Air-breathing polymer electrolyte fuel cells: A review

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A B S T R A C T

Air-breathing polymer electrolyte fuel cells have become a promising power source to provide uninterrupted power for small electronic devices. This review focuses primarily on describing how the air-breathing PEFC performance is improved through optimisation of some key parameters: the design and material of the current collector; the design and material of the cathode gas diffusion layer; the catalyst layer; and cell orientation. In addition, it reviews the impact of the ambient conditions on the fuel cell performance and describes the methods adopted to mitigate the effects of extreme conditions of ambient temperature and humidity. Hydrogen storage and delivery technologies used in air-breathing fuel cells are then summarised and their design aspects are discussed critically. Finally, the few reported air-breathing fuel cell stacks and systems are reviewed, highlighting the challenges to the widespread commercialisation of air-breathing fuel cell technology.

1. Introduction

Hydrogen fuel cells have been a central element in what is known as the "hydrogen economy", where hydrogen is produced from zero/low carbon technologies (e.g., water electrolysers powered by wind turbines), and where the overarching aim is to mitigate the detrimental consequences of global warming [1–3]. Due to their low operating temperature, high efficiency, and fast starting speed, polymer electrolyte fuel cells (PEFCs) are the fuel cell of choice for a magnitude of automotive, stationary, and portable applications [4–6]. Fuel cells designed to power portable applications are classified as battery replacement where the output power is typically under 100 W and portable power generators where the output power is normally up to 1 kW [7,8]. The scope of this review paper is mainly centred on the first classification, i.e., the battery-replacement PEFCs. As it is evident from this classification, the aim here is not to reduce CO_2 emissions but to replace batteries, which normally contain toxic heavy metals whose disposal poses an environmental challenge [9].

The portable fuel cell has the main advantage that the time taken between charges is significantly longer than batteries, potentially several days versus hours for batteries [10]. However, typical consumer devices require to be reasonably handled by consumers and thus the size and weight of the fuel cell powering these devices need to be significantly reduced to seriously compete with ever-improving batteries [11]. The cost of these fuel cells also needs to be significantly reduced to increase their competitiveness in the consumer device markets [12].

Conventional PEFCs require devices to store oxidant and fuel and pumping devices to supply the oxidant and fuel to the reaction sites in the fuel cell. Further, these reactant gasses normally need to pass through humidifiers to initially humidify the membrane electrolyte and make it functional. Evidently, these conventional PEFCs with all the above ancillary components are not an attractive option for small portable applications where size, weight, and cost play a vital role when selecting the powering devices. Therefore, most of these ancillary components should be removed in order for PEFCs to become competitive with the batteries used in small consumer devices. As the output power required to power the consumer devices is relatively small, it turns out that, in fact, most of the above-mentioned ancillary components could be removed without compromising the main functions of the fuel cell. Namely, the cathode compartment is made open so that oxygen is directly extracted from the ambient air through the process of natural convection, removing the requirement for an oxidant storage device, a pumping device to apply it to the fuel cell, as well as the valves and the

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Nomenclature

Roman symbols

a	Water activity
c_f	Fixed charge site concentration in membrane, mol/m^3
C_p	Specific heat of fluid at constant pressure, $J/(kg.K)$
D	Diffusion coefficient, m^2/s
F	Faraday's constant, C/mol
g	Gravitational acceleration, m/s^2
h	Heat transfer coefficient, $W/(m^2.K)$
h_m	Mass transfer coefficient, m/s
i	Electric current, A
I	Current density, A/m^2
k	Permeability of porous media, m^2
k_{eff}	Effective thermal conductivity, $W/(m.K)$
k_p	Hydraulic permeability of membrane, m^2
k_φ	Electro-kinetic permeability of membrane, m^2
M	Molecular weight, kg/m^3
n_d	Electro-osmotic drag coefficient
P	Pressure, atm
S	Source terms of governing equations in Table 4
T	Temperature, K
$\vec{V}$	Superficial velocity vector, m/s
V_{cell}	Overall cell potential, V
Y	Mass fraction
z_f	Charge of sulfonate site in membrane

Greek symbols

ε	Porosity
η	Surface over potential, V
λ	Water content
μ	Dynamic viscosity, $kg/(m.s)$
ρ	Density, kg/m^3
σ	Electrical/ionic conductivity, S/m
$\vec{\tau}$	Stress tensor, $kg/(m.s)^2$

Subscripts and superscripts

a	Anode
c	Cathode
eff	Effective value
f	Fluid
i	Species i
m	Membrane
ref	Reference
s	Solid
sat	Saturation
∞	Ambient

Abbreviations

GDL	Gas Diffusion Layer
MEA	Membrane Electrode Assembly
MPL	Microporous Layer
PEFC	Polymer Electrolyte Fuel Cell

flow controllers. Likewise, the water vapour that is required to initially humidify the membrane electrolyte at the start-up of the fuel cells is directly extracted from the ambient air, avoiding the need for a humidifier at the anode side of the fuel cell. All the above arrangements greatly simplify the PEFC system powering small consumer devices and make them much more technically and economically competitive with batteries. This simplified type of fuel cell is normally termed an air-breathing PEFC and this is due to the passive way to supply oxygen to the cathode of the fuel cell.

Currently, there are only two examples where air-breathing PEFCs experience market penetration. High-tech military-related portable electronics, such as night vision devices, personal cooling systems, radios, and computers, are normally used for various purposes in hostile environments, where recharging the devices is a challenge. Hence, a fast-growing deployment of air-breathing PEFCs into portable military electronic devices has been observed, and this is primarily due to long times between recharges and the light weight of the air-breathing fuel cell [13]. Furthermore, air-breathing PEFCs have been used as implantable power sources (e.g., biosensors and pacemakers) or in the operation of robots used in biomedical applications [14,15]. Their

potential use, however, is wider than these specialised applications, and Table 1 lists more small electronic devices and their corresponding power requirements where air-breathing PEFCs could potentially be used.

Notably, numerous review papers on the conventional PEFCs have been published, for example, [17–22]; however, to the best of the authors' knowledge, there have been no comprehensive review papers on air-breathing PEFC. Kurnia et al. [23] recently reviewed the open cathode PEFCs, including forced-convection and air-breathing PEFCs. However, they did not cover some important aspects of air-breathing PEFCs including some components (e.g., gas diffusion layers, catalyst layers, and hydrogen cartridge) and system designs, which have been thoroughly covered and discussed in this review paper. Namely, this review provides up-to-date research trends and reports on various aspects of air-breathing PEFCs that involve their mathematical models, components, stacks, systems, and applications; thus ultimately providing much better insights on how to improve their efficieny and cost-effectiveness. Also, the review discusses the challenges that face the air-breathing PEFC technology and the potential future work that could be unertaken to boost the penetration of this clean technology into the marketplace. The layout of this review paper is as follows: it first provides a general description of the main components and the working principles of the air-breathing PEFC in Section 2. It then lists and describes the equations that are normally used to create air-breathing PEFC mathematical models in Section 3. Section 4 looks into various ways that have been adopted in the literature to optimise the designs and the materials to maximise the performance of the air-breathing PEFC. The impact of ambient conditions in terms of temperature and humidity is reviewed in Section 5. Hydrogen delivery, air-breathing PEFC stacks, and systems are reviewed in Sections 6, 7, and 8, respectively. Section 9 discusses the present state of air-breathing PEFC and provides recommendations for future work. Finally, the main points of the review are summarised in the last section.

Table 1
Power requirements for portable small electronic devices [8,10,16].

Electronic Devices	Power Requirements
Cellular phone	1 W
Smartphone	2 W
iPhone	2 W
Video camera	1–10 W
Laptop	20–40 W
Tablet personal computer	10 W
Robot	10–15 W
Toy car	5–15 W
Toy airplane	110 W/kg
PlayStation portable	2 W
Flashlights	1–10 W
Insulin pump	10 mW

2. Overview of air-breathing PEFC

An air-breathing PEFC is a portable electrochemical device in which oxygen is taken directly from the ambient air by natural convection and reduced at the cathode and hydrogen is supplied as fuel from a storage device to the anode where it is oxidised. The key components for this type of fuel cell are shown in Fig. 1; an open cathode current collector, an anode current collector, two gas diffusion layers (GDLs), two catalyst layers, and a polymeric electrolyte. The hydrogen supplied to the air-breathing PEFC is not normally humidified [24–28]; water, which is directly extracted from the ambient air at the open cathode, should be ideally sufficient for the initial humidification of the membrane. The main functions and the commonly used materials of the fuel cell components are given in Table 2.

The polymeric electrolyte membrane, the catalyst layers, and the GDLs are assembled to form what is known as the membrane electrode assembly (MEA). The polymeric electrolyte membrane is ionically conductive, allowing protons (produced at the anode) to be transported to the cathode through the membrane. The catalyst layers are where the half-electrochemical reactions take place, and as such, they need to have voids, an electrically conductive solid phase, and a membrane electrolyte phase to allow for reacting gases, electrons, and protons to transport and/or meet. The GDL is a porous structure whose main function is to distribute the reacting gases as uniformly as possible to the catalyst layers. Also, the position of the GDLs within the fuel cell requires them to be good electrical conductors, liquid water removers and heat dissipators. The GDLs are typically coated with microporous layers to enhance electrical contact with the catalyst layer and improve water management [29,30].

The cathode in the air-breathing PEFCs is open to the ambient air to allow for the oxidant (oxygen) to be directly extracted from the ambient air through natural convection and be transported to the active areas in the cathode catalyst layer. On the other hand, hydrogen molecules are oxidised at the anode catalyst layer and split into protons and electrons. Oxygen molecules at the cathode react with protons, migrating from the anode catalyst layer through the membrane electrolyte, and electrons (forced, due to the electrically insulating nature of the membrane electrolyte, to migrate to the cathode) and form water molecules. The

Table 2
Air-breathing PEFC components: functions and materials [22,31].

Component	Main Functions	Materials
Open cathode current collector/flow field plate	• Supply of oxygen and water vapour from/to the ambient to/from the fuel cell by natural convection • Conduction of electrical charge	A variety of metallic (e.g., stainless steel) and non-metallic materials (e.g., silicon wafers and printed circuit boards (PCBs) coated with metals)
Anode current collector/flow field plate	• Supply of hydrogen to the fuel cell • Conduction of electrical charge	Graphite, carbon composite or metallic sheets
GDLs	• Uniform supply of reactant gases to the catalyst layers • Removal of excess liquid water • Conduction of electrical charge • Mechanical support to the catalyst layer • Dissipation of heat	Carbon fibre-based paper or cloth coated with a microporous layer (a mixture of PTFE and carbon black)
Catalyst layers	• Facilitating electrochemical reactions	Platinum nanoparticles supported on carbon black particles
Polymer electrolyte	• Conduction of protonic (or ionic) charge	Perfluorosulfonic acid

following are the electrochemical half-reactions and the overall reaction for the PEFCs:

$$\text{Hydrogen Oxidation Reaction (Anode)}:$$
$$H_2 \rightarrow 2H^+ + 2e^- \tag{1}$$

$$\text{Oxygen Reduction Reaction (Cathode)}:$$
$$\frac{1}{2}O_2 + 2H^+ + 2e^- \rightarrow H_2O \tag{2}$$

$$\text{Overall reaction}:$$
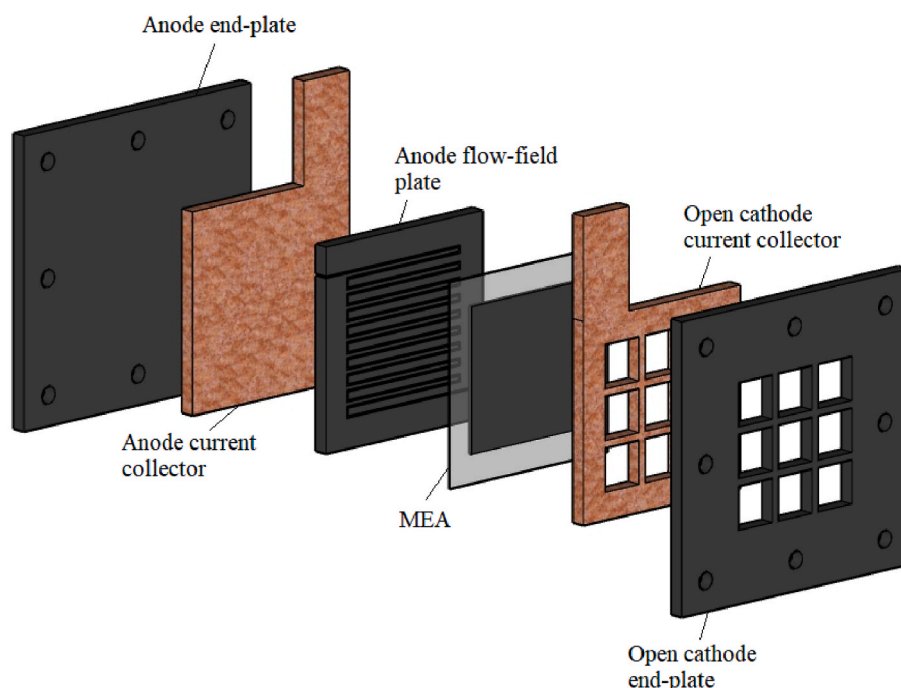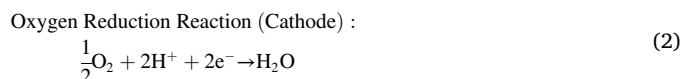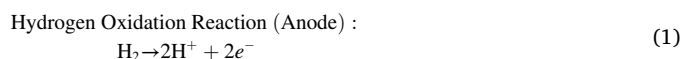$$H_2 + \frac{1}{2}O_2 \rightarrow H_2O \tag{3}$$

Fig. 1. Exploded view of an air-breathing PEFC showing its key components.

Water and most of the heat produced at the cathode catalyst layer should be adequately managed to obtain and sustain high performance. Excess water (normally in the form of liquid) results in water flooding at the cathode, thus hindering the transport of oxygen to the reactive sites in the catalyst layer. On the other hand, insufficient water leads to membrane dehydration, thus decreasing the membrane ionic conductivity and increasing the ohmic losses of the fuel cell. Likewise, thermal management is as important as water management. Excess heat may result in membrane dehydration, and a lack of heat may lead to water flooding. To this end, the amount of water and heat within the MEA of the fuel cell, particularly for air-breathing PEFCs where water and heat are passively transported, should be carefully balanced [32].

Further, in air-breathing PEFCs, the flow of air within the proximity of the open cathode of the air-breathing PEFC is driven by buoyancy effects (i.e., natural convection). Namely, the air adjacent to the surface of the heat-generating open cathode becomes relatively warm, light and in turn rises, replacing the upper and colder portion of air that flows downward adjacent to the warm open cathode. Again, this portion of air becomes relatively warm, light and in turn rises and so on [33]. Such dynamics and the fact that oxygen is consumed and water is produced at the cathode catalyst layer create gradients in temperature, oxygen and water vapour concentration which govern the heat and mass transport between the open cathode of the air-breathing fuel cell and the ambient air. As mentioned previously, the balance of water and heat within the air-breathing PEFC is crucial to avoid undesirable phenomena that degrade the fuel cell performance, such as water flooding or membrane dehydration. One of the efficient and cost-effective ways to better understand transport phenomena within air-breathing PEFCs is mathematical modelling discussed in the following section, leading to more effective designs that improve the fuel cell performance and potentially mitigate undesirable phenomena.

3. Mathematical modelling

Several modelling tools have been used in the field of fuel cells to: study the effects of some geometrical and operational parameters; understand the transport phenomena within the several components of the fuel cell; and explore the transient response of the fuel cells. In the literature, the number of models for the air-breathing PEFCs is substantially less than for the conventional PEFCs. This is evidently attributable to the significant use of the latter type of fuel cells in a wide range of applications. Typically, the use of air-breathing PEFCs is restricted to portable appliances where the small output power is required.

The models existing in the literature for air-breathing PEFCs are either: numerical, analytical or dynamic; dimensionless, one-dimensional, two-dimensional or three-dimensional; and resembling channel-based or window-based fuel cells. Table 3 lists various numerical models that have been built for air-breathing PEFCs, mentioning (among other items) their dimensionality and key findings. More details on these models are in Sections 4 and 5 where the experimental and modelling work on the optimisation of the air-breathing PEFCs and the impact of the ambient conditions on their performance are described.

For completeness, the following are brief descriptions of the mathematical equations (mainly adapted from Refs. [42,43]) that are often used to capture transport phenomena within the PEFCs, namely the equations for conservation of mass, momentum, species, charge, and energy.

The conservation of mass equation is expressed as follows:

$$\nabla \cdot \left(\rho \overrightarrow{V} \right) = S_c \tag{4}$$

where ρ is the density of the fluid, $\overrightarrow{V}$ is the superficial velocity vector, and S_c is the mass source term. Note that the mathematical expressions for all the source terms for various regions within the fuel cell are listed

in Table 4. The conservation of momentum equation is given by:

$$\nabla \cdot \left(\rho \overrightarrow{V} \overrightarrow{V} \right) = -\nabla P + \nabla \cdot \overrightarrow{\tau} + \rho \overrightarrow{g} + S_V \tag{5}$$

where P is the pressure, $\overrightarrow{g}$ is the gravity vector, $\overrightarrow{\tau}$ is the stress tensor and S_V is the momentum source term. The conservation of the chemical species equation could be expressed as follows:

$$\nabla \cdot \left(\rho \overrightarrow{V} Y_i \right) = \nabla \cdot \left(\rho D_i^{eff} \nabla Y_i \right) + S_i \tag{6}$$

where Y_i is the mass fraction of species i and S_i is the source term for species i. The effective diffusion coefficient of the species i, D_i^{eff}, is often calculated using Bruggmann's correlation [57]:

$$D_i^{eff} = \varepsilon^{1.5} \cdot D_i \tag{7}$$

where ε is the porosity of the porous medium and D_i is the bulk diffusivity of the species i, given by:

$$D_i = D_i^{ref} \left(\frac{T}{T_{ref}} \right)^{1.5} \left(\frac{P_{ref}}{P} \right) \tag{8}$$

where D_i^{ref} is the bulk diffusivity of the species i at the reference temperature (T_{ref}) and pressure (P_{ref}). The conservation of charge equation for the solid (s) or the membrane (m) phases is expressed as follows:

$$\nabla \cdot \left(\sigma_j^{eff} \nabla \varphi_j \right) + S_j = 0; \quad j = s, m \tag{9}$$

where σ_j^{eff}, φ_j, and S_j are respectively the effective electrical conductivity, the potential and the charge source term of either the solid or the membrane phase. σ_s^{eff} is given as follows:

$$\sigma_s^{eff} = \left(1 - \varepsilon_{eff} \right) \sigma_s \tag{10}$$

where σ_s is the electrical conductivity of the solid phase. On the other hand, σ_m^{eff} is given as follows:

$$\sigma_m^{eff} = \varepsilon_m^{1.5} \sigma_m \tag{11}$$

where ε_m is the volume fraction of the membrane phase which is equal to unity in the membrane electrolyte. The ionic conductivity of the membrane, σ_m, can be estimated using the well-known Springer's model [58]:

$$\sigma_m = [0.514\lambda - 0.326] \exp \left[1268 \left(\frac{1}{303} - \frac{1}{T} \right) \right] \tag{12}$$

where λ is the water content of the membrane and is calculated using the following expression:

$$\lambda = \begin{cases} 0.043 + 17.81a - 39.85a^2 + 36a^3, 0 < a \leq 1 \\ 14 + 1.4(a-1), 1 < a \leq 3 \end{cases} \tag{13}$$

where a is the water activity and is given by:

$$a = \frac{P_{H_2O}}{P_{sat}} \tag{14}$$

where P_{H_2O} is the partial pressure of water vapour and P_{sat} is the saturation pressure of water vapour which can be obtained (in atm units) by the following empirical formula [58]:

$$log_{10}P_{sat} = -2.1794 + 0.02953(T - 273.15) - 9.1837 \times 10^{-5}(T - 273.15)^2 + 1.4454 \times 10^{-7}(T - 273.15)^3 \tag{15}$$

However, Ismail et al. [50] and Litster and Djilali [59] reported that at low humidity operating conditions, the Springer model results in unrealistic predictions for the case of air-breathing PEFCs. Thus, an

Table 3
Literature survey on modelling of air-breathing PEFCs.

Authors	Analytical/ Numerical	Model Characteristics	Cathode Type	Software	Focus of Research	Model Validation	Main Findings
Hamel and Frechette [34]	Analytical	1D, isothermal, single phase	Window	N/A	Water transport in the membrane	Validated by experimental data	Anode suffers from dehydration
O'Hayre et al. [35]	Analytical	1D, non-isothermal, single phase	Window	N/A	Heat and mass transfer at the cathode side	Validated by experimental data reported in [36]	Air-breathing PEFC requires maximum heat rejection and minimum water flooding.
Schmitz et al. [37]	Numerical	2D, isothermal, single phase	Window	COMSOL Multiphysics®	Impact of opening ratio	Validated by experimental data	The larger the opening ratio, the better the cell performance.
Hwang [38]	Numerical	3D, isothermal, single phase	Window	COMSOL Multiphysics®	Impact of size and arrangement of opening ratio	Validated by experimental data	There exists an optimum size for the opening ratio, about 30%.
Tabe et al. [39]	Numerical	3D, non-isothermal, single phase	Channel	ANSYS Fluent®	Oxygen profile in flow channels	Validated by experimental data	The depletion rate of oxygen increased with decreasing channel depth
Matamoros and Bruggemann [40]	Numerical	3D, non-isothermal, multi-phase	Channel	In-house code	Concentration losses in the flow channels	N/A	Shorter stacks are needed to maximise the utilisation of the active area; low platinum is sufficient for this type of fuel cell.
Litster et al. [41]	Numerical	2D, non-isothermal, single phase	Window	ANSYS CFX	The feasibility of the use of nano-porous GDL	N/A	The nano-porous GDL could be used in air-breathing PEFCs.
Zhang and Pitchumani [42]	Numerical	2D, non-isothermal, single phase	Window	ANSYS Fluent®	Impact of cell orientation and stack height	Validated by experimental data	The cell performs better with a vertical orientation and worse with a horizontal facing upward orientation; the cell becomes less sensitive to orientation as it becomes smaller.
Zhang et al. [43]	Numerical	3D, non-isothermal, single phase	Window	ANSYS Fluent®	Impact of geometrical parameter of a stack	Validated by experimental data	There must be a minimum spacing between the adjacent cartridges and a minimum gap between the cell and the substrate.
Rajani and Kolar [44]	Numerical	2D, non-isothermal, single phase	Window	ANSYS Fluent®	Natural convection boundary layers	Validated by experimental data reported in [45]	A shorter stack gives better performance; the longer stack has thicker boundary layers and therefore experiences larger mass and thermal resistance.
Ying et al. [46]	Numerical	3D, non-isothermal, single phase	Channel	STAR-CD®	Local distribution	Validated by experimental data	The local distributions showed.
Ying et al. [47]	Numerical	3D, non-isothermal, single phase	Channel	STAR-CD®	Impact of channel width	Validated by experimental data	The channel width must be optimised.
Ying et al. [48]	Numerical	2D, non-isothermal, multi-phase	Channel	Not Mentioned	Impact of channel and rib widths	N/A	Optimum values for these two parameters exist.
Wang and Ouyang [49]	Numerical	3D, non-isothermal, single phase	Channel	STAR-CD®	Local distribution	Validated by experimental data	The membrane resistance decreases with increasing back diffusion.
Ismail et al. [33]	Numerical	2D, non-isothermal, single phase	Window	ANSYS Fluent®	Thermal situation above the open cathode surface	Validated by experimental data reported in [36]	Joule heating has a significant effect on thermal parameters.
Ismail et al. [50]	Numerical	0D, non-isothermal, single phase	Window	MATLAB	Impact of Joule heating and entropic heat sources	Validated by experimental data reported in [36]	The neglect of Joule and entropic heats results in over-prediction of the fuel cell performance.
Chen et al. [51]	Numerical	0D, non-isothermal, single phase	Window	MATLAB	Impact of hydrogen relative humidity	Validated by experimental data reported in [36]	Increased hydrogen humidity enhances the fuel cell performance.
Yalcinoz and Alam [52]	Numerical	0D, dynamic, non-isothermal, single phase	Window	MATLAB/ Simulink	Proposing a dynamic model for an air-breathing PEFC	Validated by experimental data reported in [36]	The proposed air-breathing PEFC-based system provides sufficient power supply for a laptop.
Calili et al. [53]	Numerical	0D, dynamic, non-isothermal, single phase	Window	MATLAB/ Simulink	Impact of ambient conditions and GDL parameters	Validated by experimental data reported in [36]	Both transient response and steady-state performance of the fuel cell are sensitive to ambient conditions and GDL parameters.
Calili-Cankir et al. [54]	Numerical	0D, non-isothermal, single phase	Window	MATLAB	Impact of convection type on the fuel cell performance	Validated by experimental data reported in [36]	The performance of conventional PEFC surpasses that of air-breathing fuel cell due to its superior heat and mass transfer coefficients.
Calili-Cankir et al. [55]	Numerical	0D, dynamic, non-isothermal, single phase	Window	MATLAB/ Simulink	Impact of convection type on the dynamic response	Validated by experimental data reported in [36]	The air-breathing PEFC has a substantially slower dynamic response than conventional fuel cells.
Al-Anazi et al. [56]	Numerical	3D, non-isothermal, multi-phase	Channel	ANSYS Fluent®	Impact of ambient conditions in Saudi Arabia	Validated by experimental data	The fuel cell performance is lower in the winter than in summer by around 12%.

Table 4
Source terms in the conservation equations for different regions of the air-breathing PEFC (all the symbols are defined in the nomenclature). Adapted from Refs. [7,42, 43].

Source Term	GDLs	Anode Catalyst Layer	Cathode Catalyst Layer	Membrane
S_C	0	$-\dfrac{I_a}{2F}M_{H_2}$	$-\dfrac{I_c}{4F}M_{O_2}+\left(\dfrac{I_c}{2F}+nd\dfrac{I_c}{F}\right)M_{H_2O}$	0
S_V	$-\dfrac{\mu}{k}\varepsilon_{eff}\vec{V}$	$-\dfrac{\mu}{k_p}\varepsilon_{eff}\vec{V}+\dfrac{k_\varphi}{k_p}z_f c_f F\nabla\varphi_m$	$-\dfrac{\mu}{k_p}\varepsilon_{eff}\vec{V}+\dfrac{k_\varphi}{k_p}z_f c_f F\nabla\varphi_m$	$-\dfrac{\mu}{k_p}\varepsilon_{eff}\vec{V}+\dfrac{k_\varphi}{k_p}z_f c_f F\nabla\varphi_m$
S_T	$\dfrac{i_s^2}{\sigma_s^{eff}}$	$\dfrac{i_s^2}{\sigma_s^{eff}}+\dfrac{i_m^2}{\sigma_m^{eff}}+I_a\eta_a$	$\dfrac{i_s^2}{\sigma_s^{eff}}+\dfrac{i_m^2}{\sigma_m^{eff}}+I_c\left(-\eta_c-\dfrac{T\Delta S}{2F}\right)$	$\dfrac{i_m^2}{\sigma_m^{eff}}$
S_i	0	$-\dfrac{I_a}{2F}M_{H_2}$ (H_2) 0 (O_2) 0 (H_2O)	0 (H_2) $-\dfrac{I_c}{4F}M_{O_2}$ (O_2) $\left(\dfrac{I_c}{2F}+nd\dfrac{I_c}{F}\right)M_{H_2O}$ (H_2O)	0
S_s	0	$-I_a$	I_c	0
S_m	0	I_a	$-I_c$	0

alternative empirical correlation formula is recommended to be used to estimate the ionic conductivity of the membrane under low-humidity conditions [35,50,52,60]:

$$\sigma_m=\left(3.46a^3+0.0161a^2+1.45a-0.175\right)\exp\left[1268\left(\frac{1}{303}-\frac{1}{T}\right)\right] \quad (16)$$

The conservation of energy equation can be expressed as follows:

$$\nabla\cdot\left(\rho C_p\vec{V}T\right)=\nabla\cdot\left(k_{eff}\nabla T\right)+S_T \quad (17)$$

where C_p is the specific heat of the fluid at constant pressure, k_{eff} is the effective thermal conductivity of the medium and S_T is the energy source term.

The boundary conditions typically used to solve the above conservation equations are listed in Table 5 and Fig. 2 shows the interfaces at which these boundary conditions are prescribed.

4. Optimisation of air-breathing PEFC

As mentioned in Section 2, water and heat within the air-breathing PEFC should be carefully balanced to avoid undesirable phenomena of either water flooding or membrane dehydration that badly affect the fuel cell performance. Therefore, the designs and/or materials of the various components of the fuel cell should be optimised to ensure this water and thermal balance and ultimately sustain the fuel cell performance. Further, the design and the materials are often optimised to reduce the size, weight, complexity or cost of the air-breathing fuel cell used for portable applications. Surveying the literature, the following elements are normally optimised to maximise the performance of the air-breathing PEFC or minimise cost, size, and weight: the design and the

Table 5
Boundary conditions for the layers shown in Fig. 2. Adapted from Refs. [7,42, 43].

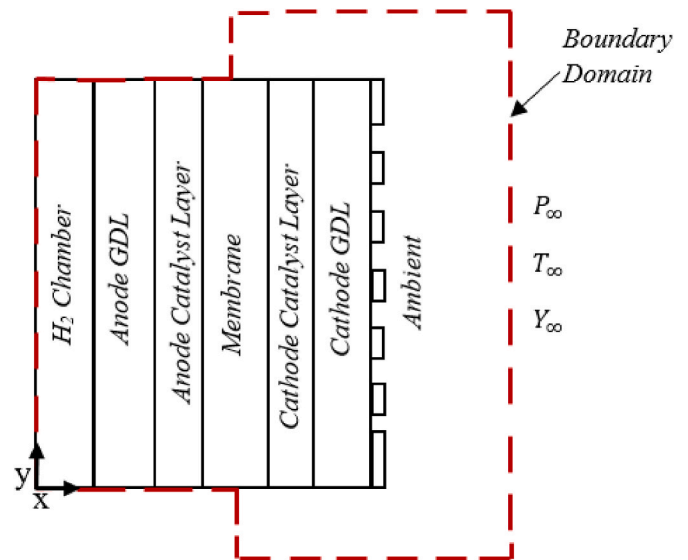| Interface	Boundary condition
Ambient | Cathode GDL	$\varphi_s=V_{cell}$ $-k_{eff}\dfrac{\partial T}{\partial x}=h(T_\infty-T_s)$ $-D_{O_2}^{eff}\dfrac{\partial Y_{O_2}}{\partial x}=h_{m,O_2}(Y_{\infty,O_2}-Y_{s,O_2})$ $-D_{H_2O}^{eff}\dfrac{\partial Y_{H_2O}}{\partial x}=h_{m,H_2O}(Y_{\infty,H_2O}-Y_{s,H_2O})$
Cathode GDL | Cathode Catalyst Layer	$\dfrac{\partial\varphi_m}{\partial x}=0$
Cathode Catalyst Layer | Membrane Membrane | Aanode Catalyst Layer	$\dfrac{\partial Y_{O_2}}{\partial x}=0;\dfrac{\partial Y_{H_2O}}{\partial x}=0;\dfrac{\partial\varphi_s}{\partial x}=0$ $\dfrac{\partial Y_{H_2}}{\partial x}=0;\dfrac{\partial\varphi_s}{\partial x}=0$
Anode Catalyst Layer | Anode GDL	$\dfrac{\partial\varphi_m}{\partial x}=0$
Anode GDL |H$_2$ Chamber	$T_a=const.;\ Y_{H_2}=const.;Y_{H_2O}=const.;$ $\varphi_s=0$

Fig. 2. A cross-section schematic of an air-breathing PEFC showing the boundary domain.

material of the cathode current collector; the thickness and the material of the GDL; the catalyst loading and thickness; and the fuel cell orientation. The following subsections review the attempts that have been made under each of the above-mentioned elements.

4.1. Design of cathode current collector

The design of the open cathode current collector (also known as the cathode flow distributor) directly influences the performance of air-breathing PEFCs, and this is due to its substantial impact on the mass and heat exchange between the ambient air and the fuel cell. The open cathode current collectors are mainly classified as follows: window-based (ribbed or open-slit) and channel-based (ducted) current collectors; see Fig. 3. The main difference between them is the airflow direction. As shown in Fig. 3a, the flow direction of the ambient air is primarily from the bottom to the top of the channel in the ducted flow fields; therefore, oxygen reacts more in the bottom part of the channel and its concentration becomes more diluted as it flows towards the upper outlet of the channel. This leads to a high degree of non-uniformity in the current density distribution. On the other hand, the whole cathode surface of the window-based type cell is exposed to the air (Fig. 3b). In other words, the concentration of oxygen is, compared to that of the ducted channel, more uniform over the cell active area. To this end, there has been a trend towards the use of window-based
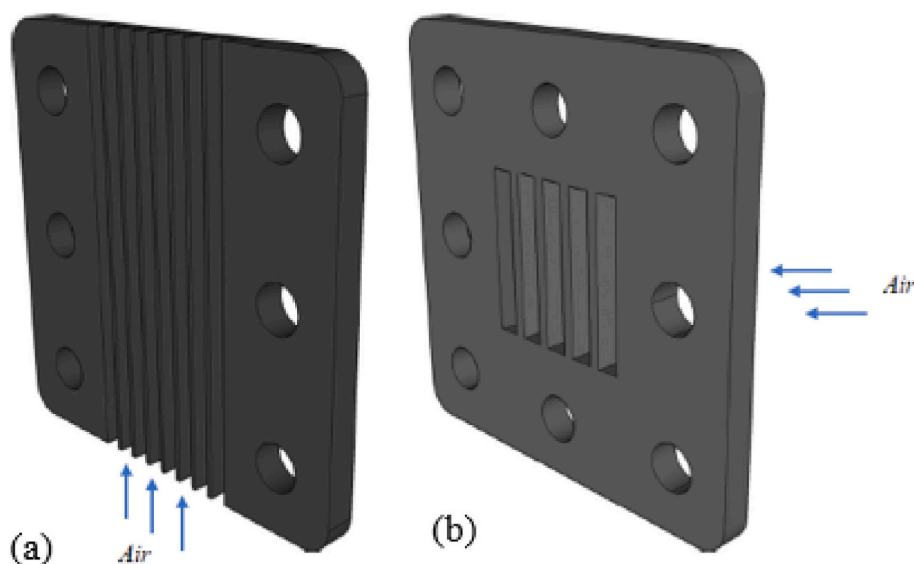
Fig. 3. (a) Channel-based and (b) window-based cathode current collectors. Reproduced from Ref. [33] with permission from Elsevier.

current collectors for air-breathing PEFC. The design criteria for each type of current collector are different; they are mainly the size and shape of the openings in the window-based current collectors and the dimensions of the channels in the channel-based current collectors. These design criteria need to be optimised since efficient mass transport to and from the cathode electrode and good contact between the collector and the MEA are typically in conflict with each other. To illustrate, in window-based current collectors, oxygen transport to the cathode and water removal rate are enhanced if the size of the openings is increased; however, the contact between the current collector and the MEA becomes poorer with increasing size of the openings. It should be noted that the term 'opening ratio' is normally used to indicate how large the openings of the collector are relative to the active area of the fuel cell. The optimisation of the design of the cathode current collectors in air-breathing PEFCs has been a major theme for a number of investigations in the literature, as will be shown in the following paragraphs.

Ying et al. [48] developed a three-dimensional mathematical model for an air-breathing PEFC and showed that the distributions of the temperature, partial pressure of gas species, the flow rate of water and gas species, local current density, and over-potential are significantly influenced by the size of the cathode opening. They concluded that a larger opening size provides an improvement in the performance of the fuel cell; however, the level of this improvement decreases as the opening ratio increases beyond an optimum value.

Schmitz et al. [61] investigated the effect of cathode current collectors with rectangular openings on the performance of air-breathing PEFCs. They found that the cell performance is more or less the same in the low current density regions; however, it significantly improves with increasing opening ratio in the high current density regions due to better mass transport of oxygen and liquid water. They experimentally showed that the amount of liquid water collected from the anode side becomes less with increasing opening ratio; this signifies that the water removal from the cathode is better for the current collectors with larger openings. Later, the same research group [37] developed a two-dimensional computational model that confirmed the above experimental results. In a relevant work [62], they demonstrated that increasing the opening ratio improves cell performance regardless of the
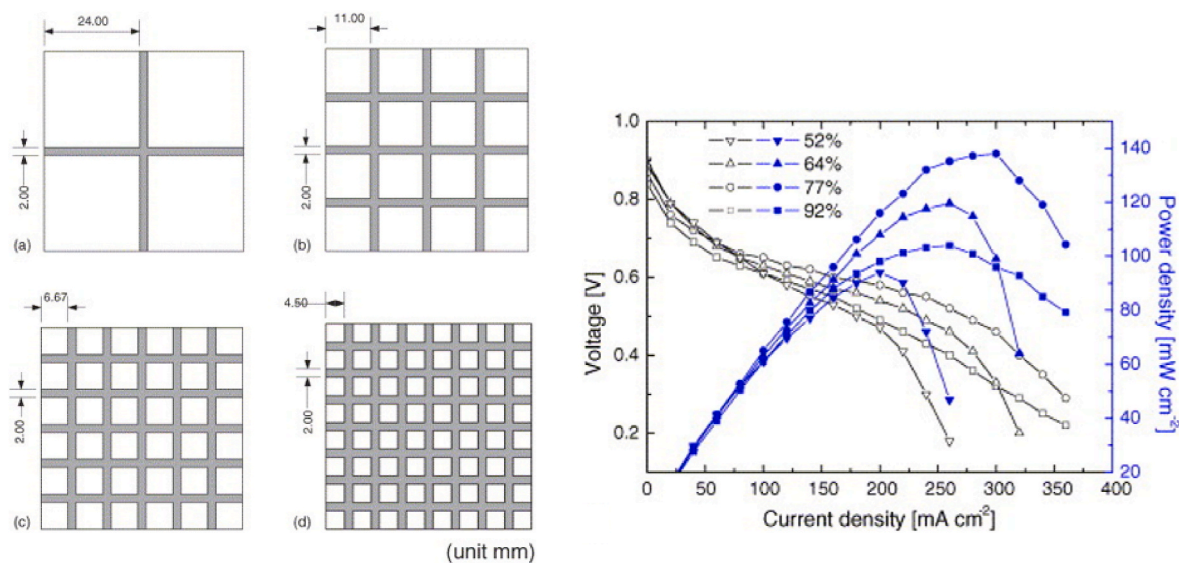

Fig. 4. Open cathode designs with opening ratio of: (a) 92%; (b) 77%; (c) 64% and (d) 52%. The left graph shows the corresponding polarisation curves at 35 °C and relative humidity of 80%. Reproduced from Ref. [63] with permission from Elsevier.

hydrophobicity of the GDL.

The effects of cathode current collectors with an array of rectangular openings were experimentally investigated by Jeong et al. [63]. They showed that, in the low current density regions, the fuel cell performance degrades with increasing opening ratio; they suggested that this is because of the increased in-plane resistance. However, in the high current density regions, there exists an optimum opening ratio at which the peak power is a maximum, namely 77% (Fig. 4). The charge transfer resistance shown by the electrochemical impedance spectroscopy measurements is a minimum for this geometry; this is most likely due to the improved activity of the catalyst layer.

Bussayajarn and co-workers [64] investigated the effects of the shape of the opening on the performance of the fuel cell. The openings investigated were parallel slits, oblique slits and circular. They found that, for a given opening ratio of 47%, the fuel cell performed better with the circular openings. The authors thought that the reason behind this was the shortest rib width and the smallest hydraulic diameter presented by the investigated circular openings. However, Kim et al. [65] found that each opening shape has its own optimum opening ratio. They experimentally showed that the optimum opening ratios for arrays of rectangular, triangular, and circular openings are about 70%, 50%, and 38%, respectively. A six-cell stack was subsequently made from cathode collectors with rectangular openings since their optimum opening ratio is sufficiently large to allow for more efficient water removal.

Hottinen et al. [45] showed that the negative effects of increased opening ratios can be significantly mitigated, especially in the low current density regions, if one employs a thick and stiff GDL. Current collectors with large openings show a slightly better performance in the high current density regions. However, the authors showed that there exists an optimum opening ratio for the openings and that the performance is significantly better than that with thick GDLs if one employs conventional thin GDLs. They also [66] designed an air-breathing PEFC consisting of a Z-shape flow field anode current collector, a window-based cathode current collector, and rigid GDLs. This study aimed to minimise the size of the cell for portable applications. There were no separate end plates in the fuel cell since the current collectors act as end plates in both the anode and cathode sides, thus reducing the size of the fuel cell and its manufacturing costs.

Babcock et al. [67] deployed a stiff and porous mesh between the GDL and cathode current collector. They showed that the use of the mesh significantly decreases the ohmic losses of the fuel cell in such a way that one can use a current collector with an extremely high opening ratio, which will significantly improve the fuel cell performance due to improved oxygen and water transport.

Kumar and Kolar [68] built a three-dimensional, single-phase, and non-isothermal model under steady-state conditions to predict the performance change of an air-breathing fuel cell with channel widths of 2, 4, and 6 mm, depths of 2, 6, and 10 mm and heights of 15, 30, and 45

mm. They found that open channels with 4 mm width, 6 mm depth and 45 mm height maximise the fuel cell power density (240 mW/cm^2). Kumar and Parthasarathy [69] carried out a similar but experimental study and found out that the best performance was obtained with the open channel of the largest cross-section (i.e., 6 mm × 6 mm) which is somewhat in line with the outcomes of their model [68].

Kumar and Kolar [70] investigated how the cathode collector type (channel- and window-based) influences the fuel cell performance using a three-dimensional, steady-state, non-isothermal, and single-phase model. They demonstrated that the transport rate of generated heat and water is higher in the fuel cell with a window-based cathode current collector than in a fuel cell with a channel-based current collector, allowing for better fuel cell performance. On the other hand, Tabe et al. [39] found that the air-breathing PEFC with a channel-based cathode current collector performs better than that with a window-based cathode current collector. This is, according to the authors, due to the increased contact resistance presented by the latter current collector. However, it appears that the authors did not optimise the opening ratio of the window-based current collector; the opening ratio of the cathode current collector used was estimated to be no more than 65%. As shown earlier in Refs. [61,63,65], the fuel cell performance is very sensitive to the opening ratio of the current collector. For the fuel cell running with channel-based current collectors, the authors reported that the mass transport and, consequently, the cell performance are improved with increasing channel dimensions [39].

Chun et al. [71] manufactured two prototype top-layers for a window-based air-breathing PEFC: thin-fin and duct top layer arrangements as shown in Fig. 5. They reported that a cathode collector with thin-fin structures offers better heat dissipation, thus preventing overheating of the air-breathing PEFC. In a later work [72], they tested the air-breathing fuel cell using two different fin structures, illustrated in Fig. 6, at four different temperatures controlled by an external heater (room temperature, 30, 40 and 50 °C). They showed that the proposed fin designs do not substantially enhance the performance of the fuel cell at room temperature, 30 and 40 °C; however, at 50 °C, the convective heat transfer rate increases with the presence of fins, thus improving heat dissipation and subsequently the fuel cell performance. The fuel cell performance was found to be better at 50 °C with the left design than with the right design shown in Fig. 6.

Karst et al. [73] developed a cover with openings for the open cathode, as shown in Fig. 7, to investigate the effect of the opening ratio on water management. They found that the amount of water ejected from the anode side increases by more than 30% at 150 mA/cm^2 when the fuel cell is equipped with a cover of 5% opening ratio.

Suseendiran et al. [74] proposed a cathode current collector consisting of two hollow semi-cylindrical parts for an air-breathing PEFC. Fig. 8 shows exploded and assembled views of the proposed cylindrical air-breathing PEFC. They reported that the fuel cell has better
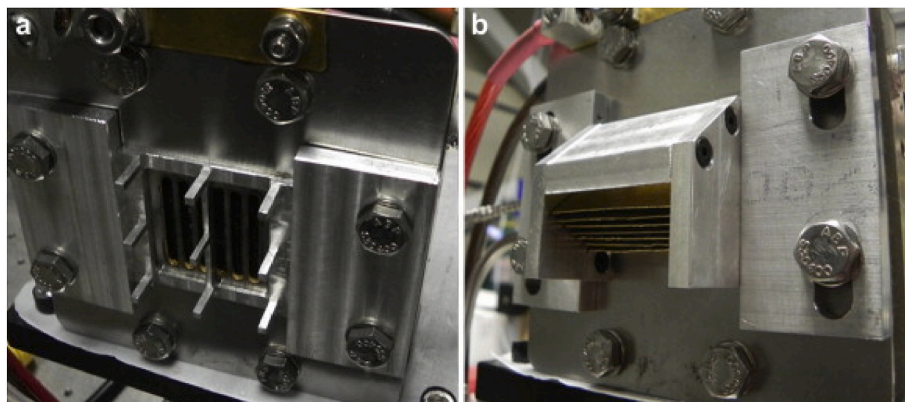

Fig. 5. Fin structures: (a) thin-fin top-layer and (b) duct top-layer. Reprinted with permission from Elsevier [71].
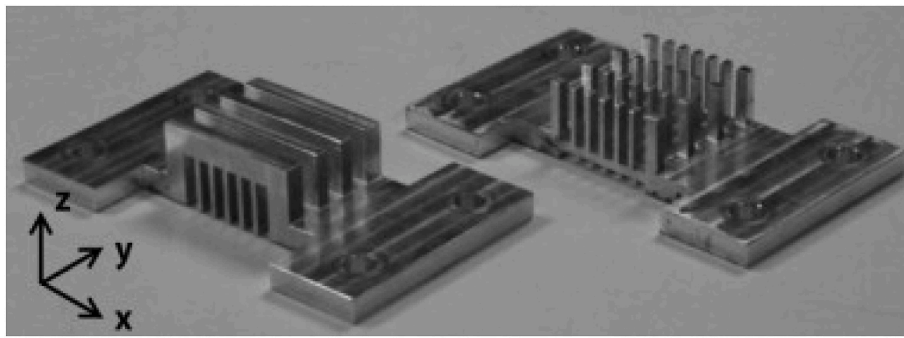
Fig. 6. The two fin structures investigated in Ref. [72]. Reprinted with permission from Elsevier.
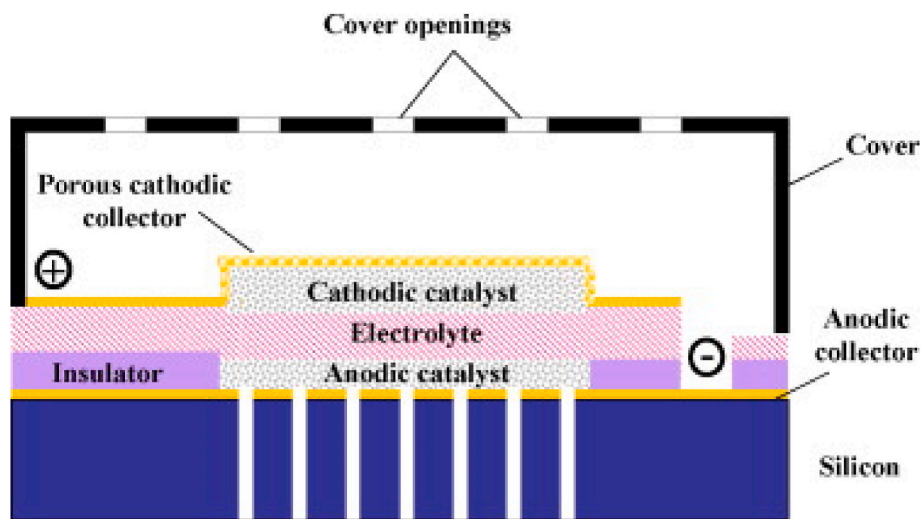

Fig. 7. A schematic of the cross-section of the air-breathing PEFC equipped with the perforated cover. Reprinted with permission from Elsevier [73].
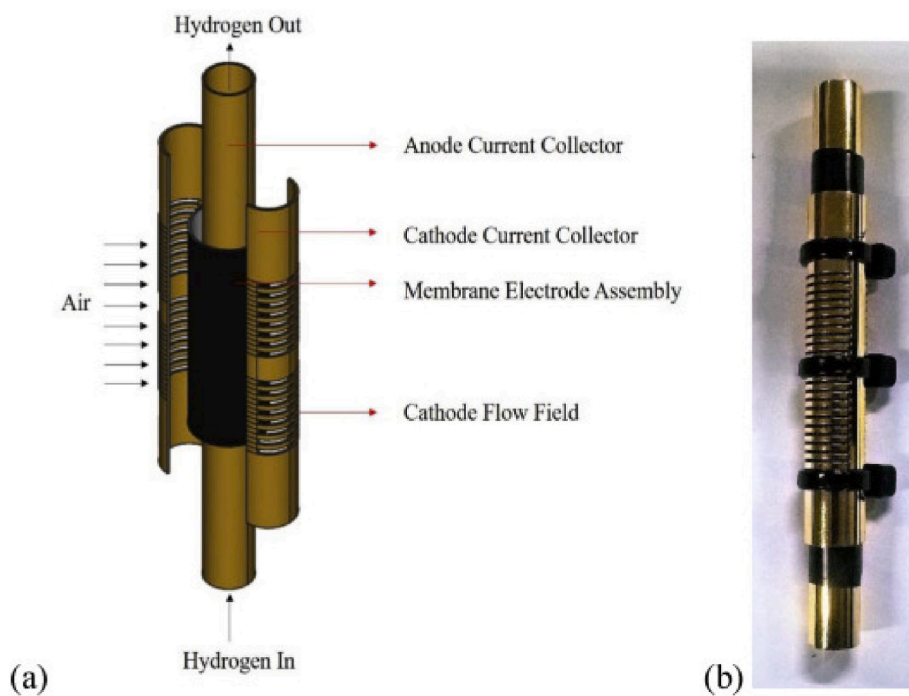

Fig. 8. A cylindrical PEFC: (a) an exploded view of the fuel cell and (b) a picture of the assembled fuel cell. Reprinted with permission from Elsevier [74].

performance with a rib width of 2.5 mm and a slot size of 1 mm, and the peak output power is 2 W at 800 mA/cm^2.

To conclude, the opening ratio for each window-based design must be optimised to achieve the required balance between good mass transport for oxygen and liquid water, and good contact between the current collector and the MEA. Thick GDLs or a stiff contact layer may be employed to enhance the electrical contact in the cathode compartment; however, care must be taken not to sacrifice the mass transport through creating undesirable long diffusion paths.

4.2. Materials for cathode current collectors

The type of material employed in current collectors directly affects the performance of the fuel cell since the properties of each material, such as the electrical conductivity and the corrosion resistance, differ [66]. A variety of metallic (e.g., stainless steel) and non-metallic materials (e.g., silicon wafers and printed circuit boards (PCBs) coated with metals) can be used as current collectors for air-breathing PEFCs [75].

Graphite is attractive to be used for air-breathing PEFC current collectors, and this is due to its high corrosion resistance; however, it is rather brittle, and as, such the current collectors made from graphite are relatively thick, resulting in "bulky" fuel cells [76]. On the other hand, current collectors made of metals are mechanically stronger than graphite, and they could be made substantially thinner than graphite collectors. However, the most commonly used metals are mostly vulnerable to corrosion, and they, therefore, need to be covered with some corrosion-resistant coating. For example, Jeong et al. [63] coated a copper cathode current collector with gold. Similarly, gold-coated aluminium-metallic current collectors were used by Bussayajarn et al. [64].

Silicon wafers have also been used as a base material for the current collectors for air-breathing PEFCs [77–79]. Namely, a silicon wafer is transformed into a porous layer by electrochemical etching and is then partially filled with platinum to form electrically conductive paths [80].

Some researchers used thin PCBs as current collectors to minimise the size of the stack volume of the air-breathing PEFCs; PCBs feature some compelling characteristics such as cost efficiency, lightweight composite materials, and fast prototype cycle times. The multilayer PCB technology enables different circuit layers to overlap so that it improves some of its features, such as functionality and mechanical strength [81]. O'Hayre et al. [82] were the first to report that PCB technologies can be applied to improve power density, design flexibility, and ease of integration. Schmitz et al. [61] designed a planar air-breathing PEFC using a standard PCB consisting of a thin copper layer (for electrical conduction) and a rigid fibreglass epoxy (to act as a mechanical support). They showed that this fuel cell achieved a power density of 100 mW/cm^2 at 0.5 V and long-term operation (more than 1500 h) without degradation. In another study by the same authors [62], an air-breathing PEFC was constructed using both anodic and cathodic plates made from PCB materials. Jaouen et al. [80] combined a PCB cathode current collector with a stainless steel net while a copper foil with an adhesive and conductive layer was used as an anode current collector. In doing so, good electrical conduction was obtained for both collectors. Kim et al. [65] coated a flexible PCB—a non-conductive polyimide film—with gold, which collects the current on both the anode and cathode sides. In doing so, they achieved a highly thin monopolar six-cell stack of 6 mm.

4.3. Gas diffusion layer

The GDL is a multifunctional layer that allows for the exchange of reactant gasses and water between the ambient and the catalyst layer, and it therefore has an influential role in terms of water and heat management in air-breathing PEFCs. A typical GDL is coated with a microporous layer (MPL) which is meant to adequately manage water within the MEA and enhance the electrical contact between the GDL and the catalyst layer. Several studies have been conducted to investigate the effects of the cathode GDL (specifically its thickness and wetting properties) on the performance of air-breathing PEFCs.

Hottinen et al. [66] employed two thick rigid GDLs in their air-breathing PEFCs. One of the GDLs was characterised by high porosity (i.e., 78% vs 58%), whereas the other was of low electrical resistance. They showed that the cell performs better with the latter GDL achieving a peak power density of 115 mW/cm^2 at 250 mA/cm^2 in the intermediate current density region, and this is due to reduced cell resistance; however, because of the reduced mass transport losses, the fuel cell performs better with the high-porosity GDL in the high current density region. In a later work [45], they used three different types of GDLs: thick carbon sheet; carbon paper; and titanium sinter to investigate the impact of the cathode structure on the cell performance. They showed that carbon paper, which is thinner and more compressible than other tested GDLs, achieved a significant performance gain with relatively high opening ratios. Ferreira-Aparicio and Chaparro [83] compared the performance of woven and non-woven carbon paper GDLs in an air-breathing PEFC. They demonstrated that the fuel cell performed better with the woven carbon paper GDLs than with the highly tortuous non-woven carbon paper GDLs as the mass transport is highly limited with the latter GDLs, particularly at high current densities (Fig. 9).

The thickness of the GDL in an air-breathing PEFC (particularly in the cathode side) should be optimised as either too thin or too thick GDLs could lead to membrane dry-out, oxygen starvation or water flooding [35]. If the GDL is too thin, the rejection rate of water from the catalyst layer becomes extremely high, leading to membrane dry-out. On the other hand, if the GDL is too thick, depending on whether the fuel cell is low or high performing, the fuel cell may experience water flooding and/or oxygen starvation due to increased mass transport resistance for product water and oxygen, or membrane dry-out due to increased thermal resistance of the GDL.

Jeong et al. [84] demonstrated that the air-breathing PEFC performance was improved by increasing the thickness of the GDL from 100 to 280 μm; however, the performance of the fuel cell degraded when using a 370 μm thick GDL. They explained these results stating that the relatively thin GDLs lead to membrane dry-out, which is due to the high evaporation rate of water while the relatively thick GDLs hinder oxygen transport from the ambient air.

Schmitz et al. [61] experimentally showed that the thickness of the cathode GDL must be optimised to improve the performance of the air-breathing PEFC. A very low limiting current was shown by the fuel cell operating with the relatively thick GDL, and this is most likely due to increased diffusion paths for oxygen extracted from the ambient air. Similarly, Tabe et al. [39] showed that, for both window and channel-based current collectors, the limiting current decreases with increasing GDL thickness. Further, they stated that, for window-based current collectors, the contact pressure becomes more uniform with increasing GDL thickness, which translates into reduced cell resistance. However, the effect of GDL thickness on the cell resistance was reported to be negligible in the case of channel-based current collectors, owing to their geometry, which allows for uniform contact pressure. Notably, in these two studies (i.e., [39,61]), the activation losses are minimal with thick GDLs. The reason is most likely that the good contact between the current collector and the GDL in these cases induces better electronic conduction, a higher reaction rate, more water produced to humidify the catalyst layer, and, therefore, more catalytic activity.

Using a dynamic model, Calili et al. [53] studied the impacts of GDL thickness and thermal conductivity on the dynamic response and steady-state performance of an air-breathing PEFC. They demonstrated that there is an optimal GDL thickness at which the load-following ability of the fuel cell is enhanced. In addition, they reported that both the dynamic responsiveness and the steady-state performance of the fuel cell could be improved with increasing GDL thermal conductivity. In later studies, they studied the influence of GDL porosity on the steady-state performance [54] and the dynamic response [55] of the air-breathing PEFC. They found that both the dynamic and steady-state
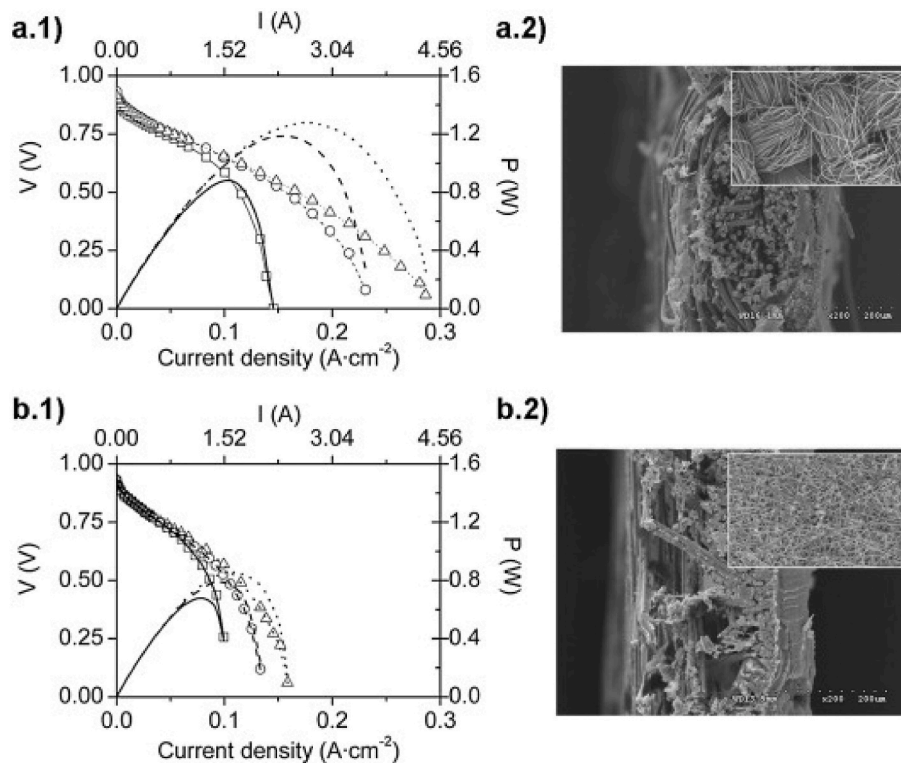
Fig. 9. Polarisation curves of the air-breathing PEFC with: a) woven GDL; b) non-woven GDL and with fan-driven air with maximum power (●●△●●), 18% of fan's maximum power (–○–), and natural convection (-□-). Reprinted with permission from Elsevier [83].

performances of the air-breathing PEFC increased with decreasing GDL porosity. This is because the rate of water removal from the catalyst layer decreases with decreasing GDL porosity, enhancing the humidification of the membrane, and therefore decreasing ohmic losses, and improving the cell performance and dynamic response of the fuel cell. Litster et al. [41] developed a two-dimensional model for an air-breathing cathode electrode consisting of a nano-porous GDL. They showed that this new design for the GDL is able to passively supply reactants and regulate the fuel cell temperature by natural convection and Knudsen diffusion.

The wettability of the GDL is another important factor that affects the fuel cell performance [84]. Carbon paper GDLs are typically treated with polytetrafluoroethylene (PTFE) to assist in driving water away from the MEA and prevent water flooding at the cathode [11]. PTFE (or any other hydrophobic agent) treatment also improves the corrosion resistance of the metal-based GDLs [85–87].

Xiong et al. [88] showed that the air permeability of the GDL (and evidently the hydrophobicity) increases when increasing the PTFE content beyond 10 wt % (i.e., 15–25 wt %), which, according to the authors, results in higher cell performance. They also investigated the impacts of the MPL thickness on the mass and charge transfer by testing the GDLs with MPLs ranging from 0 to 0.16 mm in thickness. Their results show that the optimal MPL thickness that maximises the fuel cell performance is 0.14 mm; this was explained as follows: (i) no MPL or too thin MPL potentially causes water flooding in the catalyst layer and/or the GDL, which in turn hinders the supply of the reactant gas to the reactive sites in the catalyst layer and (ii) too thick MPL evidently increases both the mass and charge transfer resistances due to the increased diffusion path and the tendency to retain condensed water within the MPL.

Open pore cellular foam has been recently increasingly used as a GDL material in PEFCs as they offer low-pressure drop, excellent gas flow and low electrical resistance [86,89–91]. Baroutaji et al. [86] designed a GDL using a PTFE-coated open cellular nickel foam that they used in an air-breathing PEFC. They demonstrated that the PTFE coating of the cellular foam improved its corrosion resistance and hydrophobicity, and subsequently resulted in better fuel cell performance. Schmitz et al. [62] investigated the impacts of the wetting properties of the GDL employed in air-breathing PEFCs. They found that the fuel cell operates more efficient with non-treated GDL, which is considered slightly hydrophobic; neither the hydrophobic nor the hydrophilic GDL improves the cell performance. The hydrophobic and hydrophilic GDLs were found to have higher contact resistance than the non-treated GDL due to reduced porosity and increased electrical resistance of the GDL after applying non-conducting coatings. Notably, the fuel cell was found to perform better with the hydrophobic GDL than with the hydrophilic GDL, although the contact resistance of the hydrophilic GDL is less than that of the hydrophobic GDL. The authors suggested that the hydrophilic GDL absorbs and uniformly distributes the produced water into its pores. This causes the evaporation rate to increase and the membrane to dry out, particularly at higher temperatures. On the other hand, the hydrophobic GDL rejects the water produced at the catalyst layer, which allows for the membrane to be reasonably humidified at high temperatures. The authors' rationales were supported by the amount of water collected at the anode side, which was found to be a minimum for the hydrophilic GDL case, signalling efficient water evaporation for this case at the cathode side.

Dang et al. [92] proposed GDLs that were made from natural wood and characterised by three-dimensional, interconnected perpendicular channels for air-breathing PEFCs. Fig. 10 shows how the natural wood-based GDL is processed and the configuration of the employed air-breathing PEFC. The wood carbon sheets were treated with PTFE dispersion and heated at 400 °C for 30 min to uniformly disperse the PTFE. The fuel cell was occupied with the proposed GDL at the cathode, and the peak power density was found to be 102 mW/cm^2 at 318 mA/cm^2 with the optimal 20 wt% PTFE.

In summary, there exists an optimum thickness for the GDL; very thick GDLs induce increased mass transport losses and increased thermal
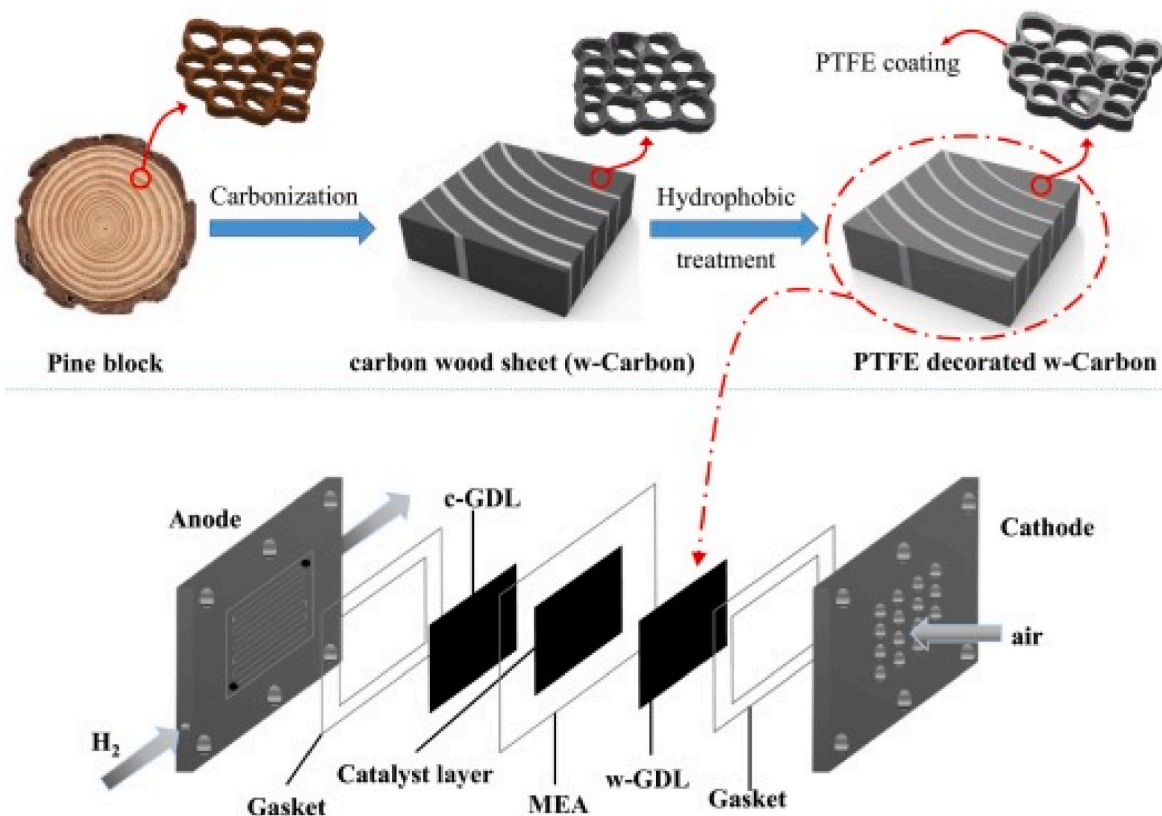
Fig. 10. A schematic diagram showing the natural wood-based GDL is processed and the configuration of the employed air-breathing PEFC. Reprinted with permission from Elsevier [92].

resistance, whereas very thin GDLs increase the likelihood of membrane dry-out and, consequently, ohmic losses. Likewise, moderately hydrophobic GDLs are recommended to be employed. Very hydrophobic GDLs might result in water flooding, whereas very hydrophilic GDLs result in membrane dry-out.

4.4. Catalyst layer

Catalyst layers (or electrodes) are where half-reactions take place and are in direct contact with both the GDLs and the polymer electrolyte membrane at each side of the fuel cell. Platinum is typically used as a catalyst in PEFCs due to its high chemical activity and stability. The catalyst layers in PEFCs consist of platinum nanoparticles supported on carbon (20–40 wt% Pt/C), Nafion (20–60 wt% Nafion content), and voids [59,61,82]. Since platinum-based catalysts are precious, lowering the catalyst loading or using alternative cheaper catalysts is of great interest to the fuel cell community. Furthermore, as will be shortly shown, optimisation of the catalyst in terms of loading and composition has proven to be vital for improving the performance of the air-breathing PEFCs.

Ferreira-Aparicio and Chaparro [83] investigated the effect of the thickness of the catalyst layer on the performance of the air-breathing PEFCs. Three catalyst layers with thicknesses of 8 (20 wt% Pt), 4.0 (40 wt% Pt), and 2.5 µm (60 wt% Pt) were prepared for the cathode side based on platinum loading of 0.17 mg/cm^2 and applied to the membrane electrolyte. They show that maximum power is obtained with the thinnest catalyst layer (i.e., 2.5 µm), particularly at the cathode side. Jeong et al. [84] investigated the effect of platinum loading (from 0.3 to 1.6 mg/cm^2) on the performance of the air-breathing fuel cell at 30 and 60% relative humidities. They showed that the platinum loading needs to be optimised: the fuel cell performance was found to decrease with substantially high platinum loadings, and this is due to increased mass

transport resistance for product water. Similar findings were reported in the numerical study undertaken by Matamoros and Brüggemann [40].

Xiong et al. [88] improved the water management in an air-breathing PEFC using a dual cathode catalyst layer including a thin hydrophilic layer in contact with the membrane electrode (where Nafion was used as a catalyst binder) and a hydrophobic layer in contact with the GDL (where a mixture of Nafion and PTFE was used as a catalyst binder). They showed that, compared to the fuel cell with a single catalyst layer, the fuel cell performs better when a dual catalyst layer is used. The hydrophilic catalyst layer enhances the ionic conductivity of the membrane phase while the hydrophobic catalyst layer traps water that is most needed for membrane humidification under low-humidity conditions and equally expels excess water produced at high current densities. Jung et al. [93] added 40 wt% hydrophilic silica nanoparticles to the anode catalyst layer so that these nanoparticles could absorb the excess liquid water migrating from the cathode. They showed that, with this arrangement, the fuel cell performance improves by around 27%, and this is due to increased water rejection from the cathode to the anode and substantially decreased mass transport resistance for oxygen.

4.5. Cell orientation

One of the main factors that affects the performance of air-breathing PEFCs is the orientation of the fuel cell as the natural convection heat and mass transfer coefficients are sensitive to this orientation [94]. As shown in Fig. 11, there are typically three different fuel cell orientations: vertical, where the fuel cell is parallel to the gravitational force (Fig. 11a); horizontal upward, where the open-cathode of the fuel cell is normal to the gravitational force and facing upwards (Fig. 11b); and horizontal downward, where the open-cathode of the fuel cell is normal to the gravitational force and facing downwards (Fig. 11c) [42].

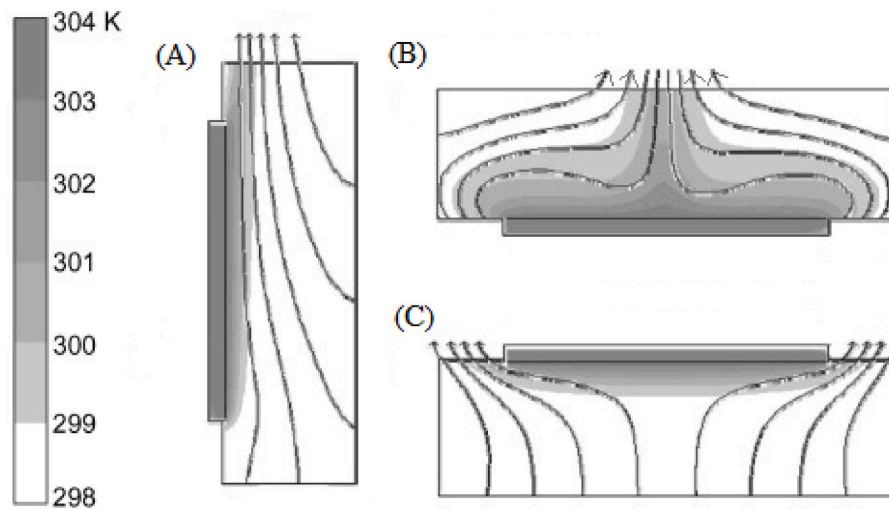Li et al. [94] developed a numerical model for an air-breathing PEFC

Fig. 11. Schematic of the temperature distributions and airflow patterns for window-based air-breathing PEFCs under three different fuel cell orientations: (a) vertical, (b) horizontally facing upward and (c) horizontally facing downward. Reproduced from Ref. [42] with permission from Elsevier.

and found that a much higher concentration of oxygen at the cathode surface could be obtained with vertical or horizontally facing upward orientations. Also, they experimentally showed that the horizontally upward-oriented fuel cell, compared to other orientations, demonstrates better performance while the downward-oriented fuel cell shows the worst performance. This phenomenon was attributed to the potential enhancement of the mass transport characteristics associated with the natural convection, which could be facilitated by the appropriate orientation of the open-cathode surface. They reported that, compared to the horizontally facing downward, the horizontally facing upward orientation resulted in a potential increase in the maximum output power of the fuel cell by around 10%. Obeisun et al. [95] evaluated the effect of cell orientation on the performance of a channel-based air-breathing PEFC by visualising water accumulation using thermal imaging, optical visualisation, electrochemical impedance spectroscopy, and gravimetric analysis. They found that the horizontally facing upward orientation is favoured for the fuel cell due to less build-up of liquid water in the channels. However, most of the relevant studies show that the best performance of the air-breathing PEFC is obtained when the fuel cell is vertically oriented [36,45]. Zhang and Pitchumani [42] developed a numerical two-dimensional model for an air-breathing PEFC and showed that the best performance is obtained with vertical orientation. They showed that, with this orientation, the air is initially drawn from the bottom of the fuel cell. Air adjacent to the open cathode of the fuel cell becomes heated, rises, and is replaced by cold air. This cold air in turn becomes hot, rises, and so on. Such dynamics create buoyancy effects and allow, compared to the horizontal orientations, for a relatively more effective supply of oxygen to the fuel cell and the removal of excess water and heat from the fuel cell. Vijay Babu et al. [96] experimentally investigated the effect of cell orientation on the performance of window-based and channel-based air-breathing PEFCs. Vertical orientation was found to be the best orientation for both types of fuel cells; this is due to higher natural convection heat transfer coefficients compared to other cell orientations. They also showed that the gravitational force assists in the removal of liquid water from the catalyst layer when the fuel cell is oriented vertically.

Hottinen et al. [66] experimentally showed that the performance of a single-cell air-breathing PEFC demonstrated similar performance when orienting it vertically or horizontally facing upwards. However, they [45] reported that, compared with horizontal orientation, an air-breathing PEFC with vertical orientation showed a longer stable operation. Similar findings were obtained by Kim et al. [65] but with a six-cell mono-polar stack attributing this to better expulsion of water

when orienting the fuel cell vertically or horizontally facing upwards compared.

Ismail et al. [33] created a two-dimensional thermal model and investigated how the fuel cell orientation affects the thermal dissipation from the air-breathing PEFCs; the heat was found to be dissipated more efficiently when the fuel cell is oriented vertically or horizontally facing upward compared to horizontally facing downward orientation. Kumar and Kolar [70] conducted a numerical study and investigated the effect of the fuel cell orientation on the performance of both fuel cells with window- and channel-based cathodes. They reported that as the thickness of the boundary layer increases along the height of the cell, the cell orientation substantially affects the natural convection heat and mass transport. Hence, they concluded that the best performance of the air-breathing PEFC is obtained when it is oriented vertically in both types of open-cathode designs.

Fabian et al. [36] visualised the thermal plumes around the cathode surface of an air-breathing PEFC in vertical and horizontal cell orientations using shadowgraphy. The average air speed above the cathode surface was found to be higher with the vertical orientation than with the horizontally facing upward orientation (11 cm/s vs 9 cm/s); this is due to the higher density gradient of the plume in the former orientation.

To summarise, the relevant literature has shown that the cell orientation of the air-breathing PEFC could have a significant impact on the natural convection heat and mass transfer coefficients and subsequently the fuel cell performance. Namely, it has been shown that, depending on the design parameters, particularly those associated with the open cathode, the performance of the fuel cell improves when orienting it vertically and/or horizontally facing upward. However, the variation in the performance between the fuel cells that are oriented vertically and those oriented horizontally facing upward is mostly small or even negligible [66].

5. The effect of ambient conditions

Since the cathode side is open to ambient air, the performance of air-breathing fuel cells is highly dependent on the ambient conditions of temperature and humidity, which are practically out of control. Instead, one may change or refine the design and the material of the components that make up the fuel cell to mitigate the detrimental consequences of some ambient conditions. As will be shown in the following paragraphs, the impact of ambient conditions on the air-breathing PEFCs has been studied by several research groups through mathematical models or

experiments.

Matamoros and Brüggemann [40] created a three-dimensional model for a channel-based air-breathing PEFC. They demonstrated that as the ambient temperature rises, the performance of the fuel cell improves. This mainly results from the improved natural convection that is induced by the temperature gradient between the fuel cell and the ambient air. They discovered, on the other hand, that the impact of ambient humidity is negligible for fully humidified inlet gasses. They also demonstrated that the current density reaches the highest value near the ends of the channel and decreases towards its centre since the natural convection is inefficient to drive air towards the central regions. Further, only a small amount of platinum was found to be required for a fuel cell with a realistic channel length; the primary rate-limiting issue is the concentration losses resulting from the insufficient oxygen supply due to natural convection. Any increase in the platinum loading would have a negligible impact on the local current densities at the channel ends. Rajani and Kolar [44] developed a two-dimensional model for a window-based air-breathing PEFC. They showed that the thicknesses of the boundary layers associated with natural convection significantly affect the cell performance. The shorter the height of the fuel cell and the lower the overall thicknesses of the velocity, thermal, and concentration boundary layers, the higher the temperature and concentration gradients at the cathode surface, leading to the higher heat and mass transfer coefficients. As a result, shorter fuel cells performs better owing to: lower concentration losses, a result of increased oxygen supply; higher activation losses, which are inversely proportional to temperature; and lower ohmic losses, a result of improved heat dissipation.

Ismail et al. [50] built a steady-state zero-dimensional model and found that favourable ambient conditions depend on the cell potential of air-breathing PEFC. Moderate ambient temperatures (e.g., 20 °C) and low humidities (e.g., 20%) are preferred at intermediate fuel cell potentials (e.g., 0.6 V) while low ambient temperatures (e.g., 10 °C) and high humidities (e.g., 80%) are preferred at low cell potentials (e.g., 0.4 V). Chen et al. [51] developed a numerical model and investigated how hydrogen relative humidity influences the performance of air-breathing PEFCs at ambient temperatures of 10, 20 and 30 °C; it was shown to have a great impact on the fuel cell performance. For instance, at an ambient temperature of 30 °C, when the relative humidity of hydrogen rises from 0% to 100%, the limiting current density could increase by more than 40%. Calili et al. [53] developed a dynamic model for an air-breathing PEFC to study the dynamic response of the fuel cell to sudden current changes at various ambient conditions: 10, 20 and 30 °C; and 20, 40, 60, and 80% RH. They found that there exists an optimum ambient temperature (i.e., 20 °C) at which overshoots are minimised during load changes and the steady-state fuel cell performance is maximised. Furthermore, they showed that both the transient response and the steady-state performance of the fuel cell are improved with increasing ambient relative humidity. Al-Anazi et al. [56] developed a three-dimensional, non-isothermal, steady-state model for an air-breathing PEFC stack to explore the influence of Riyadh City's (Saudi Arabia) ambient conditions on the performance of the fuel cell. It was discovered that the performance of the fuel cell stack is enhanced by warm and humid ambient circumstances (summer) in which the membrane is sufficiently humidified. In the winter, the output power of the fuel cell stack is approximately 12% lower than in the summer.

Fabian et al. [36] conducted a comprehensive experimental study regarding the impacts of ambient humidity and temperature on the performance of planar air-breathing fuel cells. They found that the effect of ambient humidity on cell performance is dependent on the ambient temperature. To illustrate, if the ambient temperature is 40 °C, the cell performance improves with increasing ambient humidity. When the ambient temperature decreases to 20 °C, there is an optimal relative humidity at which the cell performance is a maximum, namely 40% as higher or lower relative humidity results in flooding or membrane dry-out, respectively. Unlike the 40 °C case, the cell performance degrades with increasing ambient humidity at 10 °C. Likewise, they

showed that the effect of ambient temperature on the performance of the fuel cell is dependent on the ambient humidity; however, this dependency is rather weak. For example, the optimum temperature at a relative humidity of 20% is 20 °C. The optimum temperature slightly increases with increasing relative humidity; it is 30 °C at a relative humidity of 80%.

Hottinen et al. [97] conducted a similar but earlier experimental study. Notably, they found that, at relatively high ambient temperatures, the fuel cell performance degrades with increasing relative humidity; this appears to be in contradiction with that of Fabian and his co-workers [36]. This is not the case. The relevant polarisation curves show that, for a given low cell potential, the amount of electric current generated by the fuel cell used by Fabian et al. [36] is significantly higher than that generated by the fuel cell used by Hottinen et al. [97]. The high electric current in Fabian et al.'s case dictates a higher heat of reaction, and, as a consequence, higher heat generation. This amount of heat appears to be sufficiently high to raise the cell temperature to a level where the rate of water evaporation is higher than the rate of water generation. As a result, the membrane starts to dry out. Therefore, any increase in the ambient humidity will assist in humidifying the membrane, mitigating the ionic resistance, and improving the performance of the fuel cell. In contrast, since the amount of heat generated is relatively low in Hottinen's et al. fuel cell, the rate of water generation is higher than the rate of water evaporation. Therefore, any increase in the ambient humidity will exacerbate water flooding and oxygen mass transport resistance. This was evident from the current distribution measurements which show that the non-uniformity of the current distribution increases with increasing relative humidity [97]. The same rationales can be used to interpret the results reported by Chu and Jiang [98,99] which are similar to those of Fabian et al. and those reported by Jeong et al. [63], which are similar to those of Hottinen et al. [97]. Notably, Jeong et al. [63] showed that if the fuel cell is to be operated at low current densities, then its performance increases with increasing ambient humidity; the increased humidity assists in humidifying the membrane and the catalyst layer and, as a result, reducing the ohmic and charge transfer resistances.

As stated earlier in this section, the design of the air-breathing fuel cell and the materials from which the components of the fuel cell are made can be refined or changed to alleviate the detrimental effects of some environmental conditions on the performance of the fuel cell. It has been found that the fuel cell performance is improved with an increasing temperature difference between the fuel cell and the ambient [35,40,97]. The buoyancy force, which is the driving force for natural convection, increases with increasing temperature difference between the surface of the cell and the ambient. This leads to increased air velocity near the cathode, better oxygen transport to the cathode, and better water removal from the cathode [97]. On the other hand, as the temperature difference between the cell and the ambient becomes smaller, the heat rejection rate from the cell becomes less. As a consequence, the cell temperature increases; the rate of water evaporation increases; the membrane starts to dry-out; the ionic resistance increases; and the fuel cell performance degrades [36]. This is normally the case when the ambient temperature is high, e.g., 40 °C. In accordance with this, the fuel cell was found to perform better at moderate ambient temperatures, e.g., 20 °C [36]. At such temperatures, the effect of humidity is minimal since the rate of water evaporation is low and the water produced is largely sufficient to humidify the membrane. However, it must be stressed that water flooding typically occurs at low ambient temperatures and high relative humidities [36] owing to the decrease in the rate of water removal [35]. One way to increase the temperature gradient is to use a GDL with low thermal conductivity [35, 97]. However, as discussed in Section 4.3, this may lead to excessive self-heating and, as a consequence, membrane dry-out.

Ous and Arcoumanis [100] investigated the effect of ambient conditions on the formation and accumulation of water droplets in the flow channels of an air-breathing PEFC by using two CDD cameras. The

images of the water droplets captured during the cell operation showed that their contact angles were approximately equal when they were advancing and receding. The water droplets were found to evaporate significantly when the ambient temperature increased beyond 23 °C. This study showed that the ambient temperature significantly influences water removal from the cathode of the air-breathing PEFC. As shown above, some ambient conditions may create undesirable phenomena for the air-breathing PEFCs, such as water flooding or membrane dry-out. Below are summaries of some investigations, aimed at mitigating undesirable phenomena induced by ambient conditions.

Ma and Huang [101] innovated an air-breathing PEFC design incorporating a micro-diaphragm pump with a piezoelectric actuator to enhance both oxygen supply and liquid water removal. The piezoelectric actuator was able to pump most of the water out of the open cathode and, at the same time, transport more air towards the MEA of the fuel cell. Fabian et al. [102] introduced a water-collecting wick, which is electrically conductive and hydrophilic, to provide a water balance for an air-breathing PEFC. It was located between the cathode current collector and the catalyst layer. To test the water-rejection capability, they used an environmental chamber and set the ambient relative humidity and temperature to 80% and 10 °C, respectively, to induce severe flooding conditions at the open cathode; they showed that the wick adequately mitigated water flooding. In subsequent work, for active water management, they integrated an electroosmotic pump into the air-breathing fuel cell system [103]. Their experimental results demonstrated that, with only 2% of the cell power, the use of the electroosmotic pump in conjunction with the wick can completely prevent water flooding at the open cathode.

Coz et al. [104] positioned an insulating water management layer, i. e., a 190 μm thick microporous PTFE membrane, between a cathode current collector made of PCB and a metal grid in an air-breathing PEFC to retain liquid water. The metal grid, having no electrical contribution, was used to maintain a constant compression and dissipate the heat. They aimed to investigate the nucleation of liquid water and its relationship with natural convection. They found that the proposed method improves water condensation, thus increasing the water activity at the cathode region, and reported that the performance of the fuel cell is stable between 0.6 and 0.65 V with a power density of 150 mW/cm^2.

In summary, the impact of the ambient humidity on the air-breathing PEFC in general depends on the ambient temperature. Low ambient humidity is preferred in conjunction with low ambient temperature (e. g., 10 °C); relatively high relative humidity causes flooding. High relative humidity, on the other hand, is associated with a high ambient temperature (40 °C); low relative humidity results in membrane dry-out. There have been attempts to mitigate the negative impact of some ambient conditions on the performance of the air-breathing PEFC by innovating some passive and active means (e.g., electroosmotic pump) to appropriately manage liquid water. However, these means mostly add to the size of the fuel cell system and subsequently lower its commercial potential. It is clear that there is a need to innovate designs for the open cathode that substantially mitigate the detrimental impacts of the extreme ambient conditions on the performance of the air-breathing PEFC and minimally increase its size and weight, rendering it more practical and commercially attractive.

6. Hydrogen storage and anode outlet

Hydrogen storage and supply in air-breathing PEFCs need to be simple, compact, efficient, cost-effective, and safe. This section first reviews how hydrogen is normally stored, with a particular emphasis on metal hydrides, which are typically used for air-breathing PEFCs. It then reviews the modes of hydrogen outlets, with a particular focus on the dead-end mode that is typically adopted for air-breathing PEFCs.

6.1. Storage of hydrogen

Hydrogen can be stored in four different forms: a compressed gas form; a liquid form; a cryo-compressed gas form; and a solid form in hydrides [105]. Among these storage options, solid-state hydrogen storage is favourable for air-breathing PEFC-based portable applications since it is more convenient and safer than other storage methods [106].

Metal hydrides have been promising candidate materials to store hydrogen in solid form as they feature high energy density [107]. There are several metals and alloys that have the capability of reversibly absorbing/desorbing large amounts of hydrogen. Their hydrogen storage performance is based on their thermal stability, durability, volumetric capacity, and the kinetics of hydrogenation/dehydrogenation [108]. In short, the metal hydrides should be thermally stable and durable within the ranges of the operating temperature and pressure of the target applications.

There have been several reviews on metal hydrides, in particular their materials and applications, in the literature. For example, Rusman and Dahari [107], Bhattacharyya and Mohan [109] and Tarasov et al. [110] comprehensively reviewed studies on materials used for metal and alloy hydrides and the progress made in terms of their absorption/desorption of hydrogen. Hoffman et al. [111] discussed the chemistry of metal hydrides and, for the first time, proposed magnesium-based alloys for hydrogen storage for mobile applications, and this is due to their low material cost and favourable hydrogenation rate.

The reversible sorption process of metal hydrides is exothermic during the absorption of hydrogen, thus requiring heat removal. On the other hand, desorption of hydrogen (when, for example, supplying hydrogen to the fuel cell) is an endothermic process; therefore, heat must be supplied to release hydrogen from the metal hydride. Hence, heat transfer between the hydride and the exterior is a limiting factor that controls hydrogen absorption/desorption in/from the metal hydrides [112]. Hydrogen absorption/desorption rates are also affected by operating conditions, the geometry of the storing cartridge, and the packing density of metal hydrides [113]. Recent studies on metal hydrides have focused on how to enhance hydrogen absorption/desorption rates through optimising design parameters and heat distribution. Lototskyy et al. [114] pointed out that the components of the fuel cell system could be integrated in such a way that the heat released as a result of the exothermic electrochemical reaction taking place within the fuel cell is efficiently utilised to release hydrogen from the metal hydride storage canister.

The plateau pressure of a metal hydride, which is a significant parameter for material selection, is the pressure at which large quantities of hydrogen are absorbed or released in/from the metal hydride [113]. When the plateau pressures of the metal hydrides are close to the ambient pressure, these metal hydrides are considered suitable for lightweight cartridges used in portable air-breathing PEFC systems [113]. Further, the storage material must be thermally stable and durable at operating temperature and pressure ranges for portable applications.

The selection criteria of metal hydrides employed in air-breathing PEFC systems vary and are highly dependent on the requirements of the portable application. The physical and design parameters (e.g., hydrogen absorption/desorption rate, thermal stability, volumetric capacity, and plateau pressure) must be considered when selecting metal hydrides for portable applications. Further, the cost and manufacturability of metal hydride are the other important selection factors. Fig. 12 shows some examples of commercially available metal hydride hydrogen storage devices for air-breathing PEFCs used in portable applications.

There have been few studies on employing metal hydride cartridges in air-breathing PEFCs. Coz et al. [104] used a sodium borohydride (NaBH₄) cartridge with a hydrogen storage capacity of 24 L to conduct an experimental study on an air-breathing PEFC. They reported that the hydrogen is supplied from the cartridge through NaBH₄ hydrolysis to

Fig. 12. Commercially available metal hydrides hydrogen storage devices: (a) HYDROSTIK™ [115] and (b) HB-SC-0010-Q [116].

meet the fuel demand of the fuel cell. This process controls the total amount of hydrogen supplied to the anode chamber and mitigates safety concerns associated with the accumulation of hydrogen. Kim et al. [28] selected an AB₅ metal hydride hydrogen storage tank for an air-breathing PEFC to power a mobile phone; this is mainly because this type of metal hydride alloy can be packaged in a small hydrogen storage tank and has a sufficient hydrogen absorption/desorption rate at around 10 MPa and room temperature. Fernández-Moreno et al. [16] used a metal hydride cartridge produced by Horizon Fuel Cell Technologies [117] to supply hydrogen to an air-breathing PEFC system. They reported that the cartridge with 1 g of hydrogen capacity provided 20 h of operation above 1 W.

6.2. Anode outlet

The outlet of the hydrogen side in PEFCs could take one of the following forms shown in Fig. 13: (a) open-ended without recirculation, (b) open-ended with recirculation, or (c) dead-ended [118,119]. In dead-end mode, the outlet of the anode compartment is sealed off so that the hydrogen fed to the fuel cell can be completely consumed at the anode. The selection of the mode for hydrogen outlets largely depends on the type of application. Rodatz et al. [120] experimentally studied the effects of the hydrogen supply modes on PEFC efficiency. They reported that the dead-end mode is the simplest arrangement in which the amount of hydrogen supplied to the fuel cell is equal to the amount of hydrogen needed to sustain the electrochemical reaction; however, the performance of the fuel cell in dead-end mode was found to be poor
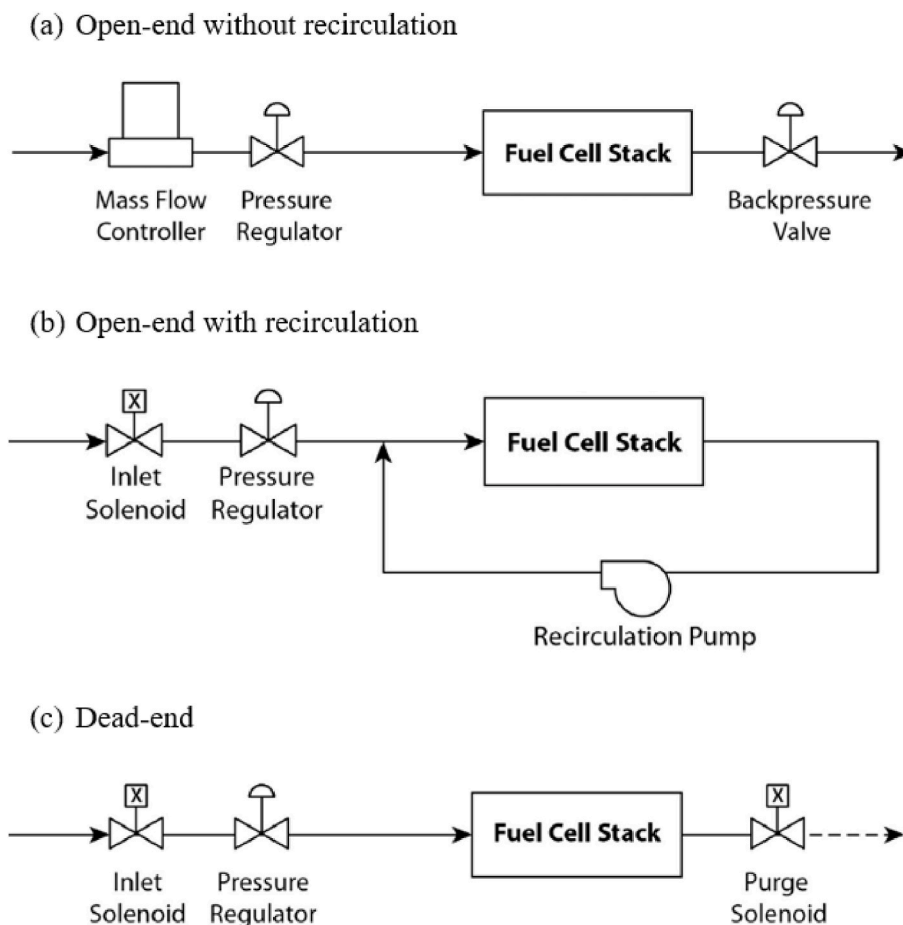

Fig. 13. Schematics of hydrogen supply modes: (a) open-end without recirculation, (b) open-end with recirculation and (c) dead-end. Reproduced from Ref. [118] with permission from Elsevier.

compared to other hydrogen supply arrangements. Hwang [118] performed a similar investigation and found out that the efficiencies of the fuel cell were similar for both dead-end and recirculation modes of hydrogen supply when the power of the fuel cell stack was less than 1.2 kW. At higher stack powers, the recirculation mode was found to be more efficient than the dead-end mode.

Evidently, the dead-end mode is the simplest mode as it does not require a downstream treatment arrangement to deal with unreacted excess hydrogen (e.g., recycling or burning of hydrogen). For this reason, it is often the mode of choice for air-breathing PEFCs where size and mass reduction are a priority. In the dead-end mode, hydrogen pressure at the anode compartment is made constant using a pressure regulating valve as shown in Fig. 13c or simply by displacement arising as a result of the reduction of volume of hydrogen in the storage device [11].

However, the use of a dead-end mode for the anode compartment of the PEFC may have some drawbacks, such as the accumulation of inert gases, contaminants, and water [119]. Namely, high purity hydrogen (i. e., >99.99%) should be used to avoid the accumulation of any contaminants and/or inert gases in the porous anode compartment [118]; otherwise, the fuel cell efficiency may be significantly reduced [121–123]. Furthermore, liquid water may form and accumulate at the anode compartment because of the absence of forced convection [124, 125]. To remedy this problem, an anode purging mechanism should be adopted to allow for regular purging and subsequently maintain good operation of air-breathing PEFCs. However, such a purging mechanism requires extra power to automatically open and shut the purging valve. Fernández-Moreno et al. [16] showed that anode purging provides performance stability for long-term operations of an air-breathing PEFC. Chiche et al. [126] proposed an experimental approach to predict the time between two anode purges for an air-breathing PEFC stack operating in dead-end mode. The relative humidity and the current load were found to be influential parameters affecting the time between two purges. They found that the time between two purges increases with decreasing relative humidity and current load; however, the performance of the fuel cell is unstable at low relative humidity and low current.

7. Air-breathing PEFC stacks

Single cells are typically connected to each other in order to meet the load of the end application, forming what is known as a fuel cell stack. Stacking air-breathing fuel cells, in particular when operating with window-based cathode current collectors, is rather challenging as the design of the stack must ensure the supply of adequate amount of oxygen to all the cells. Equally, the size and weight of the air-breathing PEFC stack should be minimised so that it could fit within the housing of the portable device to be powered. The following paragraphs list the key findings of the investigations in which air-breathing PEFC stacks were developed. Further, Table 6 shows the key features of these stacks and the cells used to form them.

Santa Rosa et al. [127] fabricated an eight-cell air-breathing PEFC stack and investigated the impact of the type of convection (forced versus natural) at the open cathode on the performance of the fuel cell stack. They showed that the performance of the PEFC stack operating with forced convection is almost five times higher than that operating with natural convection (9.7 W versus 2 W). Yang and Shi [128] fabricated a six-cell air-breathing stack where the cells are connected in series in a stair configuration as shown in Fig. 14. Such a configuration allowed for a compact design and, at the same time, allowed all the open cathodes of all the cells to be in direct contact with the ambient air. Moreover, hydrogen was circulated within the stack by fans to improve the uniformity of the fuel supply. They reported that this design produced a peak power density of 350 mW/cm^2. Kim et al. [65] designed a miniaturised air-breathing six-cell planar stack (18 cm^3) in which cells are connected in series and the anode and cathode current collectors are gold-plated PCB-based. The maximum output power from the stack was 3.5 W.

Bussayajarn et al. [64] manufactured a two-cell planar air-breathing PEFC without using endplates. They tested the fuel cell for 2 h and showed that the best performance is obtained with circular openings, where the power density (347 mW/cm^3) is stable. Isanaka et al. [129] proposed a lighter, smaller, and more cost-effective air-breathing PEFC stack design where the weight and cost were reduced by 90% and 80%, respectively. Namely, their stack did not include end plates, bolts or nuts. The stack consists of polycarbonate flow-field plates, stainless steel

Table 6
Air-breathing PEFC stack designs.

| Authors	Stack Design Features	Dimensions of Fuel Cell and MEA Properties	Fuel Cell Performance
Santa Rosa et al. [127]	An 8-cell stack; channel-based gold-plated cathode current collectors, graphite bipolar plates; a fan used for air supply and cooling	Open cathode stack: 10SR4-A (commercially available from SRE—*Soluções Racionais de Energia*); Membrane: Nafion® 111; MEA area: 3.8 cm^2	Maximum output power: 9.7 W (fan working at 5 V) and 2 W (without a fan)
Yang and Shi [128]	A 6-cell stack; window-based cathode current collectors with slit openings; stair configuration; hydrogen fans to supply and circulate hydrogen	MEA area: 5 cm^2; slits dimensions: 10 mm × 1 mm at 1 mm; Pt loading: 0.3 mg/cm^2	Maximum output power: 10.5 W at 650 mA/cm^2
Kim et al. [65]	A planar monopolar 6-cell stack using a flexible PCB-based current collector with rectangular openings; parallel-serpentine flow field anodic plates	Membrane: Nafion® 212; MEA area: 10.08 cm^2; six coplanar electrode pairs: 14 mm × 1 mm; anodic flow channel sizes: 0.5 mm × 0.5 mm with 0.5 mm spacing; cathodic opening ratio: 65%; stack size: 18 cm^3; cathode Pt loading: 1.5 mg/cm^2; anode Pt loading: 4 mg/cm^2	Maximum power density: 350 mW/cm^2 at 750 mA/cm^2
Bussayajarn et al. [64]	A planar 2-cell stack; gold plated aluminium monopolar plates; three window-based cathode collectors with parallel slits, circular openings or oblique slit	Membrane: Nafion® NRE-212; MEA area: 11 cm^2; Pt loading in cathode: 0.4 mg/cm^2; Pt loading in anode: 0.6 mg/cm^2	Maximum power density: 347 mW/cm^3 using circular openings
Isanaka et al. [129]	A stack design free from end plates, bolts, nuts, insulating washers and sleeves; polycarbonate flow field plates	Membrane: Teflon/sulfonic acid; MEA area: 50 cm^2; Pt loading: 0.5 mg/cm^2	Maximum output power: 0.25 W; reduction in weight: 90%; reduction in cost:80%
Baroutaji et al. [86]	A 4-cell stack with only two hydrogen chambers; open pore cellular foams as flow distributors	Membrane: Nafion® 212; MEA area: 25 cm^2; Pt loading: 0.4 mg/cm^2; GDL: ®SIGRACET SGL 24BCE	Maximum power density (with PTFE-coated OPCF): 0.15 W $/cm^2$ at 0.34 A/cm^2; maximum power density (with uncoated OPCF):0.09 W $/cm^2$ at 0.23 A/cm^2
Yan et al. [130]	A 15-cell stack with channel-based openings; gold-coated copper current collectors; graphite bipolar plates	Membrane: Nafion®; MEA area: 130 cm^2; Pt loading: 0.8 mg/cm^2	Maximum power density: 11.98 mW/cm^2 at 20.36 mA/cm^2 under natural convection and 244.75 mW/cm^2 at 414.36 mA/cm^2 under air-forced condition
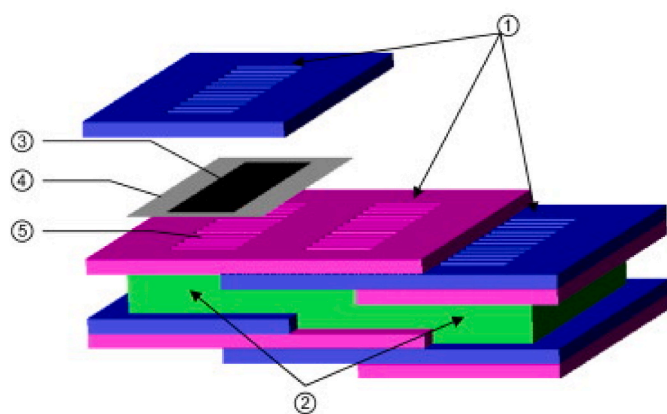
Fig. 14. A stair configuration air-breathing six-cell PEFC stack: (1) window-based cathode current collectors, (2) hydrogen fans, (3) a GDL and catalyst layer, (4) a polymer electrolyte membrane and (5) an anode flow field. Reproduced from Ref. [128] with permission from Elsevier.

current collectors, and silicone gaskets at the anode side. Notably, the peak power of the proposed stack was found to be tenfold higher than the conventional design.

Baroutaji et al. [86] proposed a design for an air-breathing PEFC using open-pore cellular foam as flow distributors. Fig. 15 shows that the design was to reduce the size and cost of the fuel cell stack by having a single hydrogen chamber for every two cells. They found that the maximum power densities of the fuel cell stack with uncoated and PTFE-coated open-pore cellular foams were 0.09 W / cm^2 and 0.15 W / cm^2, respectively. They noted that the individual cells did not perform equally, and this was probably due to the different levels of water accumulation demonstrated by each cell.

Yan et al. [130] designed a 15-cell channel-based air-breathing PEFC stack and proposed a thermal management method that improves the performance of the fuel cell stack by applying different cathode flow channel opening ratios. They compared the stack performance of the fuel cell with a 58.3% opening ratio under natural and forced convection (through using a fan) and found that the stack performance under forced convection is about twentyfold higher than that under natural convection. They also showed that the use of a combination of 50% and 58.3% opening ratios decreased the overall stack temperature and therefore improved stack performance.
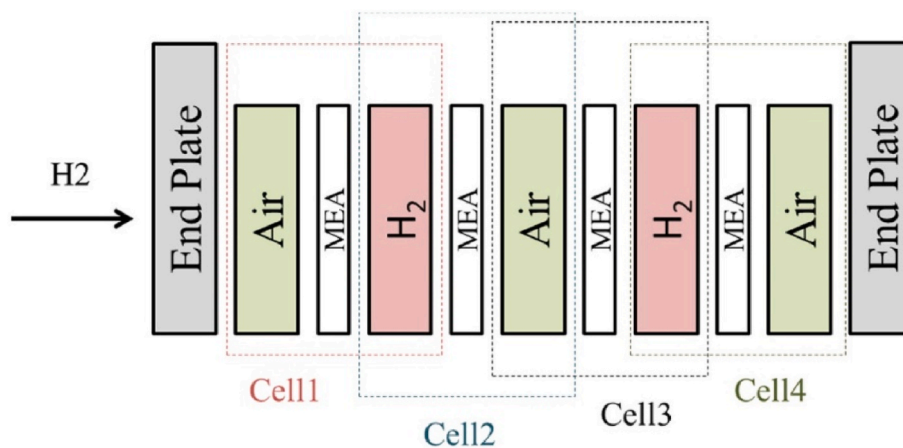
8. Air-breathing PEFC systems

Air-breathing PEFCs are a cleaner replacement to rechargeable batteries used to power small electronic devices, such as cell phones and laptops, as they do not contain poisonous heavy metals [8,131,132]. The literature has shown some experimental (and very few modelling) studies on developing air-breathing PEFC systems to power small electronic devices; the key findings of these investigations are summarised below.

Kim et al. [28] integrated an air-breathing PEFC system, consisting of an 8-cell air-breathing PEFC stack (8 cm^3), a mini dc-dc voltage converter, a miniature pressure regulator (4 cm^3), and a metal hydride hydrogen canister (8 cm^3 with a hydrogen storage capacity of 4 L at 25 °C) at the back of a mobile phone shown in Fig. 16. The volumetric energy density of this miniaturised fuel cell system (<25 cm^3) was around 205 Wh/L and was able to power the mobile phone for roughly 6 h of uninterrupted voice calling.

Fernández-Moreno et al. [16] presented a portable system including a single air-breathing PEFC cell to power a display screen and four LED lights. A dc-dc converter was used to increase the voltage of the system from 0.5–0.8 V–3.3 V. The fuel cell was operated with or without a fan installed at the open cathode, an electronic valve for anode purging, and two supercapacitors for auxiliary power requirements. They showed that this system could supply more than 1 W dc electricity with only 1 g of hydrogen for 20 h of continuous operation. The fan and the purging valve were proven to be beneficial in terms of water flooding migration. Bussayajarn et al. [64] developed and used an air-breathing PEFC system to power a cell phone charger. The fuel cell system was demonstrated to operate steadily during a 2-h cell phone charging. The specific power of the fuel cell system was found to be 150 W/kg. Han et al. [27] developed and used around 200 W air-forced PEFC system to power a freezer for outdoor and medical applications. The fuel cell system consists of an air-forced PEFC stack, a dc-dc converter, a control electronic subsystem, two metal hydride hydrogen canisters connected in parallel (to ensure continuous supply of hydrogen to the system while replacing the empty canister), and a lead acid battery (to enhance the transient response to load change). The authors demonstrated that the fuel cell system provided reliable and continuous power for the portable freezer operating at around −22 °C and an ambient temperature of around 27 °C. Note that, except for the integrated fan, this system is very similar to the air-breathing PEFC system.

Yalcinoz and Alam [52] developed a dynamic model for an air-breathing PEFC system to power a laptop. The system consists of a fuel cell stack, a dc-dc converter, a load control, and a feedback controller. The results showed that the power consumption of the laptop depends on the operating conditions (e.g., load alteration) and that it is
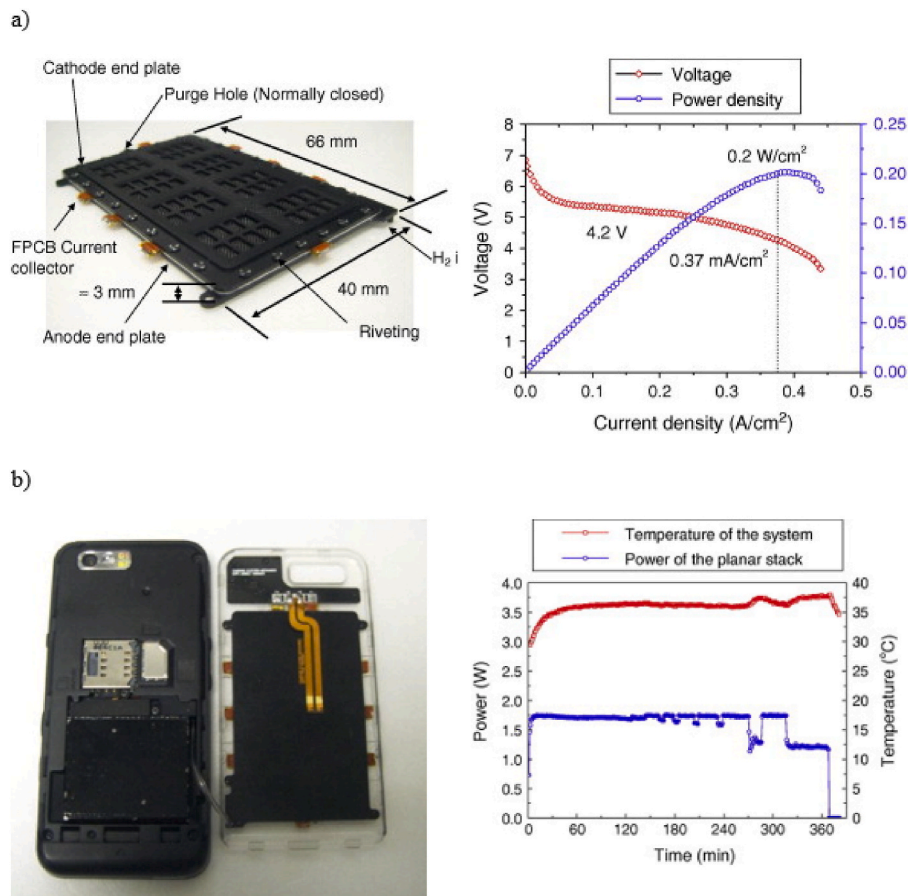

Fig. 15. Schematic representation of the 4-cell air-breathing PEFC developed by Baroutaji et al. [86]. Reprinted with permission from Elsevier.

Fig. 16. Views and performances of (a) an 8-cell air-breathing PEFC stack and (b) a mobile phone powered by an air-breathing PEFC. Reprinted with permission from Elsevier [28].

possible to keep the voltage of the system at a desirable level for the laptop by the feedback controller.

Ferreira-Aparicio [133] reviewed some of the attempts to widely commercialise air-breathing PEFCs and stated that most (if not all) of these attempts have been unsuccessful. The author discussed and analysed the key research and development bottlenecks that hinder the widespread deployment of air-breathing PEFCs; namely, the reliability of the fuel cell operation under extreme ambient conditions (e.g., extremely high and low ambient temperatures), weight reduction, the safety of hydrogen storage devices, and the high cost of materials.

9. Discussion and recommendations for future work

The air-breathing PEFC is a promising technology for a multitude of portable applications and this is due to being more environmentally friendly and less reliable on the national grid when compared to other conventional energy sources. Numerous experimental and modelling studies have been conducted to examine the effects of different design parameters and ambient conditions on the performance of air-breathing PEFC. The main motive behind these investigations is to look for ways to improve the fuel cell performance to make it more reliable and commercially attractive. However, very few studies have been conducted on hydrogen storage and delivery, air-breathing PEFC stacks, and air-breathing PEFC systems. Miniaturising the fuel cell system in order to make it more commercially viable for small portable applications is one of the primary goals of these investigations. In this work, we have exhaustively reviewed the articles on air-breathing PEFCs. Below are key findings and some recommendations for future work:

- The opening ratio of the window-based cathode current collector should be optimised to ensure a sufficient supply of oxygen and water to the cathode of the fuel cell and good electrical contact between the current collector and the MEA of the fuel cell.
- Likewise, the thickness of the cathode GDL in air-breathing PEFCs should be optimised; very thin GDLs increase the likelihood of membrane dry-out while very thick GDLs increase the mass transport and thermal resistances. Similarly, the GDL should be moderately hydrophobic as super-hydrophobic GDLs result in water flooding while hydrophilic GDLs lead to membrane dry-out.
- The impact of the ambient humidity on the air-breathing PEFC performance depends on the ambient temperature. Low ambient humidity is favoured with low ambient temperature (10 °C) to avoid water flooding while high ambient humidity is favoured with high ambient temperature to avoid membrane dry-out. The ambient conditions are beyond the control of the user and therefore, there have been some passive and active means (e.g., an electroosmotic pump) to manage better the liquid water. However, these mitigation means add to the size of the fuel cell system and may lower its commercial competitiveness.
- The air-breathing PEFC in general performs better when it is oriented vertically or horizontally facing upwards rather than horizontally facing downwards, and this is due to better heat dissipation and supply of oxygen and water to the fuel cell in the former two cases.
- Although the structures and the materials of the components (e.g., GDL, MPL, and catalyst layer) of air-breathing PEFCs are largely similar to those of conventional PEFCs, the characteristics of these components may show different effects on the performance of the fuel cell. For example, Calili-Cankir et al. [54] reported that the

performances of air-breathing and conventional PEFCs are affected by the porosity of the GDL differently: the performance of air-breathing PEFC improves with decreasing porosity while the performance of conventional PEFC improves with increasing porosity. Therefore, the parameters of the components should be optimised separately for air-breathing PEFC.

- Reducing the weight and size of the fuel cell components while maintaining good thermal and water management is one of the key challenges for air-breathing PEFCs. Light-weight gold-plated PCB [65] and polycarbonate [129] are promising materials for flow-field plates. It is, therefore, recommended that a variety of cost-effective non-conductive materials coated with highly conductive metals are used for the current collectors and the end plates to reduce the size, weight, and cost of air-breathing PEFCs.

- Many studies have been centred on reducing the catalyst loading or exploring alternative, more cost-effective catalysts for the cathode catalyst layer and this is due to the high-cost of the platinum-based catalysts [83,84]. Likewise, the above objectives are applicable to the anode catalyst layer and could be considered when seeking an overall cost reduction.

- The incorporation of the MPL between the catalyst layer and macroporous substrate is a crucial aspect in managing liquid water within the MEA. A very well-designed MPL could significantly mitigate undesirable phenomena of water flooding, particularly at the cathode side [134,135]. On the other hand, poorly designed MPLs may trap water produced at the cathode catalyst layer and consequently result in water flooding, and/or significantly increase the mass and charge transfer resistances [136]. Reviewing the relevant literature, MPL optimisation in air-breathing PEFCs was limited to the thickness of the MPL [88]. Further research is required to optimise other aspects of the MPLs (e.g., porosity and contact angle) with the aim of enhancing the water management and fuel cell performance.

- Enhancing the wettability of the porous medium (i.e., GDL and MPL) in air-breathing PEFCs is necessary to alleviate the negative effects of ohmic and concentration losses. Recently, Lee et al. [137] provided an overview of novel approaches used for the GDLs and the MPLs of PEFCs. For example, the wettability-patterned GDLs/MPLs are novel designs aiming at creating a hydrophobicity gradient within the surface of the porous media that accelerates the removal of excess water and subsequently the supply of reactant gases to the cathode catalyst layer [138]. Similarly, the perforation of GDLs/MPLs by a laser beam was found to significantly enhance the performance of conventional PEFCs [139]. It will be of great interest to investigate the impact of wettability-patterned or perforated GDLs/MPLs on the performance of air-breathing PEFCs.

- Research on the load-following capability of air-breathing PEFCs has been restricted to a limited number of studies [52,53,55]. Additional modelling analyses need to be conducted to assess the impact of the cell numbers on the dynamic response of an air-breathing PEFC. Also, the dynamic response of a small portable electronic device powered by an air-breathing PEFC should be investigated at extreme ambient and operating conditions.

- As discussed in Section 4 and Section 5, the efficiency of air-breathing PEFCs is influenced by the orientation of the fuel cell and ambient conditions. The task of rendering air-breathing PEFCs intensive to the influence of these variables poses an immense challenge. Therefore, novel methodologies need to be explored to eradicate or alleviate these adverse effects of the orientation and ambient conditions in portable air-breathing PEFC powered systems. The integration of a hybrid miniature air-breathing PEFC and battery system into a portable device has the potential to mitigate these adverse effects and provide at the same time a fast dynamic response to sudden and/or substantial load changes.

10. Summary

Air-breathing PEFCs are attractive alternative power conversion technologies, particularly for small electronic devices, as the time taken between recharges is, compared to batteries, significantly longer. Further, air-breathing PEFCs, again compared to batteries, do not involve toxic heavy metals whose disposal forms an environmental challenge. Furthermore, air-breathing PEFCs, compared to conventional PEFCs, are substantially simpler, and this is due to their reliance on natural convection to transport oxygen and water vapour between ambient air and the open cathode of the fuel cell. However, due to the low heat and mass transfer coefficients associated with natural convection, the output power and the operational stability of air-breathing PEFCs are relatively small compared to conventional PEFCs. Therefore, as reviewed in this paper, there have been considerable experimental and modelling investigations in the literature looking into the impact of various design parameters and ambient conditions on the air-breathing PEFC performance.

For completeness, the mathematical modelling of air-breathing PEFCs has been reviewed listing the conservation equations and how they are adapted to account for natural convection at the open cathode.

The literature has shown that very few investigations have been conducted concerning: hydrogen storage and delivery; air-breathing PEFC stacks; and air-breathing PEFC systems. One of the main aims behind these few investigations is to miniaturise the fuel cell system to make it more commercially attractive for small portable applications. Overall, there are still some technical and economic issues that the air-breathing PEFC system needs to overcome to make a sizeable market penetration. These issues include, but are not limited to: reliability of operation under extreme ambient conditions (very low or very high temperatures); size and weight reduction; the safety of hydrogen storage; and cost reduction. Evidently, relevant research needs to be substantially intensified to appropriately address all the above issues.

CRediT authorship contribution statement

Fatma Calili-Cankir: Conceptualization, Methodology, Investigation, Validation, Visualization, Writing – original draft, Writing – review & editing. **Mohammed S. Ismail:** Conceptualization, Methodology, Investigation, Validation, Supervision, Writing – original draft, Writing – review & editing. **Derek B. Ingham:** Supervision, Writing – review & editing. **Kevin J. Hughes:** Supervision, Writing – review & editing. **Lin Ma:** Supervision, Writing – review & editing. **Mohamed Pourkashanian:** Supervision, Project administration, Writing – review & editing.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Data availability

No data was used for the research described in the article.

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