Francisco Javier Rodríguez-Varela
Teko W. Napporn *Editors*

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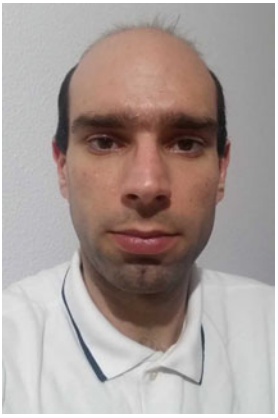

R. Oliveira is currently a research fellow in the University of Trás-os-Montes and Alto Douro at Chemistry Center of Vila Real (CQ-VR) in Vila Real, Portugal, where he performs research activities on ecofriendly catalysts for direct ethanol fuel cells, especially electrochemical experiments to evaluate Pd-based catalysts. He obtained master's degree in Chemical Engineering from the University of Akron in Ohio, USA, with a research thesis on natural corrosion inhibitors for carbon steel in ethanol media, always demonstrating a great interest in the electrochemistry field.

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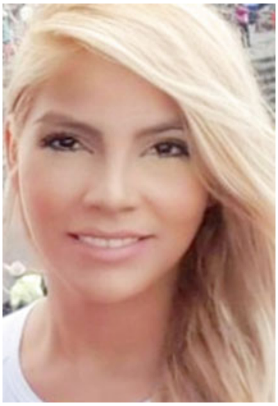

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Chapter 1
Introduction: Low-Temperature Fuel Cells

T. W. Napporn, A. Mokrini, and F. J. Rodríguez-Varela

Abstract This chapter describes the reactions occurring in low-temperature fuel cells, fuelled with from the most common H_2, to several organic molecules. The differences in the complexity of the anode reactions and their effect on the energy that may be generated from the fuel cells are discussed. It is established that, even though H_2/O_2 fuel cells are the most performing in terms of power density for large-demand systems, the use of liquid fuels is advantageous for several low-power applications. The performance of nanostructured anode and cathode catalysts in complete fuel cell systems is also covered. It is indicated that in alkaline media, some non-Pt nanocatalysts have a high catalytic activity, particularly for the ORR. Even more, the recent advances in polymer electrolyte membranes are shown, from the widely used commercial Nafion®, to the more recently developed anionic polymers for anion exchange membrane fuel cells. It is concluded that compatibility of composite and blend materials with the host ionomer is critical for the development of stable low-temperature fuel cells.

Keywords Proton exchange membrane fuel cells (PEMFC) · Anion exchange membrane fuel cells (AEMFC) · Perfluorosulfonic-acid membranes (PFSA) · Direct methanol AEMFCs (DM-AEMFCs) · Direct ethanol AEMFCs (DE-AEMFCs) · Direct ethylene Glycol AEMFCs (DEG-AEMFCs) · Direct glycerol AEMFCs (DG-AEMFCs) · Non-platinum group metal (PGM) · Perfluorinated PEMs · Nafion® membranes · Partially fluorinated PEMs · Hydrocarbon PEMs · Anion exchange

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F. J. Rodríguez-Varela, T. W. Napporn (eds.), *Advanced Electrocatalysts for Low-Temperature Fuel Cells*, https://doi.org/10.1007/978-3-319-99019-4_1 membranes (AEMs) · Hydrogen oxidation reaction (HOR) · Tafel reaction · Heyrovsky reaction · Volmer reaction · Oxygen reduction reaction (ORR) · Rotating ring disk electrode (RRDE) · Koutecky–Levich plots

1.1 Introduction

Proton exchange membrane and anion exchange membrane fuel cells (PEMFC and AEMFC, respectively) have gained the attention of academic and industrial research groups, due to their capacity to generate high-power density at low temperatures. Ever since the advancements in the 1960s for space industry applications, both systems have experienced to an extent a technological development to reach near-commercialization status. This is particularly the case of PEMFCs, whose performance has been greatly improved by the use of the perfluorosulfonic acid membranes and the demonstration of high interfacial area gas diffusion electrodes at Los Alamos National Laboratories [1, 2]. The new electrode structure proposed in those studies has reduced the catalyst loading (i.e., Pt) by an order of magnitude [1]. PEMFC is a more advanced technology than AEMFC. However, fuel cells using anion exchange membrane are being studied with a significant interest in recent years due to the development of chemically stable alkaline polymers and the capability of using non-noble metals to catalyze the electrochemical reactions in basic media. The following sections introduce the electrochemical reactions taking place in AEMFCs working with hydrogen and liquid fuels. Also, the performance of several nanostructured electrocatalysts in complete fuel cell systems is shown. Moreover, the latest developments in membranes for PEM and AEM fuel cells are discussed.

1.2 Electrocatalytic Reactions in Anion Exchange Membrane Fuel Cells (AEMFCs)

In first half of the twentieth century, the research in alkaline fuel cells (AFCs) led this type of cell to be considered for several applications. Francis T. Bacon worked in the development of H_2/O_2 AFCs, which resulted in demonstrative programs of capacity up to 5 kW output [1–3]. AFC systems reached a status that allowed the technology to be considered for space applications [1]. However, disadvantages of AFCs included several restrictions, among them, the need to use fuels and oxidants free of CO_2 due to the risk of carbonation with KOH and NaOH [1, 4]. Also, the management of liquid-phase electrolytes has been a relevant issue in AFCs [5]. With the development of the polymer electrolyte membrane fuel cells (PEMFCs) based on Nafion®, the research on AFCs somehow decreased, particularly in the 1990s and early twenty-first century.

Over the past decade, however, AEMFCs have received increased attention of fuel cells science and technology research laboratories [6]. First of all, it is generally acknowledged that the kinetics of the electrochemical cathode reactions in alkaline media is faster compared to their acid counterpart (i.e., PEMFCs). Also, perhaps one the most attracting characteristics of AEMFCs is the possibility of using non-PGM (Pt group metals) or non-noble metal catalysts in anodes and cathodes to promote the hydrogen oxidation reaction (HOR) and the oxygen reduction reaction (ORR) [6–9]. Even more, regardless of its relatively low operation temperature, AEMFCs can also operate with liquid fuels as an alternative to hydrogen [10–14].

In fact, it has been reported that AEMFCs can operate with a CH_4 containing 5% H_2 [15]. In spite of the capability of using different fuels, attention must be paid to the purity of the oxidant, since as mentioned CO_2-containing air leads to carbonation by reacting with OH^- anions. The report by Dekel et al. indicates that bicarbonate (HCO_3^-) and carbonate (CO_3^{2-}) anions are formed, changing the anion composition of the anion exchange membrane [16]. Thus, the use of air as oxidant which may contain CO_2 decreases the cell performance [16, 17].

Nevertheless, the promoted attraction offered recently by AEMFCs can be attributed to the important advances in high-performance anion exchange membranes, even though one relevant issue is the ionomer stability [6, 18–20]. As pointed out by Varcoe et al., the first publication of the so-called alkaline membrane fuel cells (AMFCs) appeared in 2005 [18]. Ever since, the number of publications has clearly increased. Dekel has reported that the number of reports has overpassed 2000 in the 2013–2017 period (Fig. 1.1) [6]. Evidently, advances in the different components of AEMFCs other than membranes, including high performance and durable catalysts, will impulse the research and applications of this technology to new grounds.

In the following sections, the electrocatalytic reactions in AEMFCs fuelled with different fuels are given. The selection of fuels goes from H_2, to several of the most common C-containing fuels: methanol (CH_3OH), ethanol (C_2H_5OH), ethylene glycol ($C_2H_6O_2$), and glycerol ($C_3H_8O_3$). Each of the liquid fuels introduces cost and energetic advantages and disadvantages. But perhaps it is worth analyzing their use from a sustainability point of view, and therefore the feasibility of obtaining them from biomass resources.

1.2.1 H_2/O_2 AEMFCs

In terms of power density and catalyst durability, the most performing AEMFC is the H_2/O_2 cell. A power density of 1.4 W cm^{-2} has been reported by Varcoe et al., with the cell operating at 60 °C, equipped with an AEM based on radiation-grafted ethylene tetrafluoroethylene and PtRu/C (anode) and Pt/C (cathode) catalysts [21]. The same research group has reported the performance of an H_2/O_2 AEMFC with non-PGM cathode catalysts (1.0 mg_{Ag} cm^{-2}) having a power density above 1 W cm^{-2} [22]. The stability of H_2/O_2 AEMFCs has also been evaluated. Yu et al.

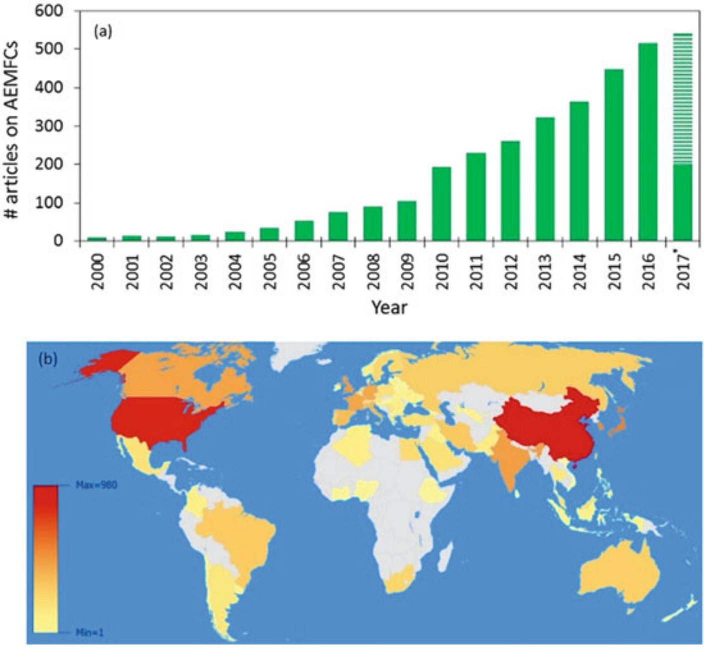


Fig. 1.1 (**a**) Reports published in the 2013–2017 period covering research on AEMFCs, (**b**) distribution by country of origin (reproduced from Ref. [6] with kind permission of © Elsevier)

have tested a cell for 500 h, with a decrease in cell voltage of 0.22 mV h^{-1}. The cell used quaternary ammonium SEBS as the ionomer [23].

In H_2/O_2 AEMFCs the electrochemical anode and cathode half-cell reactions, as well as the overall cell reaction, with their corresponding potentials at standard conditions are:

Anode reaction:

$$2H_2 + 4OH^- \rightarrow 4H_2O + 4e^-, E_a^o = 0.83 \text{ V vs.SHE} \tag{1.1}$$

Cathode reaction:

$$O_2 + 2H_2O + 4e^- \rightarrow 4OH^-, E_c^o = 0.40 \text{ V vs.SHE} \tag{1.2}$$

Overall:

$$2H_2 + O_2 \rightarrow 2H_2O, E_{\text{cell}} = 1.23 \text{ V} \tag{1.3}$$

H_2/O_2 AEMFCs are attractive from an economical point of view because of the feasibility of using non-PGM catalysts for the ORR and for the HOR [24]. However, it should be mentioned that high performances have been reported when using catalysts such as Ir or Pd to promote the HOR either in half-cell experiments or in full AEMFC tests [25, 26].

1.2.2 Direct Methanol AEMFCs (DM-AEMFCs)

The enhanced kinetics of the methanol oxidation reaction (MOR) in 0.5 mol/l K_2CO_3 and 1 mol/l $KHCO_3$ electrolytes compared with a 0.5 mol/l H_2SO_4 solution, foreseen the use of CH_3OH in AEMFCs, has been discussed by Zhuang et al. [27]. By performing in-situ FTIR analysis, the authors concluded that methanol could be oxidized to CO_2 in those alkaline solutions. Scott and Hao have evaluated extensively a direct methanol alkaline fuel cell using Pt/C anode and cathode catalyst. The cell performance increased at higher temperatures (up to 60 °C). On the other hand, with the anion exchange membranes used, the crossover of methanol to the anode increased at higher fuel concentrations [28]. Kim et al. have reported the same effect in an air-breathing direct methanol fuel cell with anion exchange membrane when increasing the CH_3OH concentration from 7 to 10 M [29]. Even though it has been reported that AEMFCs fuelled with methanol are less performing compared to other liquid fuels [30], Bianchini et al. reported an enhanced performance of a direct methanol AEMFC at 60 °C with a Pd/MWCNT anode, compared to ethanol and glycerol [31].

In DM-AEMFCs the electrochemical reactions are:

Anode reaction:

$$\mathrm{CH_3OH} + 6\mathrm{OH}^- \rightarrow \mathrm{CO_2} + 5\mathrm{H_2O} + 6\mathrm{e}^-, E_a^o = -0.81\ \mathrm{V\ vs.SHE} \tag{1.4}$$

Cathode reaction:

$$3/2\mathrm{O_2} + 3\mathrm{H_2O} + 6\mathrm{e}^- \rightarrow 6\mathrm{OH}^-, E_c^o = 0.40\ \mathrm{V\ vs.SHE} \tag{1.5}$$

Overall:

$$\mathrm{CH_3OH} + 3/2\mathrm{O_2} \rightarrow \mathrm{CO_2} + 2\mathrm{H_2O}, E_{\mathrm{cell}} = 1.21\ \mathrm{V} \tag{1.6}$$

1.2.3 Direct Ethanol AEMFCs (DE-AEMFCs)

The use of ethanol in fuel cells is of interest, since this organic molecule is considered a carbon neutral and sustainable fuel [32]. Even more, bioethanol from biomass has been used as the fuel in DE-AEMFCs, where a power density of ca. 90 mW cm^{-2} has been generated using a dealloyed PtCo/CNT anode catalyst [33]. A power density of around 50 mW cm^{-2} has been obtained elsewhere using Pd-based catalysts at the anode fuelled with 1.0 mol L^{-1} ethanol +0.5 mol L^{-1} NaOH [34]. In their study, Fujiwara et al. have compared the performance of DEFCs equipped with anion and cation exchange membranes [35]. The power density generated with the AEM was about ten times higher, compared to the cationic counterpart. Nevertheless, due to the low OH^- conductivity of the membrane, 0.5 mol L^{-1} KOH had to be provided along with the 1.0 mol L^{-1} ethanol fuel at the anode in order to sustain a high performance. Recently, a passive DE-AEMFC stack delivering a peak power density of 38 mW cm^{-2} at room temperature, using PdNi/C anode catalysts and $FeCuN_4$/C cathode catalysts, has been demonstrated by Zhao and Li [36].

The electrochemical reactions in DE-AEMFCs are:

Anode reaction:

$$C_2H_5OH + 12OH^- \rightarrow 2CO_2 + 9H_2O + 12e^-, E_a^o = -0.74\ \text{V vs.SHE} \quad (1.7)$$

Cathode reaction:

$$3O_2 + 6H_2O + 12e^- \rightarrow 12OH^-, E_c^o = 0.40\ \text{V vs.SHE} \quad (1.8)$$

Overall:

$$C_2H_5OH + 3O_2 \rightarrow 2CO_2 + 3H_2O, E_{\text{cell}} = 1.14\ \text{V} \quad (1.9)$$

1.2.4 Direct Ethylene Glycol AEMFCs (DEG-AEMFCs)

Ethylene glycol (EG) has been used in fuel cells as a feasible alternative to replace methanol and ethanol. For this application, $C_2H_6O_2$ is safer to handle than methanol, is less toxic than methanol and ethanol, and its electron transfer rate is higher during oxidation than ethanol [37–39]. EG can also be produced from biomass and its partial selective oxidation in a DEG-AEMFC can generate valuable oxalic acid without CO_2 emissions [40]. The power density generated from a DEG-AEMFC at 60 °C has been shown to become higher by increasing the fuel concentration from 0.5 to 1.0, but decreases with 2 mol L^{-1} $C_2H_6O_2$ (with a KOH concentration of 1 mol L^{-1}) [39]. Such cell used an alkali-doped PBI membrane. Cremers et al. have compared the performance of DEG-AEMFCs equipped with KOH-doped PBI and a quaternary amine alkaline AEM, with the later generating a higher power density [41]. KOH-doped Nafion ® has also been used by Forbicini et al. in a DEG-AEMFC [42]. Evidently, DEG-AEMFCs equipped with several formulations of AEMs have been tested [43, 44]. It has been reported that the power density generated by

DEG-AEMFCs is higher than those of fuel cells fuelled with methanol, ethanol, and 1,2-propanediol, but slightly lower than in the case of glycerol [10, 44–46].

The electrochemical reactions in DEG-AEMFCs are:

Anode reaction:

$$C_2H_6O_2 + 10OH^- \rightarrow 2CO_2 + 8H_2O + 10e^-, E_a^o = -0.81\ \text{V vs.SHE} \quad (1.10)$$

Alternatively, the partial oxidation of EG to oxalate is [44]:

$$C_2H_6O_2 + 10OH^- \rightarrow (COO^-)_2 + 8H_2O + 8e^-, E_a^o = -0.81\ \text{V vs.SHE} \quad (1.11)$$

Cathode reaction:

$$5/2O_2 + 5H_2O + 10e^- \rightarrow 10OH^-, E_c^o = 0.40\ \text{V vs.SHE} \quad (1.12)$$

Overall:

$$C_2H_6O_2 + 5/2O_2 \rightarrow 2CO_2 + 3H_2O, E_{\text{cell}} = 1.21\ \text{V} \quad (1.13)$$

1.2.5 Direct Glycerol AEMFCs (DG-AEMFCs)

Glycerol has several advantages for fuel cell applications: it has a relatively low toxicity, high energy density, its crossover rate is low, and is relatively inexpensive [47, 48]. It is also a versatile fuel, since DG-AEMFCs have been operated as co-generators of electricity and valuable chemicals [49, 50]. Pt and Pd-based catalysts are normally used as anode catalysts in DG-AEMFCs [47, 48, 51–54]. However, Au-based nanomaterials have also shown a high catalytic activity for the oxidation of the molecule [49, 50, 55]. Li et al. have demonstrated a higher power density generated by a DG-AEMFC in the 50–80 °C temperature range with an Au/C anode (1.0 mol L^{-1} glycerol +2.0 mol L^{-1} KOH, Fe-Cu-N_4/C cathode), compared to a PEM DGFC at 90 °C (1.0 mol L^{-1} glycerol, PtRu/C anode, Pt/C cathode) [55]. It has been shown also that higher power density is generated from the DG-AEMFC, relative to DM and DEG-AEMFCs, with the same fuel concentration [55].

One more advantage of glycerol is that it can be used in its crude composition as obtained from the bio-diesel manufacturing industry, as reported by Li′s group [51, 54–56]. Crude glycerol is cheaper than refined glycerol, methanol, and ethanol [56]. Using 1.0 mol L^{-1} crude glycerol (+ 2.0 mol L^{-1} KOH), a DG-AEMFC generated a power density of ca. 40 mW cm^2 (anode: Au/C; cathode: Fe-Cu-N_4/C; AEM: A201, 28 mm, Tokuyama, 80 °C) [55].

The electrochemical reactions in DG-AEMFCs are shown below. According to some workers, the oxidation of glycerol in alkaline media may proceed through the formation of glycerate or tartronic acid [57, 58]. Following the tartronic acid route:

Anode reaction [58]:

$$C_3H_8O_3 + 8OH^- \rightarrow C_3H_4O_5 + 6H_2O + 8e^-, E_a^o = -0.77\ \text{V vs.SHE} \tag{1.14}$$

$$C_3H_4O_5 + 2OH^- \rightarrow (C_3H_2O_5)^{2-} + 2H_2O \tag{1.15}$$

Cathode reaction:

$$2O_2 + 4H_2O + 8e^- \rightarrow 8OH^-, E_c^o = 0.40\ \text{V vs.SHE} \tag{1.16}$$

Overall:

$$C_3H_8O_3 + 2O_2 + 2OH^- \rightarrow (C_3H_2O_5)^{2-} + 4H_2O, E_{\text{cell}} = 1.17\ \text{V} \tag{1.17}$$

1.2.6 AEMFCs Operating with Other Fuels

Other fuels have been evaluated at AEMFCs. For example, the reactions at direct borohydride (DB, Eqs. 1.18, 1.19, and 1.20) and direct formate (DF, Eqs. 1.21, 1.22, and 1.23) AEMFCs are [13, 59]:

For DB-AEMFCs:

Anode reaction:

$$BH_4^- + 8OH^- \rightarrow BO_2^- + 6H_2O + 8e^-, E_a^o = -1.24\ \text{V vs.SHE} \tag{1.18}$$

Cathode reaction:

$$O_2 + 2H_2O + 4e^- \rightarrow 4OH^-, E_c^o = 0.40\ \text{V vs.SHE} \tag{1.19}$$

Overall:

$$BH_4^- + 2O_2 \rightarrow BO_2^- + 2H_2O, E_{\text{cell}} = 1.64\ \text{V} \tag{1.20}$$

and

For DF-AEMFCs:

Anode reaction:

$$HCOO^- + 3OH^- \rightarrow CO_3^{2-} + 2H_2O + 2e^-, E_a^o = -1.05 \text{ V vs.SHE} \quad (1.21)$$

Cathode reaction:

$$1/2O_2 + H_2O + 2e^- \rightarrow 2OH^-, E_c^o = 0.40 \text{ V vs.SHE} \quad (1.22)$$

Overall:

$$HCOO^- + 1/2O_2 + OH^- \rightarrow CO_3^{2-} + 2H_2O, E_{cell} = 1.45 \text{ V} \quad (1.23)$$

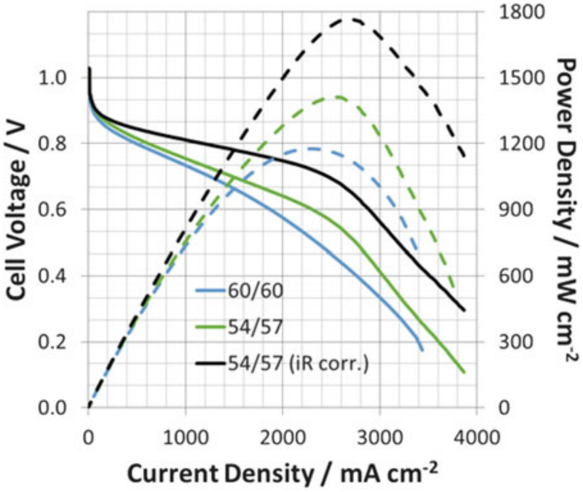
Additionally, Ogumi et al. compared the performance of fuel cells fed with the polyalcohols, erythritol and xylitol, with those of ethylene glycol, glycerol, and methanol. It has been concluded that the higher power density is delivered by using ethylene glycol with the AEMFC operating at 323 K, with a Pt-Ru/C anode and Pt/C cathode [30].

1.3 Performance of Several Types of Nanostructured Anodes and Cathodes in AEMFCs

As discussed in Sect. 1.1, several fuels are being used in AEMFCs, from H_2 to organic molecules. Advantages and disadvantages of each of them seem to be clear. Higher power densities can be delivered by H_2/O_2 AEMFCs due to the high reactivity of the gaseous fuel. Also, the absence of C atoms avoids the need of C–C bonds cleavage and the formation of reaction intermediates such as CO_{ads} during the HOR. However, hydrogen is not freely available in nature and must be produced, mainly from hydrocarbons. Renewable hydrogen, i.e., from water electrolysis using solar or wind resources, is feasible, but still more expensive than natural gas reforming on a large-scale basis.

On the other hand, easier handling of the fuels compared to H_2 can be achieved with liquid molecules. Very important from a sustainability point of view, some of the organic fuels can be produced from biomass resources. Nevertheless, the power density obtained from AEMFCs is lower when fuelled with such liquid molecules relative to hydrogen [6]. Moreover, the operational problems caused by the cross-over phenomena remain in AEMFCs (to a less extent than in PEMFCs) using methanol, ethanol, or other liquid fuels. Therefore, the selection of nanostructured cathode catalysts is of high relevance to avoid depolarization losses caused by crossed fuel or reaction intermediates. As mentioned earlier, the kinetics of the ORR in alkaline media is faster than in acid electrolytes, allowing for the use of a number of high-performance cathodes, from Pt/C and Pd/C (and their alloys or composite materials with metal oxides), to non-PGM and metal-free nanocatalysts. Taking advantage of this variety that includes low-cost nanomaterials, AEMFCs may be a cheaper technology than PEMFCs.

Fig. 1.2 Polarization curves of H_2/O_2 AEMFCs. Experimental conditions with 54/57 anode/cathode dew points: anode: 0.67 mg_{PtRu} cm^{-2} on 5% PTFE, cathode: 0.53 mg_{Pt} cm^{-2} on 5% PTFE GDL. Cell temperature: 60 °C (adapted from Ref. [21], reproduced with kind permission of © Elsevier)



Recent reports show the performance of AEMFCs under different operating conditions. Using a 0.53 mg_{Pt} cm^{-2} Pt/C cathode (40 wt. %), a power density of 1.4 W cm^{-2} has been delivered by a H_2/O_2 AEMFC operating at 60 °C (with an ETFE-g-VBCTMA membrane) as seen in Fig. 1.2 [21]. Power densities of 1.16 and 0.91 W cm^{-2} have been obtained from H_2/O_2 AEMFCs operating at 60 °C, with Pt/C cathodes, PtRu/C anodes, and RG-AEM(Cl^-) membranes [60]. The same group has reported a H_2/O_2 AEMFC delivering power densities of 1.1 and 0.699 W cm^{-2} using a non-Pt cathode (Ag/C, 1.0 mg_{Ag} cm^{-2}), operating with O_2 and CO_2-free air, respectively [22]. It has been reported by the authors that the Ag/C outperformed a Pt/C cathode with CO_2-free air at the cathode. Elsewhere, a peak power density of 1.0 W cm^{-2} has been reported with a H_2/O_2 AEMFC equipped with commercial Pt/C cathode and PtRu/C anode (metal loadings of 0.4 mg cm^{-2}) membrane of the aQAPS-Sx type and $T_{cell} = 60$ °C [61]. Also, a Pt-free H_2 (dry)/Air (<10 ppm CO_2) AEMFC operating at 73 °C delivered a power density of 0.5 W cm $^{-2}$ (cathode: Ag, 3.0 mg_{Ag} cm^{-2}; anode: Pd/C-CeO_2) [26]. Moreover, a H_2 (dry)/Air (CO_2 free) AEMFC with a silver-based alloy (3.0 mg cm^{-2}) cathode and a Pd/Ni anode generated 0.4 W cm^{-2} power density at 73 °C [62].

It is therefore feasible to use non-Pt cathode catalysts and yet generate high-power densities not only from H_2/O_2 AEMFCs, but also from fuel cells using liquid fuels. Mesoporous Fe/N/C cathode catalysts with highly active Fe-Nx/C sites have been used in a H_2/O_2 AEMFC (A901 membrane, Tokuyama), exhibiting 40% higher power density (0.272 W cm^{-2}) than commercial Pt/C in single-cell tests with $T_{cell} = 50$ °C. The high performance of the non-Pt catalyst has been in part attributed to large pores in the mesoporous structure, which resulted in a high surface area and accessibility to the active sites [63]. Elsewhere, a H_2/O_2 AEMFC (membrane Tokuyama A201) containing a Fe-NMG (a type of Fe-N-C) cathode catalyst and Pt/C anode generated 0.218 W cm^{-2}, a higher value than 0.2 W cm^{-2} of a cell with Pt/C cathode and anode catalysts with $T_{cell} = 70$ °C (Fig. 1.3) [7]. A H_2/O_2 AEMFC

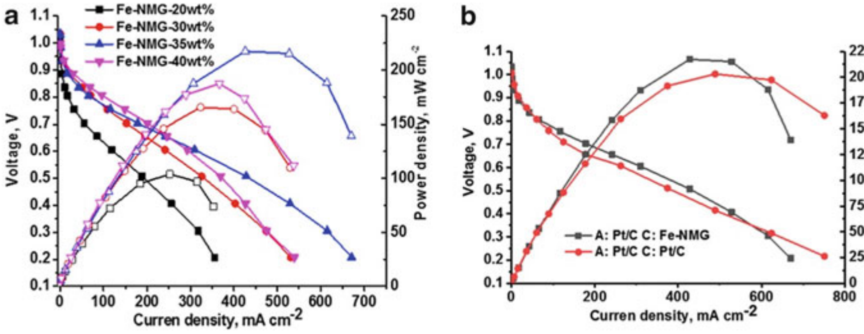


Fig. 1.3 Polarization curves of AEMFCs with (**a**) Fe-NMG cathodes at different ionomer concentration, (**b**) comparison of the performance of MEAs having Fe-NMG cathode and Pt/C anode catalysts, and Pt/C catalysts on both anode and cathode (reproduced from Ref. [7] with kind permission of © Elsevier)

composed of CoPPY/C-based cathodes and Ni-W-based anodes produced 0.04 W cm^{-2} at 60 °C, with a membrane of the xQAPS type [64].

Other types of AEMFCs have also reached a good development. It has been reported that a DM-AEMFC may produce 0.046 W cm^{-2} at 60 °C with Fe_2O_3/Mn_2O_3 (3:1) cathode and PtRu/C anode, and a polymer fiber membrane [65]. Elsewhere, a DM-AEMFC with MnO_2 cathode catalyst (membrane: Q-PVA/PECH; anode: PtRu/C) generates a maximum power density of 0.022 W cm^{-2} at 25 °C [66]. Using a similar cathode composition and a PVA/HAP membrane, an air-breathing DM-AEMFC has generated 0.011 W cm^{-2} at 25 °C (Ti-based anode with PtRu black) [67]. Recently, mesoporous 3D nitrogen-doped yolk-shelled carbon spheres have been used as cathodes in a DM-AEMFC, delivering 0.056 and 0.141 W cm^{-2} at 25 and 60 °C, respectively (polymer fiber membranes; PtRu anodes) [68].

Non-noble Fe-N-C catalyst has also been used in a DE-AEMFC, reaching a power density of 0.062 W cm^{-2} with 50 wt. % Nafion® content, Pt-Ru/C anode, and KOH-doped PBI membrane (T_{cell} = 90 °C) [8]. A higher power density (0.335 W cm^{-2}) has been generated by a DE-AEMFC equipped with a Fe-Co/C cathode, anode of the combined Pd/TNTA-web type, T_{cell} = 80 °C, and Tokuyama A201 membrane [45]. With these components, ethanol as the fuel outperformed the use of glycerol and ethylene glycol. Other fuels have been evaluated. For example, a DEG-AEMFC based on Fe-based cathode catalyst (Acta 4020, 3.0 $mg_{catalyst}$ cm^{-2}), PdAg/CNT anode (0.5 mgPdcm^{-2}), and a Tokuyama A901 membrane delivered a power density of 0.245 W cm^{-2} at 80 °C [46]. A DG-AEMFC (crude glycerol) generated 0.268 W cm^{-2} with a Fe–Cu–N_4/C cathode (Acta 4020, 3.0 mg catalyst cm^{-2}), PtCo/CNT anode (0.5 mg_{Pt} cm^{-2}), and a Tokuyama A901 membrane [52]. A Pt-free borohydride AEMFC delivered a 0.283 W cm^{-2} using $Co(OH)_2$-PPy-C cathode and anode catalysts and a co-impregnated PVA-AER membrane, with T_{cell} = 60 °C [12]. Table 1.1 summarized the components, conditions, and peak power densities delivered by several types of AEMFCs.