline fuel cells due to easy storage and transportation of alcohols. Antolini and Gonzalez presented a comprehensive review on alkaline alcohol fuel cell systems on catalysts, membranes and operational tests.<sup>18</sup> Most alcohols, except methanol, are non-toxic which make them more convenient to handle. For simple alcohols, the theoretical energy density of the fuel increases as the number of carbon in fuel molecules increases since they are able to go through complete oxidation to CO<sub>2</sub>. As more electrons are available through the fuel oxidation in the multi-carbon simple alcohols, the energy density increases. For polyhydric alcohols, even though more hydrogen and carbon are available from the fuel molecules, only partial oxidation of the alcohols occurs. As a result, the energy densities of the fuels are lower compared to simple alcohols. During the oxidation large amounts of intermediates are also produced, which could poison the catalysts.

Other types of organic fuel, such as dimethyl ether (DME), have been reported. An alkaline direct dimethyl ether fuel cell (DDFC) was assembled using a Nafion membrane and the maximum power density of 60 mW cm<sup>-2</sup> was achieved when operating at 80 °C under ambient pressure.<sup>19</sup>

Hydrogen is still the most efficient fuel because of its simple oxidation process, however, as a gaseous fuel, the storage and transport of hydrogen has been a major challenge hindering the development. Other inorganic fuels reported include ammonia,<sup>20</sup> hydrazine<sup>8–10</sup> and sodium borohydride.<sup>21</sup> The advantages of inorganic fuels are the high hydrogen contents: 17.6 wt% for NH<sub>3</sub>, 12.5 wt% for N<sub>2</sub>H<sub>4</sub> and 10.6 wt% for NaBH<sub>4</sub>. They have high reactive activity which leads to higher cell voltages from these fuel cells; however, the stability and toxicity of these fuels are the main concerns with inorganic fuels.

A summary of fuels reported for DOAFC applications and the fuel oxidation reactions involved are demonstrated in Table 1.

### 3. Recent development in anion exchange membranes

In alkaline fuel cells, the anion exchange membrane (AEM) is a critical component affecting the performance of the whole system. Recently, several reviews have been published on AEMs for alkaline fuel cells<sup>22</sup> and the polymeric materials for AEMs.<sup>23</sup> Merle *et al.* described and assessed polymeric materials potentially suitable for use in alkaline fuel cells, and of their specific properties;<sup>22</sup> while Couture *et al.* focused on summarising strategies to synthesise anion-exchange polymeric materials containing cationic (especially ammonium) groups for heterogeneous and homogeneous membranes; modify polymeric materials *via* radio-grafting or chemical reactions. They also described the approaches for chemical modifications of commercial hydrogenated aliphatic and aromatic (co)polymers.<sup>23</sup>

In the early works of DOAFCs, the AEMs used were often for other applications. For example, the commercially available

MORGANE®-ADP membranes from Solvay, S. A. were used as the solid polymer electrolyte for DMAFC in several studies,<sup>11,24</sup> which were normally used for salt electro dialysis and with a working pH range only up to 10. There was no equivalent AEM for DOAFC to Nafion in proton exchange membrane fuel cells (PEMFCs). The membrane features were far from DOAFC requirements. With the increasing interests on DOAFC, research development on novel AEM has made significant advances in recent years.

To prepare AEMs, introducing the quaternary ammonium group to the polymer matrix is considered one of the effective methods.<sup>23</sup> The process involves three major steps: chloromethylation, quaternization and alkalization.<sup>25</sup> Chloromethylation and quaternization are two key reactions that determine the ionic conductivity.<sup>26</sup> The concentration of the chloromethylation agent is crucial in increasing the chloromethyl functional group attachment onto the polymer. It was also found that using an appropriate quaternization approach could significantly improve the ionic conductivity and optimize the conductivity of the membrane.<sup>27</sup>

Non-perfluorine based polymers attract much interest due to their low cost. Several new materials, poly(phenylene oxide), quaternized polyethersulfone Cardo and polyvinyl alcohol (PVA), have been used for AEMs.<sup>28</sup> Poly(phenylene oxide) or PPO has excellent electrical properties, good resistance to various chemicals, exceptional dimensional stability, low moisture absorption, and high mechanical and dielectric strength, which makes it a desirable candidate for an ion exchange membrane.<sup>29</sup> A composite membrane with quaternised PVA/alumina (QPVA/Al<sub>2</sub>O<sub>3</sub>) was used for alkaline methanol fuel cells using air at ambient temperature.<sup>30</sup> KOH was incorporated in PVA to improve the ionic conductivity and chemical and thermal stability of the membrane.<sup>31</sup> Hybrid membranes based on PVA/3-(trimethylammonium) propyl-functionalised silica (PVA-TMAPS)<sup>32</sup> and tetraethoxysilane (TEOS)<sup>33</sup> were prepared. With the addition of TMAPS and TEOS particles, silica based material, the thermal stability and ionic conductivity of the membrane were both enhanced, and the methanol permeability was largely reduced. Polysulfone is from a family of thermoplastic polymers known for their toughness and stability at high temperatures. Polysulfone based AEMs were studied by several groups.<sup>34–39</sup> In these studies, they showed that the membrane properties, such as stability, conductivity and water uptake, are affected by the microstructure of the polymer. The study from Wang *et al.* showed that temperature and time had large impact on chloromethylation of the polymer.<sup>34</sup> Cross-linking of the polymer could increase ion incorporation which in turn improves ionic conductivity, which seems to be an ultimate strategy to enhance AEM properties.<sup>23</sup>

Fluorinated polymers such as poly(tetrafluoroethylene-*co*-hexafluoropropylene) (FEP),<sup>40</sup> poly(ethylene-*co*-tetrafluoroethylene) (ETFE),<sup>41</sup> and poly(vinylidene fluoride) (PVDF)<sup>42</sup> have also been investigated for AEM fabrication and application. Fluorinated polymers provide unique molecular properties associated with C–F bonds. The polymers are known for their good interface properties such as low surface tension and electrostatic loading, as well as excellent chemical and mechanical stability. With these properties, very thin AEMs with the thickness between 17 and 85 μm were prepared and tested with H<sub>2</sub>/O<sub>2</sub>

**Table 1** Summary of reactions in direct oxidation alkaline fuel cells

Fuel	Anode reactions: fuel oxidation	$E_a^0$ (V/SHE)	Cathode reactions: oxidant	$E_c^0$ (V/SHE)	$E^0/V$	Energy density/W h kg <sup>-1</sup>
<i>Organic fuels</i>						
Methanol CH <sub>3</sub> OH	CH <sub>3</sub> OH + 6OH <sup>-</sup> → CO <sub>2</sub> + 5H <sub>2</sub> O + 6e <sup>-</sup>	-0.81	3/2O <sub>2</sub> + 3H <sub>2</sub> O + 6e <sup>-</sup> → 6OH <sup>-</sup>	0.40	1.21	6100
Ethanol CH <sub>3</sub> CH <sub>2</sub> OH	CH <sub>3</sub> CH <sub>2</sub> OH + 2OH <sup>-</sup> → CH <sub>3</sub> CHO + 2H <sub>2</sub> O + 2e <sup>-</sup> , CH <sub>3</sub> CH <sub>2</sub> OH + 4OH <sup>-</sup> → CH <sub>3</sub> COOH + 3H <sub>2</sub> O + 4e <sup>-</sup> , CH <sub>3</sub> CH <sub>2</sub> OH + 12OH <sup>-</sup> → 2CO <sub>2</sub> + 9 H <sub>2</sub> O + 12e <sup>-</sup> , CH <sub>3</sub> CHOHCH <sub>3</sub> + 2OH <sup>-</sup> → CH <sub>3</sub> COCH <sub>3</sub> + 2H <sub>2</sub> O + 2e <sup>-</sup> , CH <sub>3</sub> COCH <sub>3</sub> + 16OH <sup>-</sup> → 3CO <sub>2</sub> + 11H <sub>2</sub> O + 16e <sup>-</sup> (CH <sub>2</sub> OH) <sub>2</sub> + 14OH <sup>-</sup> → 2CO <sub>3</sub> <sup>2-</sup> + 10H <sub>2</sub> O + 10e <sup>-</sup> or (CH <sub>2</sub> OH) <sub>2</sub> + 10OH <sup>-</sup> → (CO <sub>2</sub> ) <sub>2</sub> <sup>2-</sup> + 8H <sub>2</sub> O + 6e <sup>-</sup>	-0.77	3O <sub>2</sub> + 6H <sub>2</sub> O + 12e <sup>-</sup> → 12OH <sup>-</sup>	0.40	1.17	8030
Iso-propanol CH <sub>3</sub> CHOHCH <sub>3</sub>	CH <sub>3</sub> CHOHCH <sub>3</sub> + 2OH <sup>-</sup> → CH <sub>3</sub> COCH <sub>3</sub> + 2H <sub>2</sub> O + 2e <sup>-</sup> , CH <sub>3</sub> COCH <sub>3</sub> + 16OH <sup>-</sup> → 3CO <sub>2</sub> + 11H <sub>2</sub> O + 16e <sup>-</sup>	-0.67	9/2O <sub>2</sub> + 9H <sub>2</sub> O + 18e <sup>-</sup> → 18OH <sup>-</sup>	0.40	1.07	8600
Ethylene glycol (CH <sub>2</sub> OH) <sub>2</sub>	(CH <sub>2</sub> OH) <sub>2</sub> + 14OH <sup>-</sup> → 2CO <sub>3</sub> <sup>2-</sup> + 10H <sub>2</sub> O + 10e <sup>-</sup> or (CH <sub>2</sub> OH) <sub>2</sub> + 10OH <sup>-</sup> → (CO <sub>2</sub> ) <sub>2</sub> <sup>2-</sup> + 8H <sub>2</sub> O + 6e <sup>-</sup>	-0.72	1/2O <sub>2</sub> + H <sub>2</sub> O + 2e <sup>-</sup> → 2OH <sup>-</sup>	0.40	1.12	5200
Glycerol HOCH <sub>2</sub> CHOHCH <sub>2</sub> OH	HOCH <sub>2</sub> CHOHCH <sub>2</sub> OH + 20OH <sup>-</sup> → 3CO <sub>3</sub> <sup>2-</sup> + 14H <sub>2</sub> O + 14e <sup>-</sup> or HOCH <sub>2</sub> CHOHCH <sub>2</sub> OH + 12OH <sup>-</sup> → (COO <sup>-</sup> -COH-COO <sup>-</sup> ) + 10H <sub>2</sub> O + 10e <sup>-</sup>	-0.69	1/2O <sub>2</sub> + H <sub>2</sub> O + 2e <sup>-</sup> → 2OH <sup>-</sup>	0.40	1.09	5000
Urea CO(NH <sub>2</sub> ) <sub>2</sub>	CO(NH <sub>2</sub> ) <sub>2</sub> + 6OH <sup>-</sup> → N <sub>2</sub> + CO <sub>2</sub> + 5H <sub>2</sub> O + 6e <sup>-</sup>	-0.75	1/2O <sub>2</sub> + H <sub>2</sub> O + 2e <sup>-</sup> → 2OH <sup>-</sup>	0.40	1.15	2927
Glucose C <sub>6</sub> H <sub>12</sub> O <sub>6</sub>	C <sub>6</sub> H <sub>12</sub> O <sub>6</sub> + 2OH <sup>-</sup> → C <sub>6</sub> H <sub>12</sub> O <sub>7</sub> + 2e <sup>-</sup>	-0.85	1/2O <sub>2</sub> + H <sub>2</sub> O + 2e <sup>-</sup> → 2OH <sup>-</sup>	0.40	1.25	4430
Dimethyl ether CH <sub>3</sub> OCH <sub>3</sub>	CH <sub>3</sub> OCH <sub>3</sub> + 12OH <sup>-</sup> → 9CO <sub>2</sub> + 2H <sub>2</sub> O + 12e <sup>-</sup>	-0.80	3O <sub>2</sub> + 6H <sub>2</sub> O + 12e <sup>-</sup> → 12OH <sup>-</sup>	0.40	1.20	7100
Cellulose (C <sub>6</sub> H <sub>10</sub> O <sub>5</sub> ) <sub>n</sub>	Converted to different cellulose derivatives	Not available	1/2O <sub>2</sub> + H <sub>2</sub> O + 2e <sup>-</sup> → 2OH <sup>-</sup>	0.40	Not available	Not available
<i>Inorganic fuels</i>						
Ammonia NH <sub>3</sub>	2NH <sub>3</sub> + 6OH <sup>-</sup> → N <sub>2</sub> + 3H <sub>2</sub> O + 6e <sup>-</sup>	-0.77	3/2O <sub>2</sub> + 3H <sub>2</sub> O + 6e <sup>-</sup> → 6OH <sup>-</sup>	0.40	1.17	3300
Hydrogen H <sub>2</sub>	2H <sub>2</sub> + 4OH <sup>-</sup> → 4H <sub>2</sub> O + 4e <sup>-</sup>	-0.83	1/2O <sub>2</sub> + H <sub>2</sub> O + 2e <sup>-</sup> → 2OH <sup>-</sup>	0.40	1.23	32 160
Hydrazine N <sub>2</sub> H <sub>4</sub>	N <sub>2</sub> H <sub>4</sub> + 4OH <sup>-</sup> → 4H <sub>2</sub> O + N <sub>2</sub> + 4e <sup>-</sup>	-1.17	1/2O <sub>2</sub> + H <sub>2</sub> O + 2e <sup>-</sup> → 2OH <sup>-</sup>	O <sub>2</sub> : 0.40	1.57	5260
Sodium borohydride NaBH <sub>4</sub>	NaBH <sub>4</sub> + 8OH <sup>-</sup> → NaBO <sub>2</sub> + 6H <sub>2</sub> O + 8e <sup>-</sup>	-1.24	H <sub>2</sub> O <sub>2</sub> + 2e <sup>-</sup> → 2OH <sup>-</sup>	H <sub>2</sub> O <sub>2</sub> : 0.88	2.05	2050
			1/2O <sub>2</sub> + H <sub>2</sub> O + 2e <sup>-</sup> → 2OH <sup>-</sup>	O <sub>2</sub> : 0.40	1.64	9000
			H <sub>2</sub> O <sub>2</sub> + 2e <sup>-</sup> → 2OH <sup>-</sup>	H <sub>2</sub> O <sub>2</sub> : 0.88	2.12	



fuel cells. The highest power output was obtained from the thinnest membrane indicating the improvement of mass transport of water which normally limited the fuel cell performance with thicker membranes.<sup>43</sup>

PTFE based composite AEM was also reported for direct hydrazine hydrate fuel cells (DHFC).<sup>44</sup> The membrane was prepared by *in situ* thermal polymerisation of chloromethyl in the PTFE matrix followed by quaternary amination and alkalisation. The PTFE matrix reinforced the membrane structure and improved thermal stability and mechanical strength. The membrane hydroxide conductivity was also improved due to a high monomer uptake and the 'hydrophobic matrix confined hydrophilic domain'.

A quaternary DABCO polysulfone (QDPSU) and hybrid AEM PTFE-QDPSU were synthesised for hydrogen fuel cells recently. Fig. 2 shows the fuel cell performance and ionic conductivity of the membrane at various temperatures. The highest power density was 120 mW cm<sup>-2</sup> obtained at 50 °C. With the addition of PTFE in the membrane structure, the mechanical strength, water uptake and ionic conductivity were improved.<sup>45</sup>

Composite membranes prepared from a copolymer of various monomers instead of a single monomer have attracted lots of interests. The idea is to produce a membrane incorporated with different desired properties from different monomers through the copolymerisation process. The study by Zeng *et al.*<sup>46</sup> developed an AEM that was started with styrene, a thermoplastic phase, dispersed in elastomeric matrix ethylene/butylenes to obtain a thermoplastic elastomer with good mechanical, chemical and thermal stability, and then quaternised chloromethyl into a quaternary ammonium group. Xu *et al.* prepared an AEM from a copolymer of methyl methacrylate, vinylbenzyl chloride

and ethyl acrylate.<sup>25</sup> Ion exchange capacity, water uptake, chemical stability, thermal stability, morphology, methanol permeability and ionic conductivity of the synthesised membrane were characterised. This synthesis route eliminated the use of chloromethylether for chloromethylation, which is very toxic and carcinogenic. It provided the convenience of designing different main chain structure. The results demonstrated that the membrane may have good prospects for low-temperature anion exchange membrane fuel cell applications.<sup>25</sup>

Fuel cells using a hybrid polymer electrolyte, *i.e.* both PEM and AEM in one fuel cell system, were studied by Unlu *et al.*<sup>47</sup> With this new configuration, a self-humidified fuel cell with better water management was tested.<sup>48</sup>

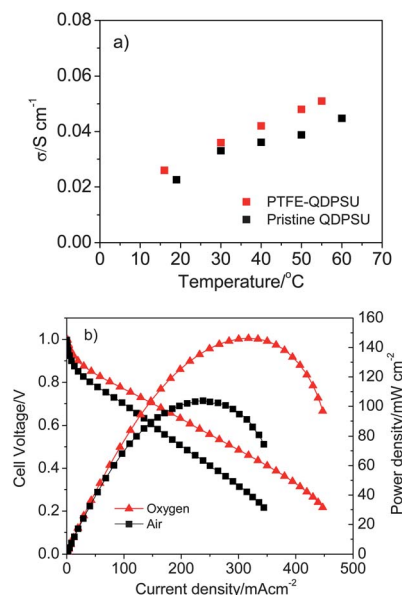
Apart from the ongoing research on anion exchange membranes, commercially available AEMs have been reported in various fuel cell studies. The main manufacturers are Solvay (MORGANE®-ADP), Tokuyama (AHA, A201 and A901), and Fumatech. Basic properties of these membranes can be found in our previous study.<sup>28</sup> The most promising fuel cell performances were reported from an alkaline ethanol fuel cell using Tokuyama A201 with Pd catalysts.<sup>12,49–52</sup>

## 4. Recent development on DOAFC catalysts

For alcohol oxidation in alkaline media, the reaction current densities obtained during alcohol oxidation at certain potentials are at least an order of magnitude greater than in acidic electrolytes. In PEMFCs, the cathode is always the limiting factor for the fuel cell performance due to low oxygen reduction kinetics, as well as potential loss from a mixed potential on the cathode as a result of fuel crossover. Nonetheless, these factors are mitigated in alkali environment. In recent years, research for DOAFCs has been focused on improving the catalytic activity and stability of non-Pt metal catalysts. New materials, such as transition-metal complexes, nitrogen-doped carbon nanotubes, and metal carbides, have drawn much attention.<sup>53</sup>

### 4.1. Non-Pt based catalysts

The cost of Pd is only one-fourth of Pt and Pd demonstrated good activity in several studies on 1-propanol,<sup>54</sup> 2-propanol,<sup>55–57</sup> ethanol,<sup>58</sup> ethylene glycol and glycerol<sup>51</sup> oxidation. It is a potential alternative to platinum when alloyed with other metals. A Pd/C catalyst promoted by Au, with the optimum ratio of Pd : Au 4 : 1, demonstrated a significant increase of catalytic activity and stability in DOAFCs.<sup>59,60</sup> A remarkable power density of 170 mW cm<sup>-2</sup> was reported for a cell operated at 80 °C.<sup>60</sup> Enhancement was also observed from Pd-Ag/C and Pd-Ru/C catalysts towards ethanol electrooxidation in alkaline media.<sup>5,61</sup> The Pd-Ag/C catalyst showed high activity, and enhanced adsorbed CO tolerance and stability for ethanol oxidation.<sup>61</sup> With Pd-Ru catalyst, the current density for ethanol oxidation was four times of that from Pt-Ru within the potential 0.3–0.4 V (SHE).<sup>5</sup> Pd-Ni as the anode catalyst was reported for a direct ethylene glycol fuel cell with a Tokuyama AEM and a non-Pt Fe-Co based Hypermec™ K-14 cathode catalyst from Acta.<sup>20</sup> The highest power density for an ethylene glycol fuel cell was achieved as 67 mW cm<sup>-2</sup>. Recently, An *et al.* used an in-house prepared PdNi anode catalyst in a direct glucose fuel cell



**Fig. 2** (a) Ionic conductivities of a PTFE-QDPSU composite membrane and pristine QDPSU membrane at different temperatures under N<sub>2</sub> atmosphere and 100% RH and (b) fuel cell performance using hydrogen at the anode and oxygen or CO<sub>2</sub> free air for the cathode, 50 °C. PTFE-QDPSU (30  $\mu\text{m}$  thickness), 0.5 mg cm<sup>-2</sup> Pt/C (60 wt%) for both anode and cathode, loading of QDPSU in catalyst layers is 6 wt%, atmospheric pressure, 100% RH at cathode.<sup>45</sup>

containing Acta non-Pt ORR cathode catalysts and achieved a maximum power density of  $38 \text{ mW cm}^{-2}$  at  $60^\circ \text{C}$  with  $7 \text{ M KOH}$  and pure oxygen.<sup>62</sup>

The addition of oxides like  $\text{CeO}_2$ ,  $\text{NiO}$ ,  $\text{Co}_3\text{O}_4$  and  $\text{Mn}_3\text{O}_4$  significantly promoted the activity and stability of Pd/C catalysts. Xu *et al.* investigated metal oxide promoted Pd/C catalysts for alcohol oxidation in alkaline media.<sup>55</sup> Some metal oxides, in particular,  $\text{CeO}_2$ ,  $\text{Mn}_3\text{O}_4$  and  $\text{SnO}_2$  have multiple oxidation states and can store and release oxygen. It is believed that the formation of  $\text{OH}_{\text{ads}}$  species on metal oxides, due to the adsorption of  $\text{OH}^-$ , at lower potential can transform  $\text{CO}^-$  or other carbonaceous species on the surface of Pd to  $\text{CO}_2$ , releasing active sites on Pd for further reaction.<sup>63</sup>

For non-precious metal catalysts for fuel oxidation, 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.<sup>64,65</sup> Different types of nickel, such as Raney-nickel, nickel particles,<sup>66</sup> electrodeposited nickel<sup>67</sup> and more recently nickel nanoparticles supported on carbon-ceramic prepared by sol-gel techniques,<sup>68</sup> have been investigated for alkaline fuel cells. Nickel was also used as the main composition in binary anode catalysts with Pd and Pt<sup>69</sup> and in cathode catalysts with Ag for direct borohydride fuel cells,<sup>70</sup> and in ternary catalysts with Pt/Ru to improve the activity of CO oxidation due to the development of electronic interaction between Ni and other catalyst compositions.<sup>71</sup> In direct borohydride fuel cells, the power densities of  $270 \text{ mW cm}^{-2}$  and  $665 \text{ mW cm}^{-2}$  were achieved for  $\text{NaBH}_4/\text{O}_2$  and  $\text{NaBH}_4/\text{H}_2\text{O}_2$  fuel cells at  $60^\circ \text{C}$  using Ni-based anode catalysts.<sup>69</sup> Silver has been used often in various alkaline fuel cells as an oxygen reduction catalyst but the activity was not comparable to Pt and metal macrocycles.<sup>70</sup>

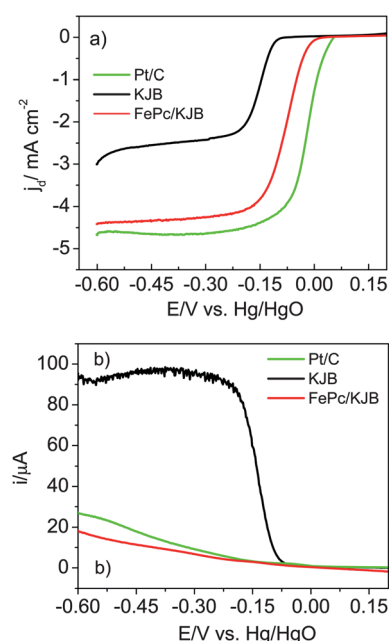
Transition metal macrocycles, such as phthalocyanine and porphyrin, have been used as effective oxygen reduction catalysts since the work of Jasinski on metal phthalocyanines in the 1960s.<sup>72</sup> The active sites of these compounds are the four-nitrogen ring coupled with transition metals, commonly Fe or Co. These catalysts have shown highly selective catalytic activity for oxygen reduction. Their stability in alkaline media and low cost make these catalysts promising alternatives in DOAFCs. A heat-treated iron phthalocyanine (FePc) supported on Ketjen-black (FePc/KJB) was prepared as the ORR catalyst. The half-cell tests, shown in Fig. 3, reveal that the FePc/KJB pyrolysed at  $800^\circ \text{C}$  has a high activity towards ORR and low hydrogen peroxide generation compared to commercial Pt/C (20 wt%, E-Tek). The  $n$  (electron transfer number) value was 3.90 at the limiting current region ( $-400 \text{ mV vs. Hg/HgO}$ ) using the following equation:

$$n = 4I_d / (I_d + I_r/N) \quad (2)$$

where  $I_d$  is the disk current,  $I_r$  is the platinum ring current, and  $N$  is the collection efficiency.

The preliminary evaluation of such a catalyst showed promising performance. Although extensive works have been done on FePc for ORR, little has been reported on fuel cell performance using such catalysts in AEMFCs.

Iron tetramethoxyphenyl porphyrin (FeTMPP) was used as a cathode catalyst in a direct borohydride fuel cell. It showed



**Fig. 3** Linear sweep voltammograms of Pt/C, KJB and FePc/KJB, the corresponding disk and ring current at a rotation rate of 2500 rpm in  $\text{O}_2$  saturated  $1.0 \text{ M KOH}$  and at  $25^\circ \text{C}$ .

better activity compared with silver and nickel catalysts.<sup>70</sup> In order to improve the activity and stability of non-platinum catalysts, hybrid catalysts with cobalt phthalocyanine (CoPc) and fluorinated cobalt phthalocyanine (CoPcF 16) on carbon supported silver nanoparticles were prepared. Lower overpotential and higher kinetics were obtained compared to macrocycles or silver used alone. The activity of the ORR catalyst could be also tuned by adjusting the composition of metal macrocycles.<sup>73</sup> Co based catalysts were evaluated for use as oxygen reduction (ORR) catalysts in liquid KOH and alkaline anion exchange membrane fuel cells (AEMFCs). Stable power density comparable to Pt was achieved although the efficiency was lower.<sup>74</sup>

Lanthanum, strontium oxides,  $\text{La}_{2-x}\text{Sr}_x\text{CuO}_4$ , and perovskite-type oxides,  $\text{La}_{2-x}\text{Sr}_x\text{NiO}_4$  ( $0 \leq x \leq 1$ ), have been investigated for methanol and EG alkaline fuel cells. All oxides gave reasonable oxidation currents in potential ranges appropriate to fuel cell operation, and no poisoning effect was detected.<sup>75-77</sup>

Transition metal carbides as catalysts received remarkable interest since the discovery of their catalytic activities. Tungsten carbides nano-powder  $\text{W}_2\text{C}$  and the mixture of  $\text{W}_2\text{C}$  and WC prepared by the microwave irradiation method have shown as promising oxygen reduction catalysts. The mixture of  $\text{W}_2\text{C}$  and WC has good methanol tolerance as its activity was not affected by the presence of methanol.<sup>78</sup> A series of interstitial metal carbides ( $\text{M} = \text{Zr}, \text{Ti}, \text{V}, \text{Mo}, \text{W}, \text{Nb}, \text{Ta}$ ) investigated by Horigome *et al.* were incorporated in Raney Ni and PTFE based gas diffusion electrodes for hydrogen oxidation. ZrC provided highest performance with respect to the electrode stability and polarization characteristics.<sup>79</sup>

Commercially available non-Pt catalysts from Acta, Italy,<sup>80</sup> have been reported by several groups in DOAFCs using alcohol

fuels.<sup>20,50,51</sup> Most applications were Fe–Co based oxygen reduction catalysts, and a Pd-based anode catalyst was reported to be used for methanol oxidation in alkaline fuel cells by Li *et al.*<sup>50</sup>

#### 4.2. N-Doped carbon materials

In alkaline media, carbon has activity for oxygen reduction although the reaction is mainly a 2-electron pathway from which hydrogen peroxide is produced. Nitrogen doped carbon materials have attracted lots of interests. The study from Gong *et al.* showed significantly enhanced ORR activity and stability from nitrogen doped carbon nanotube (NCNT) arrays<sup>81</sup> in 0.1 M KOH. In their study, the ORR onset potential for NCNTs was comparable to the Pt/C catalyst, however, the activity of NCNTs was not affected by the presence of 3 M methanol as well as H<sub>2</sub>, glucose and formaldehyde, and the activity was not decayed after 100 000 cycles of continuous potentiodynamic sweeps. They attributed the high selectivity of the NCNTs on ORR to more positive ORR potential than the fuel oxidation potentials. These NCNTs even showed a four-electron pathway for ORR. The effect of CO poisoning was also tested on NCNTs.<sup>81</sup> Unlike Pt, the non-metallic carbon catalyst was insensitive to 10% CO in oxygen.

Nitrogen heteroatoms in NCNTs play important roles in the electrocatalytic activities for ORR. There are mainly four types of nitrogen functional groups: pyridinic (N<sub>1</sub>), pyrrolic (N<sub>2</sub>), quaternary (N<sub>3</sub>) and pyridine-*N*-oxide (N<sub>4</sub>).<sup>82</sup> The enhanced ORR activity may be from pyridinic or pyrrole/pyridine type nitrogen. The importance of pyridinic nitrogen could lie in the availability of the extra lone pair of electrons on the nitrogen atom, which increases the electron density on graphitic edge planes, commonly known as reactive sites.<sup>83</sup> The nitrogen groups can transform to more thermally stable structures from heat treatment.<sup>84</sup> However, from Nagaiah *et al.*'s study, after heat treatment, NCNTs contained the highest amount of quaternary N<sub>3</sub> groups indicating the importance of these groups on enhancing activity.<sup>82</sup>

Nitrogen is also able to create defects on carbon increasing the edge plane exposure and improve the catalytic activity.<sup>85,86</sup> It was demonstrated by Chen *et al.* that the structures and morphologies of NCNTs had high influence on the ORR activity due to their impact on the surface defects. A higher degree of surface defect can enhance the activity. Their study showed that more defects formed on the NCNTs synthesised from ferrocene (Fc–NCNTs) than from iron phthalocyanine (FePc–NCNTs), which led to much higher ORR activity from Fc–NCNTs.<sup>87</sup>

Various nitrogen groups and synthesis procedures have been used to produce N-doped nanocarbon materials. HNO<sub>3</sub>,<sup>88</sup> NH<sub>3</sub> gas,<sup>82,83,89</sup> acetonitrile,<sup>90</sup> chemical vapour deposition<sup>81,85</sup> and carbonising phthalocyanines coordinated to alkali metals or alkaline earth metals<sup>91</sup> have been used to introduce N-groups on carbon materials.

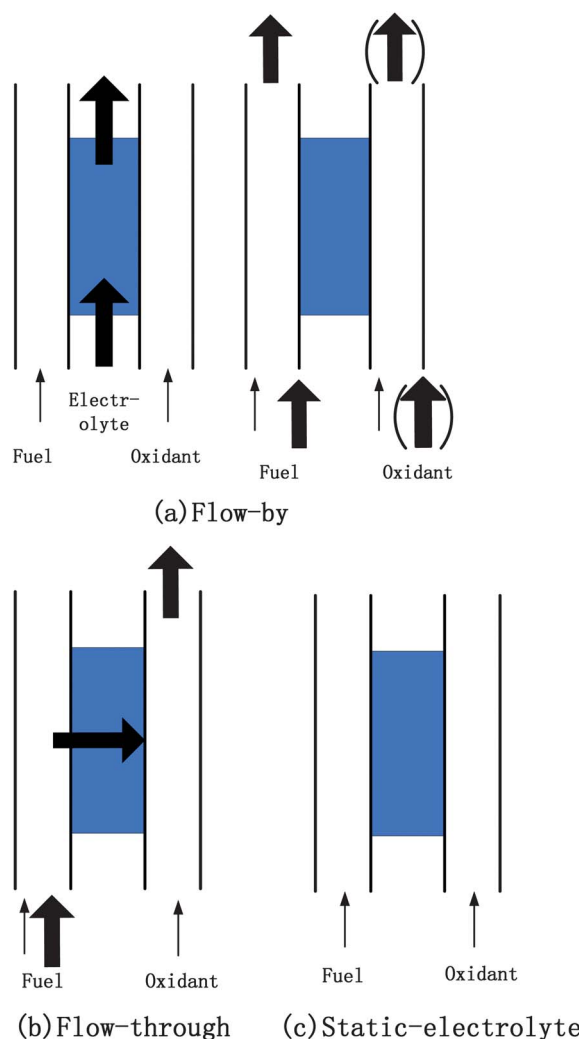
## 5. Direct oxidation alkaline fuel cell systems

DOAFCs can be classified into liquid based alkaline fuel cells and solid polymer electrolyte alkaline fuel cells, *i.e.* anion exchange membrane fuel cells (AEMFCs).

### 5.1 DOAFCs with liquid electrolytes

Liquid electrolytes were used in the early AFCs including the fuel cells used for NASA missions. In these systems, high concentrations of alkaline media, such as 5–10 M KOH, were used. Three configurations, flow-by, flow-through and static electrolyte, were applied in the system. The schematic diagrams of such systems are demonstrated in Fig. 4. For flow-by configuration, the electrolyte flows parallel to the electrodes, while in the flow-through system, the electrolyte flows perpendicular to electrodes and flows in from one electrode through the separator and flows out from the other electrode. In the static electrolyte system, the electrolyte is fixed between electrodes.

**5.1.1 Flow-by configuration.** The flow-by design was frequently used since the development of the Bacon cell in 1950s. The common design involves an electrolyte flow, 5–10 M KOH, separated by two membranes, usually made of asbestos, PP or PE, from the anode and cathode. H<sub>2</sub>, N<sub>2</sub>H<sub>4</sub>, methanol and isopropanol have been used for this fuel cell configuration.<sup>92–95</sup> Verhaert *et al.* developed a two-dimensional model for a flow-by



**Fig. 4** Schematic diagrams for configurations of an alkaline fuel cell with liquid electrolyte: (a) flow-by, (b) flow-through, and (c) static electrolyte.

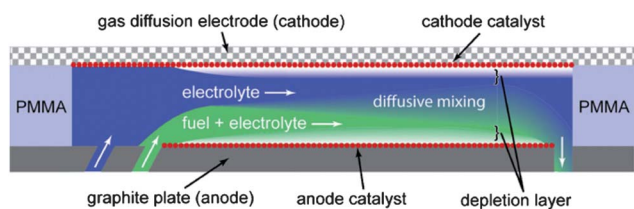


Fig. 5 Laminar flow alkaline fuel cell with flow-by configuration, reproduced from ref. 97 with the permission from Elsevier.

AFC using a control volume approach. The model was based on the steady state study on the physical flow of hydrogen, water and air in the system and not focused on the processes inside the fuel cell.<sup>96</sup>

Laminar flow fuel cells with flow-by configuration have been reported recently. Brushett *et al.* investigated the performance of air-breathing laminar flow-based fuel cells (LFFCs) operated with formic acid, methanol, ethanol, hydrazine, and sodium borohydride in either acidic or alkaline media.<sup>97</sup> The anode was a catalyst-covered graphite plate and the cathode was an air-breathing gas diffusion electrode, shown in Fig. 5. The kinetics of fuel oxidation was improved significantly in alkaline media.

**5.1.2 Flow-through configuration.** Flow-through configuration was developed in 1963 by Varta known as the Eloflux design. The EloFlux design, with its transverse flow of electrolyte, has the advantage of low-cost construction and replaceable electrolyte, but was mostly used with the  $H_2/O_2$  system. A US based company Generics developed a compact mixed-reactant (CMR) fuel cell using flow-through configuration. CMR flow-through mode gave significantly higher performance than non-flow-through modes. They explained that apart from the advantages of mixed-reactant systems, the flow-through mode significantly enhanced mass transport of reactants to the electrodes and reduced reactant pressure drops across the stack.<sup>98</sup>

**5.1.3 Static electrolyte configuration.** The use of a liquid electrolyte fixed in a separator between anode and cathode demands high purity of reactants entering the fuel cell as the electrolyte cannot be refreshed.<sup>99</sup> It was only viable for spacecrafts where high purity of  $H_2$  and  $O_2$  was available and cost was not a concern. In recent years, this configuration was used by several studies on biofuels, such as glucose, fructose<sup>100,101</sup> and cellulose,<sup>16</sup> as well as carbonized charcoal,<sup>102</sup> probably due to simplicity of the system. A direct  $NH_3$  fuel cell operated between 200 and 450 °C, and a direct carbon fuel cell operated at >600 °C were also reported using molten salt consisting of KOH and molten alkaline electrolyte, respectively.<sup>103,104</sup>

**5.1.4 Architectures of liquid fuel cells.** Qian *et al.* reviewed the architectures of direct liquid fuel cells.<sup>105</sup> They compared passive/active fuel/oxidant supply, and liquid fuel and vapour fuel feed systems. The unit cell and stack architectures, as well as various flow field configurations, were also reviewed. Based on analysing the challenges on different architectures, they concluded that the active supply fuel cell system was preferred for larger fuel cells, while the passive system was better for

portable applications.<sup>105</sup> These analyses are also applicable to liquid DOAFC systems.

## 5.2 Solid polymer electrolyte DOAFCs

Both CEMs and AEMs have been used in DOAFCs. Nafion was used in methanol,<sup>106</sup>  $NaBH_4$ <sup>107,108</sup> and  $N_2H_4$ <sup>109,110</sup> systems because of its excellent chemical and thermal stability. For inorganic fuels,  $NaBH_4$  and  $N_2H_4$ ,  $H_2O_2$  was used instead of air or  $O_2$  to obtain higher energy and power densities.<sup>108,110</sup> An alkaline ethanol fuel cell using a CEM was reported and the cell could stably discharge with a high power density at 90 °C.<sup>111</sup>

Amendola *et al.* first used an AEM in a  $NaBH_4$  fuel cell and obtained power densities >20  $mW\ cm^{-2}$  at room temperature and >60  $mW\ cm^{-2}$  at 70 °C.<sup>112</sup> Further investigations on applying AEMs in hydrogen<sup>113</sup> and methanol<sup>114,115</sup> systems were published in the following years. The development of AEMFC largely relies on the progress of AEMs, which has been discussed in the previous section.

$CO_2$  carbonation with alkaline electrolyte has been a major challenge since the early days of AFC development. It was the main reason that the status of AFC was replaced by PEMFC in fuel cells. The carbonation is largely reduced by replacing the aqueous alkaline electrolyte with solid polymer AEM as the electrolyte. The study from Varcoe and Slade revealed that in alkaline media, the continuous production of hydroxide ions on the cathode can reduce the replacement of  $OH^-$  in the membrane by  $HCO_3^-$  or  $CO_3^{2-}$ .<sup>26</sup> In this case, the carbonation process is much slower than in the aqueous electrolytes.

In most AEMFC systems to date, alkaline was still added to the fuel. The power output for fuel cells without added alkaline was significantly lower.<sup>28</sup> Lower ionic conductivity due to lower ionic mobility from  $OH^-$  compared to  $H^+$  may account for this. Although additional liquid electrolyte increases the power density of DOAFC, the use of alkaline electrolyte in the fuel solution is not favoured. The presence of free cations such as  $K^+$  and  $Na^+$  allows for the unwanted precipitation of carbonate salts. This could limit the lifetime of an alkaline fuel cell. Using fuels without KOH or NaOH can reduce the formation of carbonate salts, thus reduce the risk of decrease of membrane ionic conductivity caused by blockage of carbonate precipitation on the membrane. This, on the other hand, will require an AEM with high ionic conductivity to transfer  $OH^-$  produced from cathode readily to the anode side.

AFC stacks have been studied for stationary, transport and portable device applications<sup>92,93,116–118</sup> in addition to NASA's application for spacecrafts. A 6 kW AFC generator for small scale stationary applications was developed by VITO and Intensys.<sup>118</sup> These applications indicate AFC as a promising power source in the future.

## 6. Challenges and perspectives in DOAFC development

DOAFC has become a major research field in fuel cell research in recent years. However, for limited numbers of commercially available fuel cells, PEM fuel cells still occupy the greatest share of the market. There are challenges hindering the



commercialisation of the technology, yet opportunities for future development.

### 6.1 Variety of fuels for DOAFCs

A wide variety of fuels ranging from inorganic compounds of hydrogen, hydrazine, sodium borohydride and ammonia to organic fuels including various alcohols (methanol, ethanol, isopropanol and ethylene glycol), glycerol, dimethyl ether and sugars have been employed in DOAFCs.

There has been a major concern of CO<sub>2</sub> generation from the oxidation of carbon containing fuels. Most alcohols and other carbon containing fuels are not being oxidised completely to CO<sub>2</sub>. For example, the oxidation product of ethanol can be acetaldehyde or acetic acid,<sup>12</sup> and ethylene glycol can produce oxalate (COO<sup>-</sup>-COO<sup>-</sup>) *via* a non-poisoning path, and formate *via* a poisoning path.<sup>13</sup> Antolini and Gonzalez addressed that without complete oxidation of alcohols at anode, the degradation of DOAFC performance is insignificant by using AEMs.<sup>18</sup>

Although the carbonation process is largely reduced from the application of AEM, the readily formation of CO<sub>3</sub><sup>2-</sup> or HCO<sub>3</sub><sup>-</sup> from carbon containing fuel oxidation still can lead to decrease in ionic conductivity of AEM and catalyst activity for the oxidation reaction<sup>119</sup> in the long term. Carbon-free inorganic fuels, *e.g.* ammonia, hydrazine and borohydrides, have advantages over alcohol fuels on this. Increasing interests have been attracted in this area.

Most alcohols and inorganic fuels are produced from petroleum products, which is not sustainable. Biofuels produced from biomass have been major focal points for renewable energy research. Biofuels, mainly sugar and ethanol, are major sources of renewable energy. Apart from natural plant sources, large quantities of carbohydrates are present in industrial wastewaters, such as cellulose from paper industry, sugar and ethanol from breweries. During the production of biodiesel, a large amount of glycerol was produced as a by-product and disposed as waste. Recently, urea was also used for DOAFCs demonstrating a possibility to generate energy from human waste.<sup>120</sup> The numbers of studies on direct glucose alkaline fuel cells have been emerged rapidly recently.<sup>121,62</sup> Basu and Basu studied binary (with Au, Bi and Pd) and ternary (Pd-Au) Pt based catalysts for glucose oxidation.<sup>100,101,116,122</sup> With relatively mild conditions, *i.e.* ambient temperature and 1 M KOH, the maximum power density of 1.6 mW cm<sup>-2</sup> mg<sup>-1</sup> was obtained with Pt/Au catalyst.<sup>101</sup> Sagano *et al.* investigated direct electrochemical oxidation of cellulose in alkaline media for fuel cell application, and they found that cellulose was converted to cellulose derivatives demonstrating the feasibility of using cellulose as direct electrical based fuel.<sup>16</sup> Advances have been achieved on ethanol fuel cells using mainly Pd based catalysts.<sup>51,60,123</sup> The combination of waste treatment and application of natural biofuels can be new areas for DOAFC development. These encouraging results imply that future DOAFC development may lie on versatility of fuels.

### 6.2 Further development of anion exchange membranes (AEMs)

Compared to existing commercial PEM membranes (*e.g.* Nafion), there are still several aspects to improve for developing

AEMs. The critical properties to be improved and the targets of improvement are:

- Ionic conductivity: ionic conductivity  $\sigma > 50$  mS cm<sup>-1</sup> at 80 °C.<sup>124</sup>

The state of the art commercial Nafion membrane can reach 0.1 S cm<sup>-1</sup> at room temperature but for AEM, it is in the region of 32–39 mS cm<sup>-1</sup>, still much lower.<sup>124</sup>

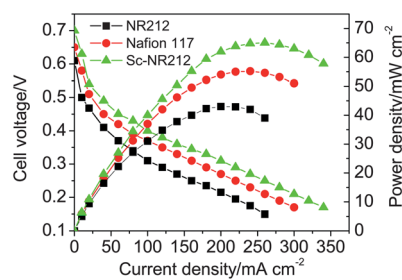
- Chemical and thermal stability: >500 h at 80 °C in 1 M NaOH aqueous solution.<sup>124</sup> Currently, in hydrogen and oxygen AEMFCs, the maximum operating temperature is 60 °C<sup>26,125</sup> and the operating time is about 380 h.<sup>124</sup>

- Mechanical property: yield stress > 10 MPa, strain > 10%.<sup>124</sup>

- Engineering property: good solubility of AEM ionomers and electrode processing of AEMs.

Based on the above discussion, there are some potential materials to be investigated. The aromatic ring polymers (*e.g.* poly(arylene ether)s) (PAEs) can be synthesised with high molecular weight at the lab scale. They have excellent thermal stability, mechanical strength, and good ionic conductivity. The latest report on quaternized block poly(arylene ether)s (QPAEs) showed that the highest ionic conductivity of QPAE was 0.144 S cm<sup>-1</sup> at 80 °C. The maximum pressure loading of such a membrane was up to 40 MPa and it was relatively stable for 5000 h in hot water. However, the Friedel–Crafts chloromethylation reaction of this kind of polymer takes approximately one week and there are risks of cross-linking to become insoluble.<sup>126–128</sup> Tanaka *et al.* recently synthesised a block poly(arylene ether)s anion exchange membrane with a excellent conductivity of 0.144 S cm<sup>-1</sup> at 80 °C.<sup>127</sup> The fuel cell performance using hydrazine and pure oxygen reached 297 mW cm<sup>-2</sup>. Kim from Los Alamos National Laboratory reported that poly(phenylene) based AEM prepared by Sandia National Laboratory using aminated tetramethoxyphenylporphyrine (TMPP) obtained good chemical and mechanical stability (stable >670 h at 60 °C in 4 M NaOH), due to the wholly aromatic structure.<sup>124</sup> This result is better than PAE based AEMs. High ionic conductivity (>50 mS cm<sup>-1</sup>) was also achieved indicating another promising material.

Ion-containing block copolymers are attractive materials holding promise as next-generation membranes for PEMFCs.<sup>129</sup> Block copolyimides, prepared by utilizing a sequential addition of sulfonated and non-sulfonated monomers, lead to phase-separated membranes with both hydrophilic (sulfonic acid-containing) and hydrophobic (non-sulfonated) domains.<sup>130</sup> In these polymer nanostructures, the hydrophilic and hydrophobic moieties are distributed in an ordered manner, which facilitates proton transport over a wide range of conditions. Such a unique structure benefits the mechanical strength of the membrane, swelling behaviour, and ionic conductivity.<sup>129</sup> In fact, a Nafion membrane is a typical block polymer. Yan and Hickner investigated anion-conducting membranes synthesised by halonethylation and quaternization of benzylmethyl-containing poly(sulfone)s through bromination and quaternization reaction with ordered distribution of functional group.<sup>37</sup> In this case, it can avoid the time-consuming chloromethylation reaction and cross-linking risk. By directing the distribution of ionic groups, the anion conductivity and water uptake of the membranes could be tuned over a wide range.<sup>37</sup> They reported a strong correlation between the water uptake and anion conductivity and suggested



**Fig. 6** Polarization curves for the MEAs fabricated with different membranes (operation conditions: 1 M methanol solution, pure O<sub>2</sub> and 60 °C).<sup>141</sup>

the importance of water uptake in these materials to promote fast anion transport.<sup>37</sup> There are limited numbers of reports on this kind of materials, however, the promising membrane and fuel cell performance indicate another means for AEM development.

The purposes of developing a composite membrane include improving water retaining inside the membrane, mechanical strength especially at elevated temperatures (above 80 °C) and reducing the membrane cost. The experience from proton exchange composite membranes is also applicable to AEM. However, the limitation of using AEMs is their stability issue at temperatures above 60 °C. Gu *et al.* reported that the hydrogen and oxygen fuelled AEMFCs can be operated at up to 80 °C and 250 kPa back pressure.<sup>131</sup> High pressure surpasses the water loss inside the membrane thus stops membrane degradation occurring.<sup>125,132</sup> The methods to improve the water retention of AEM are important for future development. Self-humidification developed for the Nafion membrane<sup>133</sup> can apply to AEMs.

Radiation-grafted and cross-linked AEMs exhibited promising performance.<sup>134,135</sup> Due to the insolubility of such materials, it cannot be applied in the catalyst layer and the lack of suitable ionomer in the catalyst layer will result in a significant fuel cell performance loss. Unlike the requirements for AEMs, the hydroxide conductive ionomer is not necessarily mechanically strong which allow more potential materials to be explored. In addition, if the ionomer can be dissolved in low boiling point solvent such as chloroform, then the catalyst ink with specific ionomer loading can be easily sprayed onto the radiation-grafted or cross-linked membrane surface to make a catalyst coated membrane (CCM), which reduces the contact resistance between the electrode and membrane.<sup>136</sup> Our most recent work using poly(vinylbenzyl chloride) (PVBC) and methylated melamine low-cost materials for anion conductive materials showed promising fuel cell performance.<sup>137</sup> Further optimization of this material is undertaking. Development of novel materials is highly desirable for AEMs.

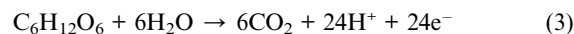
With the development of membrane technology, new methods used to prepare or improve the performance of CEM membranes will be used for AEMs. For example, nanofibers prepared through electrospinning have received attention.<sup>138–140</sup> It shows that the nanofiber ion exchange membranes would have higher ionic conductivity, lower gas permeability and longer durability. Recently, we reported a new approach assisting supercritical carbon dioxide (Sc-CO<sub>2</sub>) to enhance performance of Nafion membranes.<sup>50,141</sup> Due to the Sc-CO<sub>2</sub> induced crystallization, the crystallinity of Nafion membranes increased after such

treatment. The treated Nafion 212 membranes would not only have higher mechanical strength and dimensional stability, but also show higher ionic conductivity and lower methanol permeability. Therefore, the fuel cell performance of the thinner Nafion 212 membrane was higher than that of the thicker Nafion 117 membranes (Fig. 6). Since the AEMs mentioned above are semi-crystalline polymers, the crystallinity of these polymers will be easily increased due to the Sc-CO<sub>2</sub> induced crystallization. We expect that the performance of the AEMs will be improved after this new treatment.

### 6.3 Challenges and further development of catalyst for DOAFCs

As the price of gold and platinum hit the record high on the market, the catalyst development for DOAFCs will be more and more focused on non-noble metal catalysts. Although promising fuel cell performances have been achieved from non-Pt catalysts, particularly Pd based catalysts, further improvement on catalytic activity, catalyst stability and selectivity (on cathode) still remains as the major challenges.

Due to the complicated structure of multi-carbon fuels, complete oxidation is difficult to accomplish. For example in glucose oxidation, 24 electrons can be produced from complete oxidation:



However, under the current experimental conditions, glucose is oxidised to gluconic acid in alkaline media but with only two electrons transferred for each glucose molecule.<sup>121</sup> Also because of formation of a large amount of intermediates during oxidation, the poisoning effect caused by the intermediates on catalysts could affect the lifetime of the fuel cells. For anode oxidation, novel catalysts able to completely oxidise complex carbohydrates are vital for further development of DOAFCs.

For cathode, oxygen reduction is still the main reaction for receiving electrons. A cathode catalyst with high selectivity unaffected by fuel crossover, and promoting a four-electron transfer process to avoid the H<sub>2</sub>O<sub>2</sub> producing two-electron pathway for oxygen reduction reaction is highly desirable.

To overcome the challenges, composite catalysts with binary, ternary and even quaternary compositions other than single metal composition can offer a way to introduce desired properties to the catalysts. Applications of catalyst promoters such as metal oxides and Au have shown promising improvements on Pt catalyst activity.<sup>55,142</sup>

Recently developed N-doped carbon material showed remarkable activity for ORR in alkaline media. However, the exact mechanisms of the reactivity of NCNT are still not clear. There was a direct correlation observed between the nitrogen content and the number of reducing sites on carbon.<sup>83</sup> The reductive character in high N-doped NCNT resulted in a rise in pyridinic type N functionalities, which could enhance the chemical reactivity of NCNT. Further research on such material on better understanding of the reaction mechanisms and improvement in catalytic activity are essential to make NCNT an alternative cathode ORR catalyst for DOAFCs.

Catalyst substrates can largely influence catalyst activity and stability. Carbon materials have been commonly used as the supporting substrates for catalysts but carbon corrosion also causes catalyst degradation and activity losses.<sup>143–148</sup> In PEMFCs, novel catalyst substrates ranging from tungsten carbide WC,<sup>149</sup> TiO<sub>2</sub>,<sup>150–153</sup> conductive ceramics of TiB<sub>2</sub>,<sup>154</sup> TiN,<sup>155</sup> nanocomposite substrates of WC and TiO<sub>2</sub><sup>156</sup> to polypyrrole modified carbon nanotubes<sup>157</sup> as well as nanoscale graphite<sup>158</sup> have been investigated. The durability and high surface area of these substrates provide the catalysts and fuel cell with much improved stability and lifetime, and the catalyst loading can also be reduced. These properties are equally important in DOAFC systems. In order to enhance the catalyst and fuel cell performance and lifetime, novel catalyst substrates will need to be employed and investigated for DOAFCs.

#### 6.4 Further development of DOAFC systems

Rapid development in solid polymer membranes suggests that AEM based alkaline fuel cells will be the dominant type of DOAFCs for various applications.

In addition to AEMFCs, the DOAFC system development will also divert to different directions for various applications.

(1) Membraneless microscale alkaline fuel cells for small and portable electronic devices.

By eliminating the membrane from the system, it enables compact fuel cell design suitable for miniaturised or microscale electronics. Microfluidics,<sup>159–161</sup> planar microchannel,<sup>162</sup> laminar flow<sup>97,163</sup> and mixed reactant systems<sup>98</sup> can be used to give the system more flexibility for fuel handling and electrolyte media.

(2) An alkaline electrolyser and a combined system for hydrogen and other chemical generation.

A new avenue of applying DOAFC technology in redox flow batteries, electrolysis to produce hydrogen, can be another way for energy production and storage. Hydrogen production from methanol using a PEM electrolyser was reported in 2008 by Sasikumar *et al.*<sup>164</sup> Ammonia was studied by Hejze *et al.* in a combined system of AFCs as a hydrogen carrier.<sup>165</sup> For an electrolyser using anion exchange membranes, catalyst and membrane development for hydrogen evolution from alcohol and sodium borohydride are still a new area to explore.<sup>166,167</sup> Hydrogen generation from the systems can provide on-site hydrogen generation for mobile applications.

Bianchini *et al.* investigated the selective conversion of ethanol into acetic acid in a direct fuel cell containing a non-Pt electrode and an AEM.<sup>60</sup> This broadens up a new path to use AEMFC to produce specific chemicals.

DOAFC has special advantages over PEM fuel cells providing the possibility of developing versatile power source systems with low cost membrane and catalyst materials for various applications. We envisage that DOAFCs will play a major role in energy research and applications in the near future.

#### Acknowledgements

The authors thank Preshant Subhas Khadake for providing materials and valuable discussion, and Newcastle University URC visiting fellowship for Lei Li.

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