Review

A comprehensive review of direct carbon fuel cell technology

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A B S T R A C T

Fuel cells are under development for a range of applications for transport, stationary and portable power appliances. Fuel cell technology has advanced to the stage where commercial field trials for both transport and stationary applications are in progress. The electric efficiency typically varies between 40 and 60% for gaseous or liquid fuels. About 30–40% of the energy of the fuel is available as heat, the quality of which varies based on the operating temperature of the fuel cell. The utilisation of this heat component to further boost system efficiency is dictated by the application and end-use requirements. Fuel cells utilise either a gaseous or liquid fuel with most using hydrogen or synthetic gas produced by a variety of different means (reforming of natural gas or liquefied petroleum gas, reforming of liquid fuels such as diesel and kerosene, coal or biomass gasification, or hydrogen produced via water splitting/electrolysis). Direct Carbon Fuel Cells (DCFC) utilise solid carbon as the fuel and have historically attracted less investment than other types of gas or liquid fed fuel cells. However, volatility in gas and oil commodity prices and the increasing concern about the environmental impact of burning heavy fossil fuels for power generation has led to DCFCs gaining more attention within the global research community. A DCFC converts the chemical energy in solid carbon directly into electricity through its direct electrochemical oxidation. The fuel utilisation can be almost 100% as the fuel feed and product gases are distinct phases and thus can be easily separated. This is not the case with other fuel cell types for which the fuel utilisation within the cell is typically limited to below 85%. The theoretical efficiency is also high, around 100%. The combination of these two factors, lead to the projected electric efficiency of DCFC approaching 80% - approximately twice the efficiency of current generation coal fired power plants, thus leading to a 50% reduction in greenhouse gas emissions. The amount of CO_2 for storage/sequestration is also halved. Moreover, the exit gas is an almost pure CO_2 stream, requiring little or no gas separation before compression for sequestration. Therefore, the energy and cost penalties to capture the CO_2 will also be significantly less than for other technologies. Furthermore, a variety of abundant fuels such as coal, coke, tar, biomass and organic waste can be used. Despite these advantages, the technology is at an early stage of development requiring solutions to many complex challenges related to materials degradation, fuel delivery, reaction kinetics, stack fabrication and system design, before it can be considered for commercialisation. This paper, following a brief introduction to other fuel cells, reviews in detail the current status of the direct carbon fuel cell technology, recent progress, technical challenges and discusses the future of the technology.

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1. Introduction

Fuel cells have long been heralded as a replacement for current less efficient power generation technologies and have been under development since about 1960 even though the first fuel cell was demonstrated by Grove in 1839 [1–3] about 160 years ago. "The Birth of the Fuel Cell 1835–1845" gives an interesting account of the history of early fuel cell research [3]. Since these early experiments, a wide range of fuel cell devices have undergone research, development and demonstrations [4–18]. The applications of fuel cells are enormous and include large scale stationary power generation (MW range), distributed combined heat and power (CHP) (e. g. for remote areas, residential and commercial dwellings), transport (e. g. cars, buses, locomotives, submarines, scooters, auto-rickshaws, auto-bicycles, and other small transporters) and portable power (e. g. electronic appliances, portable power packs, emergency power). The operating temperatures of different types of fuel cells vary considerably from room temperature to 1000 °C. Therefore,

there is a large variation in the electrode, electrolyte and other stack construction materials with the overall system and control requirements varying accordingly [5,6].

Research and development into fuel cells is continuing at both commercial and early stage research levels with a large number of products undergoing early stage trials or being delivered to the market [16,19–35]. These systems range from small micro-fuel cells producing only 2–3 W [23] to large scale multi-megawatt systems [24]. Depending on the dimensions and type of fuel cell, a single cell may produce less than 1 W of electricity at less than a volt. Thus, to deliver the desired power for a given application and to increase the output voltage, most systems connect multiple cells together in series with modules of multiple cells connected in series or parallel. This modular nature offers size flexibility (better load matching with end user application) and increases overall reliability. Fuel cells are also less susceptible to efficiency penalties, as the size decreases to kW range, compared to conventional power generation technologies such as steam or gas turbines. There is no

Abbreviations and acronyms

AFC	Alkaline Fuel Cell
APU	Auxiliary Power Unit
ASR	Area Specific Resistance
BOP	Balance-of-Plant
CCE	Clean Coal Energy Inc.
CHP	Combined Heat and Power
DARPA	Defence Advanced Research Projects Agency
DBFC	Direct Borohydride Fuel Cell
DCFC	Direct Carbon Fuel Cell
DEFC	Direct Ethanol Fuel Cell
DHFC	Direct Hydrogen Micro/Portable Fuel Cell
DMFC	Direct Methanol Fuel Cell
EPRI	Electric Power Research Institute
GDC	Gadolinia Doped Ceria
HHV	High Heating Value
IGCC	Integrated Gasification Combined Cycle
LHV	Low Heating Value
LLNL	Lawrence Livermore National Laboratory
LMA	Liquid Metal Anode
LSCr	Lanthanum Strontium Chromite
LSM	Lanthanum Strontium Manganite
LST	Lanthanum Strontium Titanate
LTA	Liquid Tin Anode
MCFC	Molten Carbonate Fuel Cell
LPG	Liquefied Petroleum Gas
MC-DCFC	Molten Carbonate Direct Carbon Fuel Cell
NEDO	New Energy and Industrial Technology Development Organization
NGCC	Natural Gas Combined Cycle
OCV	Open Circuit Voltage
PAFC	Phosphoric Acid Fuel Cell
PCC	Pulverized Coal Combustion
PDA	Personal Digital Assistant
PEM	Proton Exchange Membrane
PEMFC	Polymer Electrolyte Membrane Fuel Cell
PROX	Preferential Oxidiser
SARA	Scientific Applications and Research Associates Inc.
SASOL	South African Synthetic Oil Limited
ScSZ	Scandia Stabilised Zirconia
SDC	Samaria Doped Ceria
SOFC	Solid Oxide Fuel Cell
SRI	Stanford Research Institute
TPB	Triple Phase Boundary
TZ3Y	Tetragonal Zirconia with 3 mol % Yttria
UPS	Uninterrupted Power Supply
USCC	Ultra-supercritical Coal Combustion
UTC	United Technologies Company
WVU	West Virginia University
XRD	X-ray Diffraction
YSZ	Yttria Stabilized Zirconia

fundamental reason why fuel cells in a small system should not operate with the same efficiency as those in much larger systems. However, fuel processing and thermal management on a larger scale is significantly less challenging which may lead to larger systems having a greater overall efficiency. Fuel cells do not rely on pressure or thermal gradients to produce power and are not governed by the Carnot cycle. Thus they have much higher theoretical efficiencies than heat engines. The absence of a high pressure, high temperature combustion chamber and the fact that air and fuel are separated in a fuel cell, also leads to significantly lower emissions (such as nitrous oxide or particulate matter). The combination of high operating efficiencies at almost any scale and low emissions is driving the development of a wide range of systems for a number of markets. In general, early market entry points appear to be battery chargers [23,25–28] and, micro-CHP units [16,21,22,29–34]. Other key markets going forward include decentralised stationary power, embedded generation and the transport sector with the automotive industry taking a lead role. Numerous organisations are at an advanced stage of product development within these market sectors [6,20,35–51]. However, despite these recent advances there is considerable uncertainty about the reliability, lifetime and cost of fuel cell systems.

Direct carbon fuel cells (DCFCs) are still at the very preliminary stage of development with only few authors or industrial organisations reporting performance parameters on single cells or small stacks which are somewhat similar to those obtained for gas fed fuel cell systems. Although a wide range of designs and concepts have been tested, there is currently no clear leader within the field with respect to optimal design or operating parameters. Even fundamental design parameters such as operating temperature are currently undecided. An EPRI report has given assessment of direct coal conversion fuel cells for utility applications [52]. This report concludes that potential benefits of the technology are rather large such as high conversion efficiencies, relatively low cost coal as the fuel with further cost benefits from concentrated CO_2 as the by-product for sequestration, and a simple system to operate. The report

further concludes that the technology has the potential to address a number of key issues related to coal utilisation with very low carbon pollution compared with coal fired power plants in a carbon constrained world. The technology is at an early stage of R & D, however, there is a compelling case for its future development.

DCFCs convert the chemical energy in a carbon fuel directly into electricity without the need for gasification. Fine (submicron) carbon particles in an electrochemical cell are electrochemically oxidised at high temperatures (600–900 °C) with the overall fuel cell reaction being: $C + O_2 = CO_2$. The reactions in DCFC produce almost pure CO_2, provided high purity carbon is used as the fuel, which can be contained in a concentrated stream and easily captured for downstream use or disposal avoiding the need for costly gas separation technologies. The fuel and products are distinct separate phases (solid and gas), so their separation is easy and the fuel utilisation can be almost 100% (typically 80–95% for other fuel cells). To avoid downstream processing of exit effluent, some processing of coal is required to remove impurities and to turn the fuel into submicron size particles. However, this processing is not as extensive or energy intensive as that required to gasify solid carbon fuels for use within traditional fuel cells or gas turbines. A variety of fuels including coal, coke, tar, biomass and organic waste can be used.

There are three basic types of direct carbon fuel cells. These can be distinguished by the type of electrolyte used: molten hydroxide; molten carbonate and oxygen ion conducting ceramic [52–56]. In addition to the use of different electrolytes, there are further subcategories of DCFCs which are differentiated from each other via the materials used within the anode, the design of the anode chamber and the method of fuel delivery to the electrode/electrolyte interface. For example, systems with ceramic electrolytes may adopt a range of strategies to deliver fuel to the electrode/electrolyte interface including a fluidised bed, carbon mixed with a molten metal or carbon mixed with a molten salt.

Overall effort in the development of DCFC technology has been relatively small in comparison with other major fuel cell

technologies. However, more recently due to concern over global warming and air pollution combined with the realisation that coal is going to remain as a major primary fuel for power generation for several decades, there has been increasing effort in developing technologies which offer a step increase in fuel conversion efficiency. Most other coal technologies such as oxy-fuel firing, pulverised coal combustion (PCC), ultra-supercritical coal combustion (USCC), integrated gasification combined cycle (IGCC) offer an incremental increase in the conversion efficiency for power generation. Therefore, the emphasis is on the development of low cost carbon capture and storage technologies. However, in coal fired power plants, carbon capture and storage can result in a 20–25% energy penalty leading to net power generation efficiency of approximately 30%. This further increases the amount of CO_2 to be captured and stored per unit power delivered.

The theoretical or thermodynamic efficiency in DCFC is close to 100%. Actual stack efficiencies (determined by the thermodynamic efficiency, fuel utilisation factor and voltage efficiency) are projected to be ~80% with total system efficiencies estimated to be above 60% [52,55,57,58] - almost twice those of current generation coal fired plants and significantly higher than other fuel cell types. Thus, compared with conventional coal fired power plants, there is a potential for 50% reduction in greenhouse gas emissions and significantly less CO_2 to be sequestered. The projected cost, including balance-of-plant (BOP) of around US$1500/kW is lower than most other fuel cell types with substantially lower operating costs due to the availability of cheap fuel sources [52].

The DCFC technology has many obvious benefits as discussed above, however, it is at an early stage of development with considerable effort required to take it to the commercialisation stage. Some major challenges that need to be resolved before commercialisation include: mode of solid fuel delivery to electrode electrolyte interface (fluidised bed, molten salt or molten metal); fuel processing and fuel quality requirements (effect of ash and other contaminants in coal on DCFC performance); understanding the electrochemical reaction kinetics and mechanism for carbon oxidation; corrosion of cell components especially where molten salts are used either as the electrolyte or fuel carrier; lifetime (currently far too short even for reasonable demonstration); degradation rates and causes; improvement in materials performance and power densities; overall systems design; and technology up-scaling.

In this paper, a comprehensive review of this new technology and its current status has been given along with an overview of other fuel cell types.

2. Background to fuel cells

A fuel cell is an electrochemical device that converts chemical energy (of a fuel) directly into electrical and heat energy when supplied with a fuel and an oxidant. It consists of an electrolyte, anode and a cathode (an example is shown in Fig. 1). The anode and cathode are electronic conductors and the electrolyte conducts only ionic species. The anode and cathode facilitate anodic and cathodic reactions respectively at the anode/electrolyte and cathode/electrolyte interfaces. Fuel is supplied to the anode and oxidant to the cathode. The fuel oxidises at the anode by an anodic reaction that involves generation of electrons and either formation of ionic species which are transported through the electrolyte to the cathode or formation of compounds by reaction between the fuel and the ionic species transported through the electrolyte from the cathode to anode. The electrons generated in the anodic reaction travel through the outer electrical circuit to the cathode and are responsible for generating power from the fuel cell. The cathodic reaction involves consumption of electrons, and either reaction
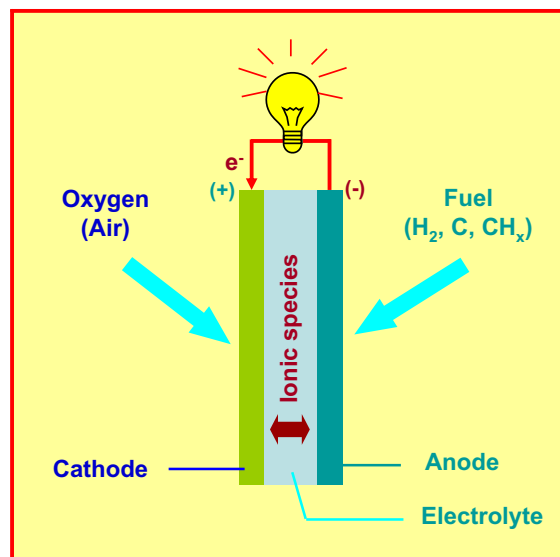

Fig. 1. The basic operating principle of a fuel cell.

between oxygen and ionic species transported through the electrolyte (such as the reaction of protons with molecular oxygen in PEMFC) or the formation of oxygen anions which are transported through the electrolyte from the cathode to the anode (such as in the reaction of oxygen or carbonate ions with molecular hydrogen and/or CO in SOFC or MCFC).

As distinct from batteries which are essentially storage devices, fuel cells can operate continuously through the supply of fuel to the anode and oxidant (typically air) to the cathode. Fuel cells offer several advantages over conventional methods of power generation, such as high efficiencies with combined heat and power (CHP or tri-generation — heating, cooling and power, systems offering efficiencies approaching 90%), high power densities, simpler balance-of-plant (small foot print), low particulate and gas emissions, low noise and high quality power (no spikes or electrical noise). Fuel cells are modular in nature and do not suffer large energy penalties when scaled down to a small size (1–10 kW) when compared to other power producing technologies such as gas turbines or reciprocating engines which can be 50% less efficient at 1 kW scale compared to multi-megawatt systems using the same technology. This makes them ideally suited for distributed power generation which avoids transmission and distribution losses.

2.1. Fuel cell efficiency

The majority of methods used to convert chemical energy into electrical energy rely on pressure and thermal gradients to first convert the chemical energy into kinetic energy which is then converted into electrical energy. Efficiency of these systems is typically governed by the Carnot cycle. Fuel cells, however, generate electricity via electrochemical reaction of the fuel and are thus not limited by the Carnot cycle. The total amount of energy available to produce electricity is known as the free energy and is often referred to as the Gibbs free energy. The Gibbs free energy for a fuel oxidation reaction is given by:

$$\Delta G = \Delta H - T\Delta S \tag{1}$$

ΔH is the enthalpy of the fuel oxidation reaction,
ΔS is the entropy term, and
T is the temperature at which the reaction occurs.

Only free energy (ΔG) of the fuel oxidation reaction is available for conversion to electricity with the remainder consumed via the entropy change. The open circuit or reversible voltage (E_{ocv}) of the cell is given by the free energy (ΔG) of the fuel oxidation reaction:

$$E_{ocv} = -\Delta G / nF \qquad (2)$$

where n is number of electrons transferred in the fuel cell electrochemical reaction and F is the Faraday constant. The reversible voltages of different fuel oxidations reactions are given in the Table 1.

The thermodynamic (maximum) fuel efficiency (ϕF_{th}) of a fuel cell (based on all the fuel being utilised) is defined as the ratio of free energy (ΔG) and enthalpy (ΔH) of the fuel oxidation reaction:

$$\phi F_{th}(\%) = (\Delta G / \Delta H)100 = (1 - (T\Delta S / \Delta H))100$$
$$= (-nE_{ocv}F / \Delta H)100. \qquad (3)$$

Fuel cell efficiency increases or decreases with temperature depending on whether ΔS is positive or negative (see Table 1 and Fig. 2), thus it varies with the type of fuel reaction. For example for carbon, methane (91–93% of natural gas is methane), hydrogen and CO, fuel cell efficiencies are 100, 92, 83, and 91% at 25 °C [9] and 101, 100, 69 and 61% respectively at 980 °C based on the high heating value (HHV) of the fuel. For some fuel reactions, ΔS is negative and in this case efficiency higher than 100% can be achieved but only by the system absorbing heat from the surroundings. Fig. 2 shows how the maximum or theoretical efficiency would vary with operating temperature of the fuel cell. The Figure suggests that, from a thermodynamic perspective, in order to maximise efficiency it would be beneficial to operate fuel cells on either methane (at elevated temperature) or carbon. Direct oxidation of methane within solid oxide fuel cells at high temperature has indeed been reported [59–61]. However, dry reforming or direct electrochemical oxidation of methane in a SOFC has very poor conversion efficiency and also leads to the deposition of carbon on the anode [15,59–61]. To internally reform methane, a large quantity of steam (steam/carbon ratio above 2.5) is needed to be introduced into the fuel cell stack. This potentially reduces efficiency and substantially increases system complexity.

Clearly no system ever operates at its maximum theoretical efficiency and fuel cells are no different in this respect. The overall electrical efficiency of a fuel cell stack is relatively simple to measure and is a product of the thermodynamic efficiency, fuel utilisation factor and voltage efficiency as discussed below. When the cell is loaded, internal cell losses cause the cell open circuit voltage (E_{OCV}) to reduce to cell operating voltage (E_{OP}). The cell losses are a consequence of the ohmic and electrode (anode and cathode) overpotential losses. The ohmic polarisation occurs due to
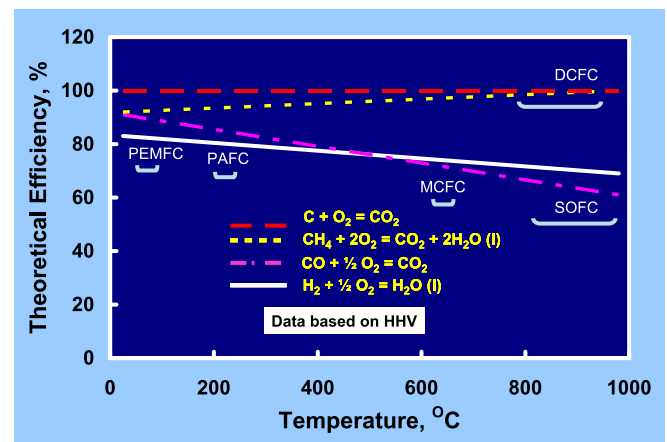

Fig. 2. The theoretical efficiency of different fuels calculated from free energy of the fuel oxidation reaction as a function of temperature. Different types of fuel cells and their operating temperature regime are also shown as an indication of their theoretical efficiency for a particular fuel.

the resistance of the cell components (electrode, electrolyte, interconnects, current collectors, etc.) and contact resistances. Several different rate limiting processes such as diffusion (mass transport of ionic or gaseous species from or to the electrode/electrolyte interface), charge transfer or surface adsorption/dissociation of fuel or oxygen may contribute to the total overpotential losses for a given operating condition.

Under load (i. e. when current is drawn from the fuel cell), the cell operating voltage, E_{OP}, is given by:

$$E_{OP} = E_{OCV} - I_d R - \eta_a - \eta_c - I_d r - \eta_{concn} \qquad (4)$$

r = resistance of air and fuel electrodes, interconnect and other components

R = resistance of the electrolyte

I_d = current density (current normalised per unit area)

η_a = anodic polarisation or overpotential losses at anode/electrolyte interface

η_c = cathodic polarisation or overpotential losses at cathode/electrolyte interface

η_{concn} = concentration polarisation related to slow diffusion of reactant/product species to and from elelctrode/elelctrolyte interface and usually is noticeable when fuel cells are operated at high current densities.

Both $I_d R$ and $I_d r$ are pure ohmic voltage losses and increase linearly with current density, whereas, overpotential losses follow a non-linear relationship with current density and are highly

Table 1
Thermodynamic properties, reversible voltages and thermodynamic efficiencies of different fuel oxidation reactions.

Reaction	n	$-\Delta H°$ (kcal/mol)	$-\Delta G°$ (kcal/mol)	$E_{ocv}°$ (V)		Thermodynamic efficiency (%)	
				25 °C	980 °C	25 °C [9]	980 °C
$H_2 + ½ O_2 = H_2O_{(l)}$ (HHV)	2	68.14	56.69	1.23	–	83	69
$H_2 + ½ O_2 = H_2O_{(g)}$ (LHV)	2	57.84	54.64	1.19	0.97	94	72
$C + ½ O_2 = CO$	2	26.4	32.81	0.71	1.16	124	197
$C + O_2 = CO_2$	4	94.05	94.26	1.02	1.03	100	100
$CO + ½ O_2 = CO_2$	2	67.62	61.45	1.33	0.90	91	61
$CH_3OH + 3/2O_2 = CO_2 + 2H_2O_{(l)}$	6	173.66	167.9	1.21	1.46	97	97
$CH_4 + 2O_2 = CO_2 + 2H_2O_{(l)}$ (HHV)	8	212.91	195.6	1.06	1.06	92	100

The higher heating value (HHV) (the gross calorific value or full energy content of a fuel) is defined as the amount of heat released by a specified quantity (initially at 25 °C) once it is combusted and the products have returned to a temperature of 25 °C. In calculating efficiency, it is more meaningful to use HHV rather than LHV value of a fuel. The HHV is always greater than the LHV, and the difference is largest for hydrogen, less but still significant for natural gas (lower hydrogen content), less still for liquid fuels as the hydrogen content decreases, and not much for solid fuels.

dependent on electrode materials and microstructure, fuel composition, reaction mechanism, operating temperature and the cell design. The voltage efficiency of the fuel cell is the ratio E_{OP}/E_{OCV}. In general in a fuel cell, like many other electrochemical devices, the voltage efficiency decreases with increasing current density whereas power density (product of net cell/stack voltage and current density) shows a peak at a certain current density. The typical data for an operating fuel cell is shown in Fig. 3. On the primary vertical axis of this figure is also plotted the voltage efficiency (a ratio of operating cell voltage to reversible cell voltage of 1.2 V) as a function of current density. The fuel utilisation has been assumed to be 100% for all current densities in calculating voltage efficiency in this Figure. It can be seen in the Figure that the power density reaches a peak value at certain value of current density (650 mA cm^{-2} in this case), however, the voltage efficiency continues to drop with increase in current density. The power density is a function of cell/stack design and construction materials, their respective performances to either the fuel oxidation or oxidant reduction reactions and ion and electron transfer through various materials at the fuel cell operating temperature. The example given here shows that the maximum power density achieved is 442 mW cm^{-2} at 650 mA cm^{-2}, and the corresponding voltage efficiency achievable is 55%. Another interesting attribute to be noticed in this figure is that at some values of current densities on either side of the peak value of power density, the achievable power densities are same. For example at current densities of 600 and 700 mA cm^{-2}, the power density value is 432 mW cm^{-2}, but the corresponding voltage efficiencies achievable are respectively 58.5% and 50%. Therefore, the preference would be to operate the cell at 600 mA cm^{-2}, which would be further advantageous in prolonging the life of the fuel cell. Thus there is a complex relationship and trade-off between power density (including peak power density) and cell/stack voltage efficiency.

Internal electrical short circuiting is a phenomenon often ignored in fuel cell operation and calculating overall electrical efficiency. However, it can occur due to membrane rupture (e. g. in PEMFC) and development of electronic conductivity in the electrolyte under reducing conditions (e. g. ceria based electrolytes in SOFC and DCFC). If internal electronic shorting occurs, this would reduce OCV and electrical efficiency.

In addition to the electrical and electrochemical losses within a fuel cell another major limiting factor is the fuel utilisation. The fuel utilisation factor (F_U) is the ratio of fuel utilised for electric power generation to total fuel consumed and it varies significantly with fuel cell stack design, operating variables and current density.
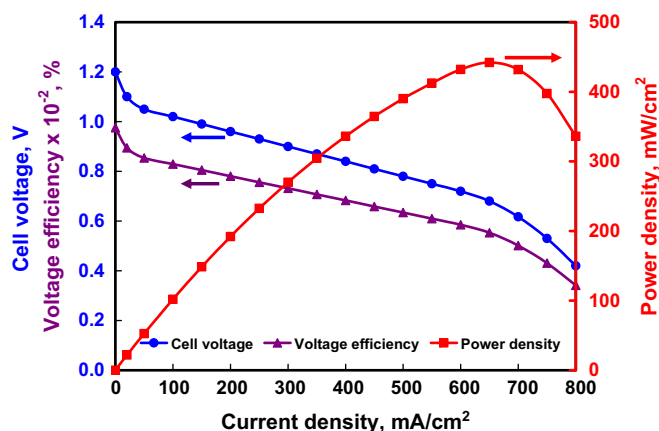
In fuel cells with flowing fuel system and where products are formed on the fuel side, it is practically impossible to operate a fuel cell at greater than 80–90% fuel utilisation. With hydrogen or other gaseous fuels such as CO, there is increasing fuel dilution with product gases from entry to exit sides leading to kinetic and diffusion limitations for cell reactions and also have an effect on the available cell voltage. Other factors that may lead to lower fuel utilisation are fuel leaks and fuel cross-over from anode to cathode compartment. Furthermore, separation of un-reacted gaseous fuels from product gases (e. g. CO_2), downstream from the fuel cell stack, are difficult and less cost effective. This is not an indication that 10–20% of the fuel is totally wasted within real systems with most being designed to further utilise this un-reacted fuel downstream of the fuel cell system either through hybrid gas turbine/fuel cell systems [47,48,62], recycling the spent fuel back to the incoming gas stream [62] or through the use of combined heat and power [16,63]. None of these approaches are ideal as they add system complexity and can lead to fuel being used in less efficient sub-systems (e. g.combustion for heat or steam generation). With respect to fuel utilisation direct carbon fuel cells have a clear advantage over existing fuel cell systems because a solid fuel can be easily separated from the waste products that are all gaseous. This could simplify the system design and increase fuel utilisation to near 100%. Similarly, the cell potential does not decrease as the fuel is consumed, further simplifying the system design with all the cells within the system being held at a common potential. However, in real DCFC systems, the fuel utilisation may not be 100% with some losses expected due to side chemical reactions leading to some efficiency penalty.

The overall electric efficiency of a fuel cell stack is product of three terms discussed above ($\phi F_{th}(\%)$. (E_{OP}/E_{OCV}). F_U). There will be further system related efficiency penalties for operating auxiliary sub-systems (compressors, blowers, fuel and oxidant delivery, control/monitoring/safety, power conditioning equipment, etc.).

2.2. Different types of fuel cells

Fuel cells are generally named based on the type of electrolyte or fuel used. For example, Proton Exchange Membrane (PEM) fuel cells use a polymer electrolyte for conducting protons and Molten Carbonate Fuel Cells (MCFC) use molten carbonate as electrolyte for conducting carbonate ions, Direct Methanol Fuel Cell (DMFC) although using proton exchange membrane as the electrolyte is named after the fuel it uses in order to differentiate it from conventional PEMFC. Fuel cells may also be divided according to their operating temperature regime: low temperature (AFC - alkaline, PEMFC − polymer electrolyte membrane, DMFC − direct methanol); medium temperature (PAFC − phosphoric acid); and high temperature (MCFC, DCFC and SOFC). Fig. 4 shows various types of fuel cells and their characteristics, i. e. fuel and oxidant, anodic and cathodic reactions, electrolytes and operating temperature range. A summary of various fuel cell types is given below and general features of main fuel cell types are given in Table 2. Only the direct carbon fuel cells will be discussed in sections which will then follow. For detailed descriptions of other main fuel cell types see references [5−7]. In addition to the main families of fuel cells, there are an increasing number of systems being developed that do not fit easily into any of the above mentioned families. These include the direct ethanol fuel cell [64], biological fuel cells [65], composite solid oxide/molten carbonate fuel cells [66], direct ammonia fuel cells [67] and the direct carbon fuel cell (which is the subject of this review). In addition to those mentioned above, there are many other types of fuel cells currently being developed a selection of which can be found in references [64,68−75].

Fig. 3. Diagram showing fuel cell voltage, efficiency and power density plots versus current density.

Fuel Cell	Fuel / Anod. Reaction	Electrolyte	Oxidant / Cath. Reaction	T, °C
PEMFC	H_2 $H_2 = 2H^+ + 2e^-$	PEM $H^+ \rightarrow$	Air as oxidant $\frac{1}{2} O_2 + 2H^+ + 2e^- = H_2O$	60 - 120
DMFC	H_2 $CH_3OH + H_2O = CO_2 + 6H^+ + 6e^-$	PEM $H^+ \rightarrow$	Air as oxidant $3/2 O_2 + 6H^+ + 6e^- = 3H_2O$	60 - 120
AFC	H_2 $H_2 + 2OH^- = 2H_2O + 2e^-$	KOH $OH^- \leftarrow$	Air as oxidant $\frac{1}{2} O_2 + H_2O + 2e^- = 2OH^-$	<100
PAFC	H_2 $H_2 = 2H^+ + 2e^-$	H_3PO_4 $H^+ \rightarrow$	Air as oxidant $\frac{1}{2} O_2 + 2H^+ + 2e^- = H_2O$	160 - 220
MCFC	CH_x, CO, H_2 $H_2 + CO_3^{2-} = H_2O + CO_2 + 2e^-$	Molten Carbonate CO_3^{2-}	Air as oxidant $\frac{1}{2} O_2 + CO_2 + 2e^- = CO_3^{2-}$	600 - 800
SOFC	CH_x, CO, H_2 $H_2 + O^{2-} = H_2O + 2e^-$	O^{2-} conducting ceramic $O^{2-} \leftarrow$	Air as oxidant $\frac{1}{2} O_2 + 2e^- = O^{2-}$	800 - 1000
DCFC	Carbon	Molten salt, or O^{2-} conducting ceramic	Air as oxidant	500 - 1000

Fig. 4. Major types of fuel cells currently under development.

2.2.1. Alkaline fuel cell (AFC)

AFCs are one of the earliest fuel cell systems developed and have provided electricity and hot water for many US space missions. AFCs use concentrated aqueous solution of potassium hydroxide (KOH) as the electrolyte. The concentration of hydroxide solution ranges between 35 and 85 wt% depending on the intended operating temperature. The operating temperature can vary from less than 80 °C to approximately 250 °C. Most systems operate at the lower end of this window to avoid loss of water from the electrolyte. Unlike other forms of low temperature fuel cell AFCs do not require precious metal catalysts with nickel commonly being used as an electrode material. The major drawback of this technology is that AFCs show a significant degradation when exposed to CO_2 either within the oxidant stream or within the fuel stream. There have been a number of solutions proposed to this issue including oxidant and fuel scrubbing to remove CO_2 and electrolyte circulation with outside scrubbing. Despite these solutions being relatively effective, performance loss and long term durability of the alkaline fuel cells are still major issues especially when using atmospheric air as the oxidant [76].

There is now only a modest global effort on this type of fuel cell technology with only a limited number of organisations currently pursuing this technology commercially [9,19,77–79]. AFC Energy is developing low cost AFCs for large scale industrial applications (e. g. alkali market, underground coal gasification) which operate around

70 °C using non-platinum electrodes and injection moulded plastic and rubber sealants [19]. Siemens and UTC have demonstrated a lifetime of 20, 000 h and 15, 000 h respectively, but this performance was only achieved with pure (CO_2 free) oxygen and hydrogen [77]. Further details of the technology can be found in references [5,6,9,19,76,79].

2.2.2. Polymer electrolyte membrane fuel cell (PEMFC)

PEMFC consists of a polymer membrane (e. g. NAFION) with proton conductivity as the electrolyte, and anode and cathode materials are typically finely divided Pt supported on high surface area carbon with carbon backing paper or cloth as gas diffusion layers on both air and fuel sides. However, CO tolerance of the Pt anode is poor, once the CO level in the gas stream exceeds 10–20ppm, at the typical fuel cell operating temperature of 60–80 °C. Each cell is separated by an electronically conducting interconnect plate. These plates connect all the cells in series. A number of different materials (graphite, metal or conducting plastics or metal/plastic composites) have been used as the separator plate. Also, in addition to the NAFION membrane, a number of other membrane materials (including those which can operate above 100 °C), have been the subject of research, development and commercialisation. Heat and water management systems need to be carefully considered in PEMFC stacks as the membrane must maintain a certain water content in order to function. As the water

Table 2
General characteristics of main fuel cell types.

Parameter	AFC	PEMFC	PAFC	MCFC	SOFC	DCFC
T_{op}, °C	<100	<100	200–215	650	700–1000	650–900
Heat output		60–70	150–200	500–600	600–900	500–800
Electrical efficiency (%)	45–60	40–45	40–45	45–55	40–50 Planar, 50–65 Tu/MT	>80
CHP efficiency (%)	>80	>80	>80	>80	>80	>90
Thermal insulation	Low	Low	Medium	High	High	High
Internal reforming	Not possible	Not possible	Not possible	Only with steam	Only with steam	Not applicable
Electrolyte	KOH	PEM	H_3PO_4	Molten carbonate	O^{2-} conducting ceramic	Molten carbonate/molten hydroxide/O^{2-} conducting ceramic
Impurity sensitivity	CO_2, CO, S	S, CO ~20ppm	Sulphur	Sulphur	Sulphur	Unknown
Power at cold start	>50%	>50%	Nil	Nil	Nil	Nil
Thermal cycling	Unlimited	Unlimited	Good	Restricted	Restricted	Restricted
Start-up/shut-down	Very fast (sec)	Very fast (sec)	Slow (hrs)	Several hrs	Several hrs[a]	Several hours
Load following	Excellent	Excellent	Limited	Limited	Limited	Limited
BOP	Simple	Simple	Medium	Complex	Complex	Complex

Tu = Tubular, MT = Microturbine, sec = seconds.

[a] Some small tubular design units may heat up to the operating temperature in less than 1 h.

content of the membrane is reduced and the membrane dries, the ionic conductivity drops, whereas excess water may flood the electrode/electrolyte interface reducing reaction kinetics. Other technical and operational issues include slow oxygen reaction kinetics, high noble metal catalyst loading, unsatisfactory membrane lifetime (degradation due to swelling and softening in operation, leaching of sulphonic acid groups and fluoride ions, cation contamination, pin holes and rupture) and anode catalyst poisoning in the presence of fuel containing >20ppm CO. Therefore, external reforming of fuel and gas cleaning to reduce CO levels to <20ppm is absolutely critical to reduce degradation and increase the stack lifetime. Due to the rapid start-up and shut-down, thermal cycling and load following capability of PEMFCs, the market potential is substantial. Major markets for PEMFCs are: residential micro-CHP; remote area power supplies; various forms of transport applications (including cars, buses, trucks, locomotives, submarines, wheel chairs, scooters, auto-bicycles, auto-rickshaws, delivery vans, armoured vehicles, and small transporters at airports, shipyards and railway stations); auxiliary power units (APU) for vehicles electric needs and for un-interruptible/back-up power. The electric efficiency is 35−60% depending on the load whereas for applications where the low grade heat produced by the fuel cell can be effectively utilised, the system efficiency may be between 60 and 80%. Most major automobile manufacturers have a program in PEMFC technology developments and several prototype vehicles are undergoing evaluation. PEMFC units up to 10 kW in size for stationary applications and 50−200 kW units for transport vehicles are now commercially available but at a high cost and with limited warranties. The readers are referred to references [5,6,8−10,14,45,80,81] for further details on technology challenges and status.

2.2.3. Direct hydrogen micro/portable fuel cell (DHFC)

PEMFC operating on hydrogen fuel in the 1−500W power output range are also under development for portable power applications (soldier packs, laptops, cellular phones, PDAs, portable electronic appliances, remote communication, emergency power, camping lights, variable message signs, etc.) [82]. Micro fuel cells are similar in operation to normal PEMFCs with many common cell materials. However, they have stringent requirements on the design and operation in terms of near room temperature operation, near 100% fuel utilisation, minimum balance-of-plant items (possibly without any moving parts), self-air breathing (no air supply or pumps), self heat and water management, no membrane humidification and compact size (no more than the battery pack) [74,82,83]. Since micro-fuel cells are low power devices, they typically operate at low current densities compared with conventional PEM fuel cells. Mass manufacturing and micro fabrication techniques are being employed for miniaturisation, large volume manufacturing and to reduce cost. Angstrom Power, a Canadian based company, has been developing a planar design hydrogen based fuel cell system since 2001 to substitute for lithium ion batteries in mobile phones and other portable power appliances [26]. The technology is based on a novel thin film fuel cell architecture design, metal hydride based high energy density hydrogen storage and micro fluidic components for safe operation of the device in a wide range of environmental conditions. The company has successfully demonstrated integration of its micro-fuel cell with a mobile phone handset which has twice the run-time of batteries and recharge times of the order of 10 min. Another company based in Singapore, Horizon Fuel Cell Technologies has launched a pocket size 1.5−2 W (5 V, 400 mA) fuel cell charger MiniPak® which is able to continuously deliver power through a USB port. It is now available at a cost of US$99 and the price is expected to drop to $29 at higher volume production [23]. It has

been designed to charge electronic portable devices such as mobile phones, MP3 players and Global Positioning Systems (GPSs). The charger device comes with ready to use two refillable solid state hydrogen cartridges able to store 12Wh net energy. Kundu et al. have carried out a detailed review of the developments and applications of micro-fuel cells until 2007 [84]. Giddey et al. have also reviewed the literature on micro-fuel cells and have reported on fabrication, life time performance and degradation issues of several self-air breathing PEM micro-fuel cells. They report life times of over 10,000 h with micro-fabricated interconnects having corrosion resistance coatings [74,83].

2.2.4. Direct methanol fuel cell (DMFC)

The direct methanol fuel cells convert methanol directly into electricity and are under development mainly for portable power applications. The direct methanol fuel cell (DMFC) uses a polymer electrolyte membrane as the electrolyte and is similar in operation to a PEMFC. The difference being that methanol participates directly in the fuel cell reaction. This eliminates the requirement for an external reformer. There are significant advantages in terms of high volumetric specific energy density associated with liquid methanol compared to gaseous hydrogen. However, disadvantages include: methanol cross-over through the membrane leading to the loss of fuel to the cathode side, high precious metal catalyst loading (more than an order of magnitude higher compared to the direct hydrogen fuel cell), poisoning of catalysts by intermediate reaction products, sluggish electrochemical reactions involving CH_3OH and H_2O (6e$^-$ transfer), low power density, water management, methanol concentration maintenance, CO_2 removal, complex balance-of-plant (compared to hydrogen PEMFC) and fuel toxicity [74,84]. More recent advances in polymer membrane technology have led to a substantial reduction in methanol cross-over and improved performance of DMFC and a number of companies are now commercialising the technology [25,28]. The current status of the technology is reviewed in reference [84].

2.2.5. Direct ethanol fuel cell (DEFC)

The DEFC has only recently attracted the attention of the fuel cell community and is at a very early stage of development. It is similar in operation to DMFC and PEMFC technologies. However, it uses ethanol directly in the fuel cell reaction in place of methanol or hydrogen. The liquid ethanol (C_2H_5OH) is oxidised at the anode in the presence of water, generating CO_2, hydrogen ions and electrons. Ethanol is an attractive alternative to methanol as it is non-toxic and has a higher energy density (8030 Wh/kg as compared to 6100 Wh/kg for methanol). However to realise the benefit of the higher energy density, the ethanol molecule must be oxidised completely to CO_2. Efforts are being made to develop new catalysts that show higher activity towards ethanol and to develop anion exchange membranes which would increase the activity of existing catalysts by allowing them to operate in an alkaline environment, with some success reported in this area [85−88].

2.2.6. Regenerative or unitised Fuel cell

A regenerative fuel cell is similar in operation to other fuel cell types and generates electricity and heat like a conventional fuel cell. However, the regenerative fuel cell also performs the reverse of the fuel cell reaction (water electrolysis) where on supply of electricity to electrodes, water is split and pure hydrogen and oxygen are generated. These gases are then stored and the hydrogen is used as the fuel on demand. This type of fuel cell is particularly advantageous when integrated within a power grid. This is because it can be used to balance the load cycle of the grid, producing fuel during periods of low demand and electricity during periods of high demand. This will be particularly advantageous as renewables are

often intermittent in nature and are increasingly incorporated into national electricity grids. These systems would only need to be supplied with water and thus do not require additional large capital investment associated with a hydrogen supply infrastructure. Both PEMFCs and SOFCs are prime candidates for this type of fuel cell operation. The major issues with this technology are the low round-trip (combined electrolysis and fuel cell modes) efficiency, low power density, high cost and rapid degradation of the cells. A considerable effort is therefore being made to develop bifunctional electrocatalysts that function equally well for oxygen evolution (electrolysis mode) as well as oxygen reduction (fuel cell mode) and to develop catalysts that are less prone to anodic corrosion [89].

2.2.7. Indirect methanol or ethanol fuel cell

The fuel either methanol or ethanol is processed to produce CO and hydrogen or just hydrogen depending on the use in low or high temperature fuel cells. Here a range of fuel cells can be used including PEMFC and SOFC. The major fuel related issue with direct hydrogen micro-fuel cells (PEM) is finding a hydrogen storage media to achieve desired energy densities. Therefore, hydrogen generation by methanol or ethanol reforming and its direct use without storage in micro-fuel cells for portable power applications is gaining considerable attention of fuel cell researchers. This kind of system consists mainly of a fuel vaporiser, steam reformer, catalytic combustor to maintain the reformer temperature, and preferential oxidiser (PROX) to oxidise any CO generated in the reforming process [90]. Ultracell has been developing indirect methanol fuel cell technology based on a methanol reformer to supply hydrogen to a PEM fuel cell [27]. These units are integrated with a battery pack to supply peak power well above the capability of the fuel cell and can supply power (from 25 to 250 W) for long periods of time with hot swappable fuel cartridges for satellite communication equipment, remote and mobile power and field battery charging applications. The only drawback is that the start-up time can be several minutes as opposed to few seconds for the direct hydrogen fuel cell. Bio-ethanol in addition to being a renewable (CO_2 neutral) fuel is non-toxic, inexpensive, easily available, offers ease of transportation and storage. Therefore, there is a significant interest in developing fuel cell systems running on reformed bio-ethanol. Recently researchers at the Fraunhofer Institute for Solar Energy Systems ISE in Freiburg, Germany have developed a 250 W PEM fuel cell system with an ethanol reformer for portable outdoor applications [91]. The overall system consists of a 300 W PEM fuel cell, a reformer with gas purification (CO removal) and a tail-gas combustor to utilise the off-gas from the anode chamber of the fuel cell and provide heat for the ethanol vaporiser and pre-heating the feed streams. Another bio-ethanol based 5 kW PEM fuel cell system (GH2-5000) is being developed by Greek based Helbio at the request of University of Milan in Italy [92]. The system produces 5 kW electrical and 5 kW of thermal energy and is designed to operate in remote locations, without any need for an external power supply. This system employs a steam reformer to reform bio-ethanol into hydrogen, and CO content is reduced to less than 20ppm by two water-gas shift reactors and a methanation reactor. The system complexity (BOP), overall response to fluctuating load demand, integration, miniaturisation in case of portable power applications and cost are the major issues that still need to be resolved for the commercialisation of this technology.

2.2.8. Phosphoric acid fuel cell (PAFC)

The electrolyte in a PAFC system is concentrated phosphoric acid. This is held in a porous matrix of Teflon bonded silicon carbide. The anode and cathode are carbon supported platinum metal catalyst with an average loading of around 0.2–0.3 mg/cm^2

held within a Teflon bonded carbon support structure. Individual cells are connected together through separator bipolar plates made of impervious graphite in the form of corrugated sheets or ribbed plates. An operating temperature of 200–215 °C is required for high proton conductivity in the acid. The acid used as the electrolyte is stable at the cell operating temperature. This higher operating temperature also reduces susceptibility to CO poisoning of the Pt catalyst leading to less stringent gas processing and longer overall system lifetimes when compared to PEMFC.

The majority of PAFC systems are designed for use in stationary combined heat and power applications. The power output of these systems is typically between 200 kW and 1 MW in size, although larger (up to 11 MW [93]) size plants and smaller systems (250 W [94]) have been operated. The PAFC is by far the most developed and technically mature and commercialised fuel cell technology with lifetimes well in excess of 40, 000 h demonstrated. As with most new technologies, cost and system lifetime remain a concern [95]. However, UTC Power has recently began marketing the PureCell™ 400, which is reported to have a stack lifetime of 80, 000 h (∼9 years) and a total installed cost of US$3, 000 per kW [20,96]. This is a significant improvement over pervious systems for which the lifetimes were limited to 40, 000 h (∼5 years) with installed costs almost 50% higher. However, these costs are still significantly higher than traditional heat engine technologies leading to these systems generally only being competitive in markets where government subsidies are available or where there is stringent air pollution legislation in place. In addition to UTC Power, Fuji Electric have also been active in the development of this technology including extensive field trials in the 1990s involving 88 units of between 50 and 500 kW capacity with a number of these units operating in excess of 30, 000 h [5]. Fuji Electric started commercial sales of PAFC systems around the turn of the century. These systems have a capacity of 100 kW and a stack lifetime of 40, 000 h (∼5 years) [50]. There are a number of other organisations that have deployed first generation products or are engaged in advanced field trials of phosphoric acid fuel cells. These include Sanyo, Toshiba and Mitsubishi Electric [5,94,97,98]. There are in excess of 250 PAFC systems currently in operation globally [99]. Further details of the technology can be found in references [5,8,9,20,95].

2.2.9. Molten carbonate fuel cell (MCFC)

In a molten carbonate fuel cell, a mixture of molten lithium and potassium (or sodium) carbonates held in a porous ceramic matrix or tile is used as the electrolyte. The porous ceramic matrix made from $LiAlO_2$ is a few hundred microns thick and is fabricated via tape casting. The operating temperature is generally between 600 and 650 °C. For effective electrolyte management, the ceramic matrix pore size and distribution need to be carefully controlled. The cathode is normally a porous Li doped NiO and the anode is a porous Ni or a Ni/Cr alloy (2–10% Cr). Each cell is connected via bipolar plates which are corrugated pressed steel structures. Since CO_2 is consumed in the electrode reaction on the cathode side, to maintain electrolyte balance, some of the CO_2 formed at the anode needs to be recycled to the cathode compartment. The cost of manufacturing is generally accepted to be low compared to other high temperature fuel cells such as solid oxide fuel cells, due to the use of cheaper materials and inexpensive fabrication techniques. However, molten carbonate fuel cells generally offer inferior power densities (120–160 mW/cm^2 vs 400–500 mW/cm^2 for SOFCs) which will most likely lead to very similar overall system costs once both technologies have reached a similar level of maturity. Due to the high operating temperature of this fuel cell type, internal reforming of natural gas, within the fuel cell stack, is possible. The hydrogen and CO produced are electrochemically consumed and

the water vapour formed in the anode chamber is utilised in the reforming reaction. The latter helps the reforming reaction to occur at the lower operating temperatures ($\sim$650 °C) of the molten carbonate fuel cell as compared to the usual reforming temperatures of $\sim$900 °C. This reduces system complexity and leads to higher electrical efficiencies when compared to lower temperature fuel cells (PEMFC or PAFC). The loss of electrolyte by vaporisation, coarsening of the $LiAlO_2$ matrix structure and corrosion of cell components leading to cell performance degradation (and low reliability) are some of the major material problems which are affecting the long term stability of the system [100,101]. The stack life of this fuel cell type is a significant concern with high degradation rates limiting the stack life to less than 5 years.

Due to the high temperature of operation and relatively low power densities, MCFCs are generally used for stationary combined heat and power applications with a typical electrical power output of 250 kW to 1 MW, although larger systems are available [35]. A number of organisations are currently developing MCFCs systems for stationary combined heat and power applications. This includes CFC solutions, Alsaldo Fuel Cells, Ishikawajima-Harima Heavy Industries, GenCell Corporation, a consortium of POSCO/KEPCO, Doosan Heavy industries and Fuel Cell Energy. As with PAFCs, extensive field trials of this technology were carried out in the 1990s [102] with commercial sales beginning in the early part of this century. There are currently around 100-150 stationary CHP systems and one MCFC powered ship in operation [99,103].

2.2.10. Solid oxide fuel cell (SOFC)

Solid oxide fuel cells comprise of an oxygen-ion conducting solid electrolyte (tens of microns thick) such as partially or fully stabilised zirconia doped with 3–10 mol% Y_2O_3. The anode is generally a Ni/YSZ cermet and the cathode is a ceramic composite usually comprising of the electrolyte material and doped lanthanum manganate $(LaSr)MnO_3$, typically referred to as LSM [6,15,18,104–107]. A number of other electrode and electrolyte materials have also been considered and are reviewed in references [15,18,104–107]. Due to the poor ionic conductivity of the electrolyte at low temperatures, SOFCs typically operate at high temperatures (800–1000 °C range). This leads to the majority of the fuel cell stack being constructed out of ceramics, ceramic metal composites and high temperature metal alloys. A number of designs have been considered with the two most common being planner and tubular [12,15]. Planner SOFCs comprise of flat planar cells that are connected in series via a dense and electronically conducting doped $LaCrO_3$, metal/ceramic cermets or high temperature oxidation resistant alloys [5,6,104] with gas flow fields for fuel and oxidant supply to reaction sites. This repeating unit is stacked to increase the system voltage and to increase the power output. For the tubular design, no sealing is required, whereas it is a serious issue for the planar design to avoid mixing of air and fuel and retain its integrity during thermal cycling. The high cost of these materials, complex balance-of-plant requirements and to reduce cell degradation stemming from corrosion of cell components, there has been a significant effort to reduce the overall operating temperature of SOFCs which also allows for the use of lower cost stainless steels as the separator plate [5,15,104,108]. For both planar and tubular designs, electrode supported cells with a thin (10–20 μm) layer of the electrolyte have been considered. In general, a more complex geometry of tubular designs requires complex manufacturing processes and leads to systems with lower overall power densities.

A large number of organisations and companies have been involved with the development of solid oxide fuel cells. Reviews of the SOFC research and developments can be found in references [12,15,18,104–107,109,110]. During the 1970s, 80s and 90s

Westinghouse and later Siemens-Westinghouse were key developers of tubular SOFC technology, demonstrating a number of units in the late 1980s and early 1990s [111]. From the mid-1990s onwards a large number of companies began programs developing SOFCs most of which have demonstrated these technologies at some scale. Large scale demonstration plants (>50 kW) have been either constructed or planned by Siemens-Westinghouse, Mitsubishi Heavy Industries, Rolls Royce Fuel Cells and Bloom Energy with smaller CHP units being demonstrated by Sulzer-Hexis, Ceres Power, Ceramic Fuel Cells Limited, Topso Fuel Cells, Delphi, Acumentrics, Fuel Cell Technologies, Global Thermoelectric Inc. and ZTEK Corp. Due to the large number of companies involved in the commercialisation activities around SOFCs, it is difficult to assess the exact status of this technology. Fuel Cells 2000 indicated that there are around 150 SOFCs installed for stationary power applications globally, this number including planned installations, demonstration units and decommissioned demonstration units [99]. Both Bloom Energy and Ceramic Fuel Cells Limited are offering first generation products with limited warranties [22,46].

2.2.11. Direct borohydride fuel cell (DBFC)

Direct borohydride fuel cells (DBFC) utilise metal borohydrides as a fuel. Metal borohydrides such as sodium borohydride contain up to 10.5% hydrogen by weight [112]. Theoretical specific energy density of DBFC, considering BH_4^- as the electroactive ion and 8 electrons participating in the electrochemical reaction, is 9.3Wh/g compared to 6.2Wh/g in case of methanol for direct methanol fuel cell (DMFC) [113]. This makes DBFCs an attractive candidate for the applications in devices such as mobile phones and laptops. Depending on the cell configuration and the type of electrolyte used, the electrochemical reaction involves transport of either hydroxyl (OH^-) or a cation such as H^+ and Na^+ [113]. The designs similar to AFC and PEMFCs have been tested. Power densities up to 290 mW/cm^2 with air as the oxidant and up to 600mw/cm^2 with hydrogen peroxide as the oxidant [113,114] have been achieved by employing Nafion membrane. This technology has a number of advantages over more traditional fuel cell designs. However, hydrolysis of BH_4^- causing loss in fuel and evolution of hydrogen at the fuel electrode, fuel (as BH_4^-) cross-over, lack of suitable catalysts for efficient electro-oxidation of fuel and electro-reduction of oxidant (O_2 or H_2O_2) and high costs of sodium borohydride are the major issues that still need to be resolved before DBFCs can be commercialised on the large scale. Furthermore, the stacking of these cells have been a major issues due to gas evolution resulting from hydrolysis of BH_4^- at the anode and decomposition of hydrogen peroxide at the cathode. For further information on this fuel cell type the reader is referred to the review article [115].

2.3. Fuels for fuel cells

A wide range of fuels have been suggested for the operation of fuel cells including ethanol, methanol, natural gas, liquefied petroleum gas (LPG), kerosene, diesel, naphtha, hydrogen and coal to name a few [61,64,116,117]. Despite the large variety of fuels that have been suggested for fuel cell systems at a cell level there is very little variation in what a fuel cell operates on. Essentially, with the exception of direct alcohol and direct borohydride fuel cells, all commercial or near commercial fuel cells operate on pure hydrogen or a mixture of pure hydrogen and CO. These gases are produced via external reforming, internal reforming or via partial oxidation of a wide range of commercially available fuels. All fuel cells are somewhat sensitive to sulphur containing impurities. Low or medium temperature fuel cells also require relatively pure hydrogen as the fuel (only 10–20ppm CO for PEMFC and <1% for PAFC). High temperature fuel cells, such as SOFC and MCFC, can

operate on hydrogen and/or CO as a fuel [118] although they generally operate on reformed hydrocarbon fuels which are a mixture of CO, CO_2, hydrogen and steam. If a high grade hydrocarbon fuel is used, such as pipeline natural gas, only sulphur needs to be removed (desulphurisation) before the fuel can be used within a high temperature fuel cell system. These systems normally have a reformer that is integral to the system and can generally use the waste heat and water from the fuel cell reactions to reform the incoming fuel. It is possible to reform fuels within the anode chamber of a high temperature fuel cell provided the steam to carbon ratio is kept high (typically over 2.5), however, this adds to system complexity. Fuel processing for PEMFC and PAFC systems needs to be more rigorous due to the lower tolerance of these fuel cell types to CO within the fuel gas and thus normally incorporates additional steps such as hydrogen separation and selective oxidation of CO over a catalyst. The lower operating temperature of these fuel cells also leads to the fuel processing being carried out externally, with any waste heat produced from the fuel cell reactions generally being lost or used mainly for space heating or hot water.

If pure hydrogen is available as the fuel, there is generally no fuel processing required for most types of fuel cells. The exceptions being direct alcohol fuel cells (which require either ethanol or methanol to operate), molten carbonate fuel cells (which generally require a source of CO_2 to maintain the carbonate concentration within the electrolyte) or direct borohydride systems (which use borohydride as the fuel). There are two major sources of hydrogen - fossil fuels and water. Hydrogen at present is produced either by steam reforming of natural gas or by electrolysis of water. Hydrogen produced by electrolysis of water can be directly used within any type of compatible fuel cell without any further processing. On the other hand hydrogen produced from fossil fuels would require desulphurisation (generally carried out at a fuel pre-processing stage) and CO removal (if used in lower temperature fuel cells). The major fossil fuels being considered as feed stocks for hydrogen fuel cells are natural gas, LPG, diesel, methanol, ethanol, gasoline, coal and biomass. While hydrogen from natural gas is produced by steam reforming, liquid fuels can be either steam reformed or partially oxidised. Steam reforming is generally carried out at high temperature (900 °C) in large chemical plants, whilst partial oxidation systems can be incorporated into comparatively small systems that do not require external heat energy inputs. Reforming can use high grade waste heat from other chemical processes and thus converts the majority of the chemical energy in the fuel into hydrogen. Partial oxidation reactors use some of the chemical energy within the fuel to heat the system and thus convert a lower proportion of the chemical energy within the fuel to hydrogen. Hydrogen from solid fuels (coal and biomass) is produced by gasification or pyrolysis. The gas mixture produced from fossil fuels after reforming/gasification can either be used directly within high temperature fuel cells [119] or is further treated in gas-shift reactors and preferential oxidation reactors to remove CO impurities before being used in lower temperature fuel cells. Further details on fuels for fuel cells can be read in the references [120,121].

2.4. Fuel cell applications

The major applications of fuel cells are for distributed power generation either stand alone or integrated with renewable energy sources (combined heat and power generation at homes, apartment blocks, remote area settlements, offices, shopping centres, restaurants, hotels, hospitals, nursing homes and other commercial dwellings), transport (family cars, buses, trucks, ships, barges, aeroplanes, locomotives, small transporters at airports, railway stations and shipyards, fork lifts, scooters, bikes, delivery vans, etc.) and portable power (battery replacement or add-on devices for laptops, mobile phones, portable electronic appliances, UPSs, back-up and emergency power, remote communication, etc.). The application of fuel cells vary depending on their operating characterics, efficiency, cost, lifetime, fuel availability and processing requirements, requirements for the quality of heat in combined heat and power applications. However, despite some major environmental advantages, most market segments are looking for high degree of reliability and costs which are competitive with existing technologies.

High temperature fuel cells (SOFC and MCFC) are more fuel flexible, not poisoned by CO or CO_2, do not require precious metal catalysts, can be combined with low pressure steam or micro turbines to improve efficiency, offer high quality waste heat and can reform hydrocarbon fuels internally by introducing steam or can be integrated with an external steam reformer. However, these systems are generally fragile, have slow start-up and shut-down times, have significant thermal load management issues in fluctuating load environments, require significant thermal shielding, can degrade rapidly on thermal cycling, are constructed from expensive high temperature materials and have complex BOP and thermal management systems [122–125]. Generally, high temperature fuel cells are most suited to large scale base load applications. However, small scale SOFCs (1–3 kW) are being considered for applications where the heat load demand outweighs the power demand. A number of different systems are being developed at various scales [5,15,21,22,33,35,46,48,49,51].

Low temperature systems (PEMFC, AFC) are simple to construct, have rapid start-up and cool–down cycles, do not have expensive refractory metals or ceramic components, exhibit excellent load following capability, are mechanically robust, and depending on design, have high power densities. However, these systems are sensitive to fuel impurities at the ppm level (CO for PEM cells and CO/CO_2 for AFCs), often require complex humidification systems, produce only low quality heat, cannot internally reform fuel, have short electrolyte lifetimes and often require expensive precious metal catalysts [74,126–128]. For small scale stationary applications where load demand can fluctuate regularly, low temperature fuel cells for power generation alone or combined heat (low grade heat such as hot water or space heating) and power generation are most suitable [19,20,24,29–31,44,45,50].

Micro-fuel cells and automotive (primary power) applications generally have more stringent requirements relating to rapid start-up, thermal management, weight, mechanical robustness and load following characteristics. Thus, these application areas are dominated by low temperature systems such as PEMFC and DMFC with a number of fuel cell products being offered in these markets [20,23,25–28,34,44,45].

Both high and low temperature systems are under investigation for use within automotives as auxiliary power units (APUs) in the 1–3 kW range. The simpler design, lower operating temperature, rapid start-up and shut-down capability and more mature low temperature systems offer a number of advantages relating to construction, installation and maintenance. However, the greater fuel flexibility and higher overall system efficiencies of high temperature systems also make them attractive to this market. At this early stage of product development it is unclear if either high or low temperature systems will be successful within these markets. Due to the size of and diversity of these markets it is possible that a number of different fuel cell types will be adopted. There are currently a number of companies at various stages of product development within these markets and most have working prototypes or are carrying out field tests [129,130].

Although there are a number of fuel cell 'products' now on the market, most of these come with limited warranties and are often offered to a select customer base. There are still a number of issues

that need to be resolved before any of these systems can transverse the gap between novelty and mainstream technology. The major issues generally relate to limited system lifetime, low reliability and substantially higher capital and operating costs in comparison with other available power sources in the market [5,6,10–15].
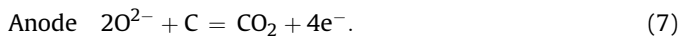
3. Direct carbon fuel cell (DCFC)

Researchers have been attempting to operate fuel cells on solid carbon fuels for well over a century with the first large scale demonstration of this technology by William Jacques in 1896 [131]. Useful reviews of devices tested in the early years of development have been conducted by Howard (1945) [132] and Liebhafsky et al. (1968) [109].

The basic structure of a direct carbon fuel cell is identical to any of the other fuel cells described in section 2. Essentially each cell consists of a cathode and anode separated by an ionically conducting but electronically insulating electrolyte. The only difference is that rather than being fed gas or liquid fuel streams, the anode chamber is supplied with a solid fuel that reacts directly at the electrode to form a gaseous exhaust product. For the fuel cell to operate at its maximum efficiency the overall cell reaction must be:

$$C + O_2 = CO_2 \qquad (5)$$
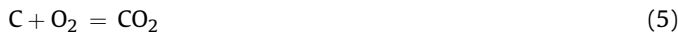
with the overall half cell reactions being:

$$\text{Cathode} \quad O_2 + 4e = 2O^{2-} \qquad (6)$$

$$\text{Anode} \quad 2O^{2-} + C = CO_2 + 4e^-. \qquad (7)$$

Key features of a DCFC, as distinct from other fuel cells and power generation technologies are as follows:

- A DCFC operates at high temperatures (500–900 °C) and converts the chemical energy in solid carbon directly into electricity through its direct electrochemical oxidation.
- The fuel utilisation can be almost 100% as the fuel feed and product gases are distinct phases and thus can be easily separated.

- The theoretical efficiency is also high, around 100% (Fig. 2).
- The by-product is pure CO_2 requiring no gas separation and can be directly sequestered avoiding cost and efficiency penalties.
- The solid fuel feed system for delivery of fuel to reaction sites can be quite complex compared to gaseous or liquid fuel fed fuel cell systems.

There are three basic families of direct carbon fuel cells under development, distinguished by the type of electrolyte used (molten hydroxide, molten carbonate or solid oxygen ion conducting ceramic) as described in Fig. 5. In addition to the use of different electrolytes, there are further sub-categories of DCFCs differing in materials and design of the anode chamber. The various families and sub-groups of fuel cell are listed below:

1. Aqueous hydroxide – operating temperature <250 °C.
2. Molten hydroxide (KOH, NaOH) – operating temperature 500–600 °C.
3. Molten carbonate (Li, Na, K) – operating temperature 750–800 °C.
4. Oxygen ion conducting ceramic (doped zirconia or ceria) – operating temperature 500–1000 °C:
   a. Fluidised bed (direct contact of carbon particles with anode).
   b. Molten metal anode (carbon in contact with molten metal anode).
   c. Molten salt (carbon particles suspended in a slurry).

In addition to solid electrolyte direct carbon fuel cells described above and in Fig. 5, there is a further class of carbon fuel cells in which carbon is first chemically oxidised either inside the cell as a part of the system design or externally to CO (C + CO_2 = 2CO). It should be noted that this reaction is not electrochemical in nature and would not produce any cell voltage. It is the secondary reaction involving reaction between CO and oxygen ions supplied from the electrolyte which would produce an electrochemical potential. This class of fuel cell is essentially similar to a normal SOFC in operation with the only difference being that the fuel supplied to the cell is pure CO (rather than the more commonly used reformate fuel which is a mixture of CO and hydrogen) and the carbon gasification

Fuel / Anode	Electrolyte	Cathode	T, °C
Solid graphite rod as fuel & anode $C + 4OH^- = 2H_2O + CO_2 + 4e^-$	Molten Hydroxides $OH^- \longleftarrow$	Air as oxidant $O_2 + 2H_2O + 4e^- = 4OH^-$	500 - 600
Carbon particles as fuel in MC & anode $C + 2CO_3^{2-} = 3CO_2 + 4e^-$	Molten Carbonates $CO_3^{2-} \longleftarrow$	Air as oxidant $O_2 + 2CO_2 + 4e^- = 2CO_3^{2-}$	800
Concept1 — Carbon particles in a fluidised bed $C + 2O^{2-} = CO_2 + 4e^-$	Oxygen ion conducting ceramic electrolyte $O^{2-} \longleftarrow$	Air as oxidant $O_2 + 4e^- = 2O^{2-}$	700 – 900
Concept2 — Molten tin + C $Sn + 2O^{2-} = SnO_2 + 4e^-$ $SnO_2 + C = Sn + CO_2$		Air as oxidant $O_2 + 4e^- = 2O^{2-}$	
Concept3 — Molten salt + C particles $C + 2O^{2-} = CO_2 + 4e^-$		Air as oxidant $O_2 + 4e^- = 2O^{2-}$	

**Fig. 5.** Main types of direct carbon fuel cells and fuel cell reactions.

process may be integral to the fuel cell system design. Such a fuel cell system may be classed as an indirect carbon fuel cell. The advantage of using an external unit for $C + CO_2 = 2CO$ reaction (with partial CO_2 recycling from fuel cell exit) is that fuel delivery to the fuel cell stack is simple and any issues related to slag formation or impurity processing can be dealt with externally with minimal damage to the fuel cell stack. This type of system would also still produce a pure CO_2 exhaust stream which would be advantageous if it was to be combined with carbon dioxide capture and sequestration. The main disadvantage is that for CO fuel, the maximum theoretical electrical efficiency is much reduced (Fig. 2). Thermodynamic system modelling by Lee et al. suggests that integrated systems operating with CO_2 and an external gasifier can produce efficiencies of around 58% [133], significantly lower than the potential >80% electric efficiency that may be offered by direct electrochemical reaction of carbon.

A tree diagram of various DCFCs is given in Fig. 6 to clarify various technologies under development.

In reality inside the anode chamber, a combination of direct and indirect carbon oxidation reactions can occur. The carbon particles which make direct contact with the electrolyte can react with oxygen ions and are converted to CO_2 via the following reaction sequence:

$$C + O^{2-} = CO + 2e^- \qquad (8)$$

$$CO + O^{2-} = CO_2 + 2e^-. \qquad (9)$$

The carbon particles which do not make direct contact with the electrolyte being oxidised by the following reaction sequence:

$$C + CO_2 = 2CO(\text{chemical reaction}) \qquad (10)$$

$$2CO + 2O^2 = 2CO_2 + 4e^-(\text{electrochemical reaction}) \qquad (11)$$
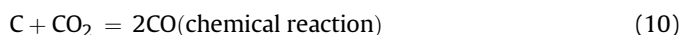
It should be noted that not all CO formed by reaction (8) or (10), will be consumed by reaction (9) or (11). Once gaseous CO forms, it is not possible to separate it from CO_2 produced within the fuel cell. This may lead to some of it leaving the anode chamber with the exhaust gas. CO is essentially a partially combusted fuel and thus if part of it leaves the fuel cell compartment before being oxidised at the anode, the fuel utilisation is effectively reduced and hence the overall system efficiency. CO can form either chemically or

electrochemically. The electrochemical formation of CO (reaction (8)) is not particularly a serious issue with direct carbon fuel cells because the reaction only takes place during cell operation, contributes to the cell voltage and occurs within the anode. The CO thus formed is likely to react electrochemically to form CO_2. Chemical formation via reaction (10) does, however, present a significant challenge. This reaction is known as the Boudouard or more accurately the reverse Boudouard reaction. The free energy of this reaction is given by: $\Delta G = 170000 - 174.5T$ Joules, where T is temperature in degree K. This relationship shows that the free energy for the Boudouard reaction is zero at 978K (705 °C). Fig. 7 shows percentage of CO and CO_2 in the $C/CO/CO_2$ system as per reverse Boudouard reaction, and standard free energy (ΔGo) values for the following reactions: $2C + O_2 = 2CO$; $C + O_2 = CO_2$; and $2CO + O_2 = 2CO_2$ as a function of temperature. The reverse Boudouard reaction and equilibrium concentrations of CO and CO_2 are very much dependent on temperature as determined by thermodynamic and kinetic considerations. At temperatures above 705 °C, the reverse Boudouard reaction is strongly favoured and the reaction (10) shifts to the right and has been reported to produce significant volumes of CO above this temperature within direct carbon fuel cells of various designs [54,134,135]. The reaction can occur anywhere in the anode chamber, does not contribute to the cell voltage and can occur in the presence of CO_2 even when the cell is not under load (i.e. no current flow through the fuel cell - the cell is at open circuit). The formation of CO further away from the anode or at open circuit is particularly problematic because under these conditions as it is unlikely that all of it will oxidise electrochemically and some of it will be lost to the exhaust. This, however, can be minimised or eliminated if the amount of residual CO_2 at open circuit is minimal or CO_2 is purged from the anode chamber for a fuel cell operating above 700 °C.

These series of observations lead to a number of obvious operation rules that may be of use to the engineer looking to build a direct carbon fuel cell:

1. Reduction in operating temperature reduces both the thermodynamic driving force and kinetics of chemical reactions that form CO (experimental studies have shown that below 700 °C, CO formation is almost reduced to zero [54,134,135]).
2. Continuous operation of a direct carbon fuel cell is advantageous as it avoids formation of CO within the anode (making this technology less suitable for on demand applications where the cell may have to be left on standby for a large proportion of its operating life).
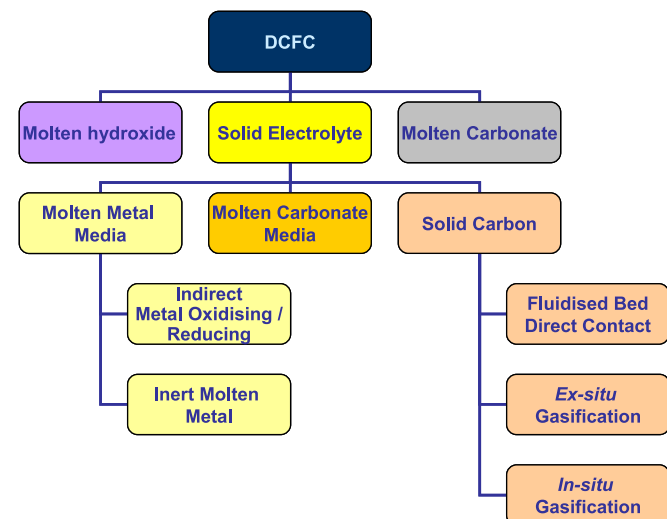

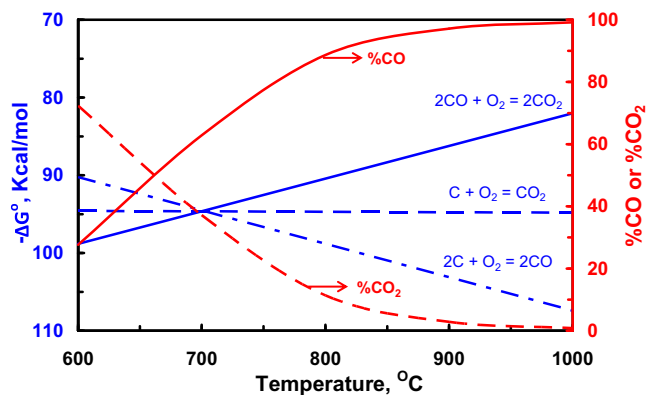Fig. 6. A tree diagram of various DCFC technologies under development.

Fig. 7. Equilibrium percentage of CO and CO_2 in the $C/CO/CO_2$ system as per reverse Boudouard reaction, and standard free energy (ΔG^o) values as a function of temperature for reactions: $2C + O_2 = 2CO$; $C + O_2 = CO_2$; and $2CO + O_2 = 2CO_2$.

3. Exposure of the carbon fuel to CO_2 in an unloaded fuel cell at the operating temperature should be minimised.

If the chemical formation of CO can be avoided then the fuel and exhaust (mainly CO_2) exist as distinctly separate phases, making the separation of reactants and products easy. This would also ensure almost 100% conversion (utilisation) of the carbon fuel in the DCFC and stabilise the cell voltage making it independent of what fraction of the fuel has been consumed. In other types of high temperature fuel cells using gaseous fuels, the un-reacted fuel is diluted with product gases and its gas phase separation is cumbersome. The conversion of carbon to CO_2 has a small entropy change and therefore the theoretical or maximum thermodynamic efficiency approaches 100%. Furthermore, this efficiency is almost independent of the operating temperature as shown in Fig. 2. The stack electric efficiency, as discussed in section 2.1, is a product of the theoretical efficiency, fuel utilisation factor and net cell voltage efficiency after taking into consideration the internal cell losses. With fuel utilisation factor for a DCFC close to one, the combination of all of three factors in a DCFC make it likely that actual fuel cell stack electric efficiency could be as high as 80–90% with 10–20% internal cell losses. In real systems, the fuel utilisation factor may be less than one due to side chemical reactions leading to some efficiency penalty. Typical auxiliary subsystem related losses in fuel cells are no more than 10%. Thus an overall system electric efficiency around 65–70% can be expected for a DCFC. Patton and Zecevic et al. [136] for the molten hydroxide and Cooper [54] for the molten caronate based DCFCs have indicated that system efficiencies above 65–70% can be achieved. These efficiency values are almost twice those of current generation coal fired plants. Even in comparison with current gas fed fuel cells, the electric efficiency of DCFCs is 15–30% higher (Table 2).

Due to the early stage of development of direct carbon fuel cells there is only limited data reported on the actual operating efficiency of a complete systems. Lee et al. have carried out system modelling based on gasification of carbon to CO which is then subsequently reacted within a conventional SOFC. This work suggests that total system efficiencies for gasification type DCFC systems will be limited to below 60% [133]. There has been very little systems modelling based on fuel cell devices in which there is a direct electrochemical reaction of carbon. Cooper and Selman reviewed the performance of a series of cells that react carbon directly within molten carbonate [57]. They combined the coulombic efficiency (fuel utilisation factor) with voltage efficiency to define a term they refer to as the 'Fractional efficiency' which they plotted against power density [57]. This data suggests that it is possible to obtain an efficiency of above 80% for an individual fuel cell operating at 40 mW/cm². The data used were not from an optimised fuel cell and the authors felt that obtaining efficiency in the region of 80% at 100 mW/cm² should be practically attainable [57].
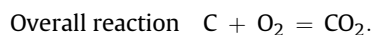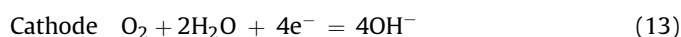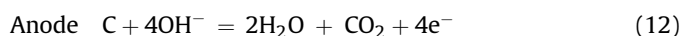
3.1. Aqueous hydroxide electrolyte technology

DCFCs operating at temperatures below 250 °C have been tested. These systems use an aqueous hydroxide electrolyte and thus must operate at greatly elevated pressures (30–35 bar) in order to maintain the electrolyte as a liquid. This concept was first explored in the 1920s, and reviewed in references [109,132] and has recently been revisited by Nunoura et al. [137]. Early work was carried out within autoclaves at 200 °C and 30 bar pressure with raw brown coal as the fuel. The autoclave body was used as the anode with an iron rod used as the cathode. The fuel, brown coal, was dispersed in an aqueous alkaline electrolyte. These trials resulted in an OCV of 0.55 V which rapidly dropped to zero. Little

information is available on the reason for the rapid drop in performance with Howard suggesting that is was related to reaction of the fuel (or fuel impurities) with the cathode [132]. More recent studies have been carried out by Nunoura et al. who developed a system that operated at 35 bar between 80 and 245 °C [137]. This system used a range of aqueous electrolytes which were various mixes of potassium, magnesium, sodium, lithium and caesium hydroxides. Similarly a range of cathodes were investigated including gold, silver, platinum and palladium. A conductive carbon bed was used as the anode in all cases. The best performing cell consisted of a potassium/lithium hydroxide electrolyte and silver/platinum cathode operated at 245 °C and 35. 8 bar (3.58 MPa) pressure.This cell had an OCV of 0.574 V and gave a peak power density of 6.5 mW/cm². The performance of this fuel cell is orders of magnitude lower than would be required for commercialisation. However, little work has been carried out on this design and it remains to be seen if the performance can be improved and if this concept can be scaled to a size where it can produce significant power. If this could be achieved the reduced operating temperature could potentially offer significant advantages with respect to system cost (i. e. cheap construction materials) and/or increased system lifetimes.

3.2. Molten hydroxide electrolyte technology

Generally this type of direct carbon fuel cell uses molten hydroxide (NaOH or KOH) as the electrolyte which is contained within a metallic container which also acts as a cathode. A carbon rod made from graphite or coal derived carbon is dipped into the electrolyte and used as both the fuel and anode of the cell. William Jacques was the first person to build a large scale direct carbon fuel cell of this type in 1896) [131] (Fig. 8a). This system, crude and rather large in size used carbon rods as both the fuel and the anode, molten hydroxide as the electrolyte and a cast iron casing that contained the electrolyte as the cathode (Fig. 8b). He was successful in putting together a series of 100 cells generating over 1 kW of electricity. The cells produced a current density of 100 mA/cm² at 1 V [131]. In this design, as with all fuel cells that use a hydroxide based electrolyte, the mobile charge species is the hydroxide ion and the cell reactions are:

$$\text{Anode} \quad C + 4OH^- = 2H_2O + CO_2 + 4e^- \tag{12}$$

$$\text{Cathode} \quad O_2 + 2H_2O + 4e^- = 4OH^- \tag{13}$$

Overall reaction $\quad C + O_2 = CO_2$.

The Jacques design exhibited high degradation rates due to the formation of carbonates within the electrolyte and chemical contamination caused by impurities in the carbon fuel rods used [131] and did not achieve commercial significance.

In the mid 1990s, Scientific Applications and Research Associates (SARA) Inc. started an R & D program on molten hydroxide based direct carbon fuel cells. Such a system was considered to have a number of advantages over the molten carbonate electrolyte DCFC. The advantages of using sodium hydroxide electrolyte include high ionic conductivity (especially when associated with water) [138,139], high reactivity towards carbon [140,141] and a low melting point (318.4 °C [142]), which allows for reduced operating temperatures (400–650 °C) [143]. The high reactivity towards carbon leads to a higher electrochemical activity at the anode which in turn leads to higher anodic oxidation rates and lower overpotential losses [144]. The reduced operating temperature allows for the use of less expensive materials for cell construction [138]. The lower temperature operation also favours
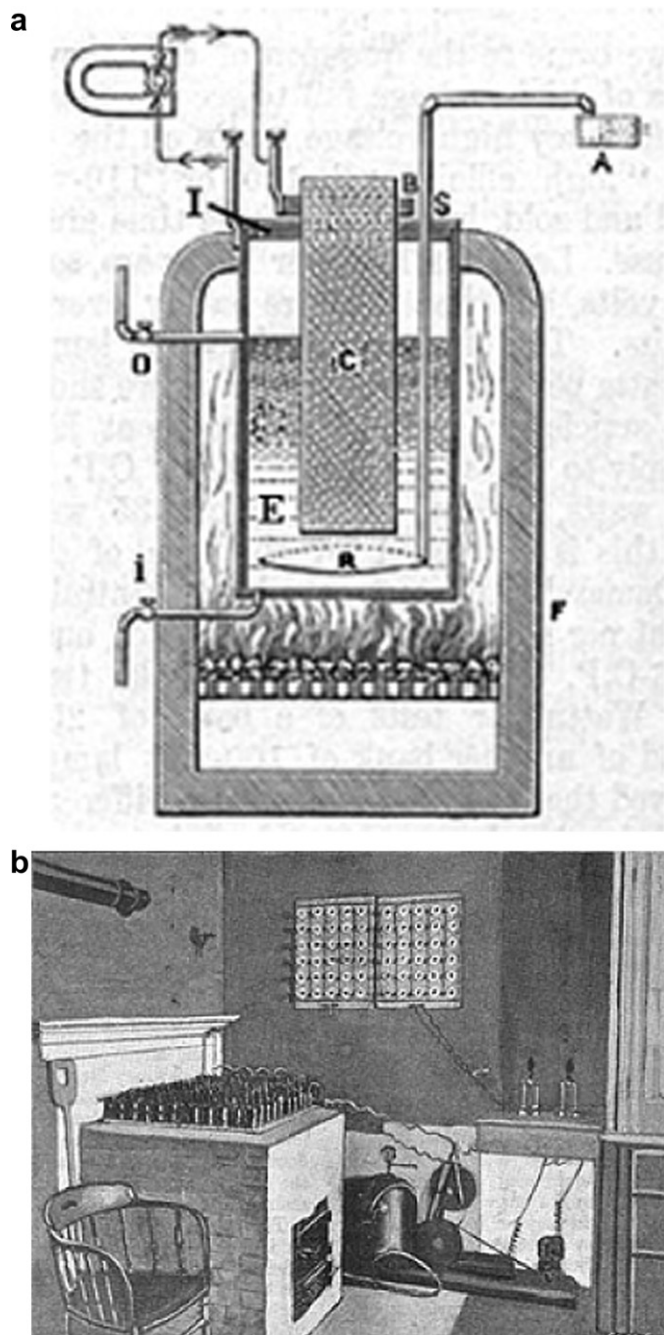
Fig. 8. (a) A sketch of a DCFC built by William Jacques in 1896. (b) A 1 kW direct carbon fuel cell apparatus used by William Jacques. After Reference [131].

the oxidation of carbon to CO_2 rather than CO (the reverse Boudouard reaction is favoured above 700 °C), which should result in higher fuel utilisation and thus overall higher system efficiencies.

Despite the advantages of hydroxide electrolytes, the fundamental issue of carbonate formation experienced by Jacques still remains and must be mitigated in any cell design using a hydroxide based electrolyte. The formation of carbonates in molten sodium hydroxide via reaction with a hydrocarbon fuel or CO_2 is well studied. In addition to Jacques early work looking at the reactions of coal (and CO_2) with molten sodium hydroxide there was also a significant amount of work done in the 1920s looking at the reaction of molten hydroxides with various hydrocarbon fuels

[145–147]. However, understanding of the mechanisms behind the CO_2 reaction with molten sodium hydroxide has largely been attributed to Goret et al. who proposed that carbonate formation occurs via either a chemical process (reaction (14)) or an electrochemical process (reaction (15)) [148,149]:

$$2OH^- + CO_2 = CO_3^{2-} + H_2O \qquad (14)$$

$$C + 6OH^- = CO_3^{2-} + 3H_2O + 4e^- \qquad (15)$$
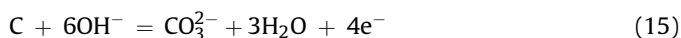
With reaction (15), electrochemical production of carbonate, occurs in two stages - an initial rapid chemical stage (reaction (16)) followed by a slower electrochemical stage (reaction (17)) as shown below:

$$6OH^- = 3O^{2-} + 3H_2O \qquad (16)$$

$$C + 3O^{2-} = CO_3^{2-} + 4e^-. \qquad (17)$$
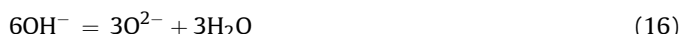
It has been found experimentally that the concentration of water within the electrolyte can dramatically impede the formation of carbonate ions within sodium hydroxide electrolytes [143]. It is unclear if the addition of water forces the equilibrium to shift to the left in reaction (14) (i. e. stops the chemical formation of carbonate) or if the increase in water concentration reduces the concentration of oxygen ions within the electrolyte, thus impeding electrochemical formation of carbonates ions by inhibiting the reaction described in reaction (16) [143]. The addition of water also increases the ionic conductivity of the molten electrolyte and helps reduce corrosion of metallic components [150]. The use of water to control the formation of carbonate ions can also be complemented through the addition of magnesium oxide which was reported by Jacques to improve the life of the electrolyte [131]. Other additions have been discussed by Zecevic et al. including SiO_2, Sb_2O_3, ZnO and oxyanions such as pyrophosphate and persulphate [143,151] although no data was presented or mechanism suggested for why these additions would restrict the formation carbonates within the electrolyte.

3.2.1. Systems investigated

SARA has continued to develop the technology with emphasis on solving problems and development and optimisation of cell/ stack materials and designs [138]. Fig. 9 shows a schematic view of
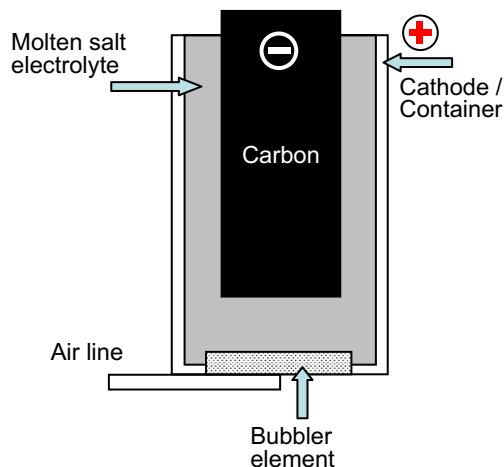

Fig. 9. A schematic drawing of a DCFC used by SARA in most of their investigations. Figure redrawn based on Reference [152].

the hydroxide based direct carbon fuel cell design used by SARA in most of their investigations [143]. It is similar in design to the cells pursued by William Jacques (Fig. 8). These cells use molten sodium hydroxide as the electrolyte and a solid carbon rod as both the fuel and anode. The molten electrolyte is contained in a metallic container which serves as an air electrode (cathode).

The shape of the container used is cylindrical or prismatic. The materials of construction for this container found to be suitable are nickel foam lined low carbon steel (C-1018) and mild steel doped with 2 wt% Ti (Fe2Ti). Humidified air is fed at the bottom of the electrolyte container using an air bubbler made of low carbon steel. The carbon rod is made of graphite or coal derived carbon. The cell is operated at temperatures from 400 to 650 °C. The overall simplicity of this design combined with the cheap construction materials makes it commercially attractive. However, there are a number of drawbacks [136]. The air bubbles and air dissolved in the electrolyte come in direct contact with the anode resulting in the chemical (rather than electrochemical) reaction of the fuel rod reducing the cell efficiency and open circuit voltage. The carbon fuel is required to be a solid rod or plank that has a good electrical conductivity which restricts fuel choice to pure carbon (some forms of coal are electrically insulating) and makes it difficult to continually fuel the cell. A metallic basket to hold the fuel cannot be used in this design as the basket would act as a cathode due to the presence of an oxygenated melt. There is also only one exhaust stream that is a mixture of both depleted air and CO_2 which makes this design less compatible with CO_2 capture technologies.

SARA has implemented a new design of the cell to overcome a number of the above mentioned drawbacks [136]. The new design of the cell (shown in Fig. 10) has a separator that allows transport of ionic species but electrically isolates the anode and cathode chambers. The separator allows hydroxyl ions to move between the electrodes but prevents air (oxygen) to come in contact with the anode. This design also prevents mixing of CO_2 with the air bubbled through the melt making it more compatible with carbon dioxide capture technologies. The separation of the anode and cathode chamber also allows the use of a metallic basket type current collector that can hold carbon in a particulate form removing the requirement for the fuel to be highly conductive and making it possible to easily refuel the design. It may also be possible in the future to fill the anode and cathode chambers with materials of different compositions. The materials investigated for the separator include porous alumina, porous zirconia and a perforated nickel foil wrapped stainless steel tub [136].

3.2.2. Technology status

SARA has built four successive generations of prototypes to demonstrate the technology based on molten hydroxide as the electrolyte [143]. The latest prototypes built are MARK II-D and MARK III-A. The various design parameters and materials used in these prototypes are given in Table 3.

Fig. 11 shows the voltage and power density versus current density characteristics of SARA's MARK II-D and MARK III-A DCFCs at 630 °C. The voltage − current density characteristics show that a limiting current condition is reached above 250 mA/cm^2 for MARK II-D and at 150 mA/cm^2 for MARK III-A. The figure shows that the peak power densities achieved are 42 mW/cm^2 by MARK III-A and 58 mW/cm^2 by MARK II-D. It was reported that Fe2Ti cathode produced lifetimes of over 540 h as compared to ∼100 h by Ni foam lined steel cathode. The open circuit voltage varied between 0.75 to 0.85 V. The maximum efficiency measured in the MARK III-A prototype was 60% at 50 mA/cm^2.

The investigations on the above two prototypes revealed that the cell operation was under mixed − ohmic and mass transfer control. The ohmic losses are mainly due to the large spacing between the anode and cathode. The performance can be improved by reducing the electrode spacing, and also by increasing the cathode surface area, optimisation of air flow, improved current collector-anode contact and using a carbon anode derived from coal instead of graphite [144,151,152]. SARA has applied for several patents on Ti doped steel for cathode, humid atmosphere above melt, new cell design and liquid hydrocarbon reformer that makes solid carbon [138,143,153].

3.2.3. Technical issues

High corrosion rates of metals used in the cell at the operating temperatures leads to high levels of degradation. In order to lower the operating temperature as well as keep the electrolyte sufficiently molten, a eutectic of sodium hydroxide and lithium hydroxide is used. This allows operation of the cell at lower temperatures. As with molten carbonate fuel cells, lithium in the melt also helps to reduce corrosion rates of anode and cathode current collectors. Other general issues are related to fuel pretreatment of coal. These mainly centre around the removal of volatile hydrocarbons and mineral ash that are known to reduce the performance of the electrolyte [138,144,151−153].

3.2.4. Technology outlook

SARA has planned to build new prototype DCFCs and to carry out tests to optimise cell geometry. There is also significant work to continue at a cell level on the optimisation of operating temperature, air humidity, gas bubbling rate and electrolyte composition
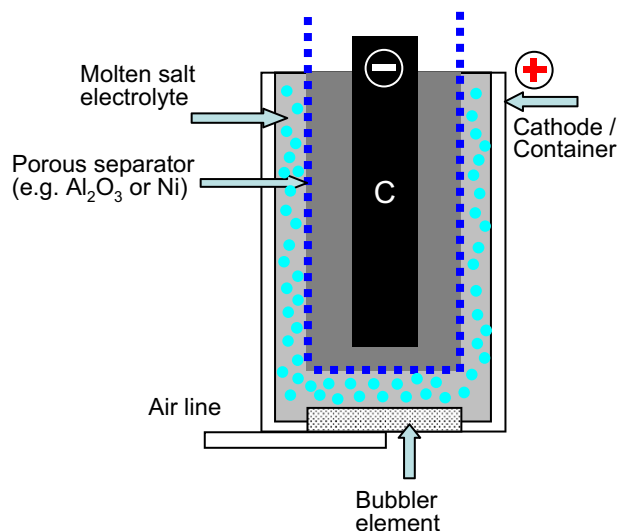

Fig. 10. A schematic drawing of a DCFC used by SARA in their investigations with a porous separator. Figure redrawn based on Reference [136].

Table 3
Design parameters and materials used in SARA's MARK II-D and MARK III-A prototypes.

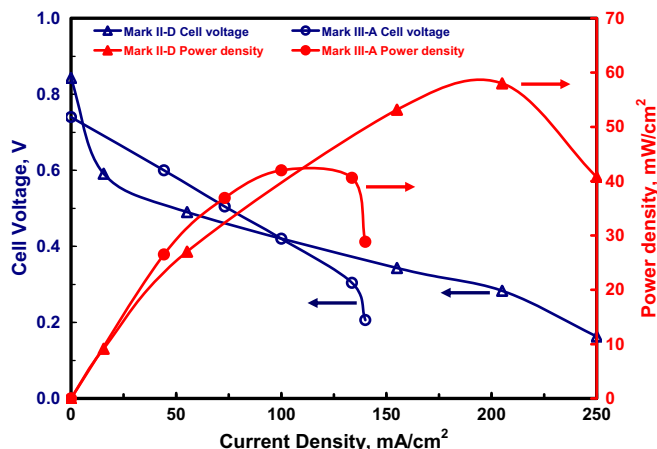| Prototype	Cathode container shape	Cathode material	Anode	Anode surface area	Electrode spacing
MARK II-D	Cylindrical	Ni foam lined C-1018 steel	2 cm dia. 4.1 cm long graphite rod	26 cm^2	1.3 cm
MARK III-A	Prismatic	2 wt% doped mild steel (Fe2Ti)	7.6 cm dia. 12.6 cm long graphite rod	300 cm^2	3 cm

Fig. 11. Voltage − current density and Power density − current density characteristics of SARA's MARK II-D and MARK III-A molten hydroxide electrolyte based DCFCs at 630 °C. Figure redrawn based on Reference [143].

(single and mixed hydroxides of Na, K, Li and use of oxygen additives such as SiO_2, MgO, Sb_2O_3, $Na_2S_2O_8$, $Na_4P_2O_7$) [152]. Other areas of development are finding suitable separator materials that can survive the aggressive cell environment and fuel pre-treatment to remove impurities to ensure no contamination of the electrolyte occurs.

Fig. 12 shows SARA's DCFC concept sketch for a commercial prototype based on a new cell design with a porous separator
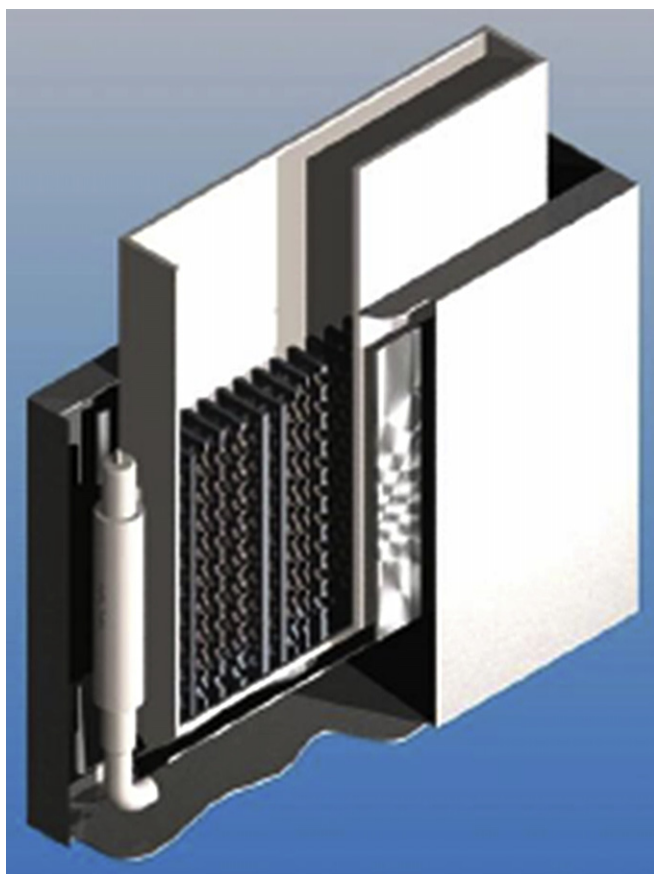

Fig. 12. SARA's commercial DCFC concept sketch. Figure reproduced from Reference [136] with permission of the publisher.

[136,153]. The cell in this design has a screen type anode current collector that can hold carbon particles. A rectangular porous separator surrounds the anode compartment. The cathode compartment surrounds the porous separator and contains the cathode (air electrode). There is an electrolyte circulation system that employs a pump to circulate catholyte and introduces air into the hydroxide melt.

SARA is now pursuing coal derived anode fuels for its experiments. West Virginia University (WVU) is supporting SARA to develop fuels for their DCFCs [136]. Hackett et al. from WVU investigated solid carbons from several sources including some derived from coal [154]. They used a simple cell design with carbon rods as the anode, iron-titanium alloy (98-2%) as the cathode and sodium hydroxide as the electrolyte. Air humidified at 70 °C and heated to the cell operating temperature (600−700 °C) was distributed to the cathode by a spider-type sparger. The cell voltage was measured as a function of current density and area specific resistance (ASR) was calculated from this data. Graphite rods produced an open circuit voltage (OCV) of up to 0.788 V and current densities up to 230 mA/cm^2 as compared to coal derived rods that produced an OCV of up to 1.044 V but current densities of only up to 35 mA/cm^2. The ASR values for graphite and coal derived rods were 2 and 6 Ωcm^2 respectively, which were also reflected in the achieved power densities of 84 and 33 mW/cm^2 respectively. These power densities are too low for a commercially viable system, however, with research and development in progress there is a potential for further improvements.

3.3. Molten carbonate electrolyte technology

Gas fed molten carbonate fuel cells are one of the most commercially mature types of fuel cell systems (see section 2). Essentially the direct carbon version of the cell (i. e. the electrodes, current collectors and electrolyte) is similar to the gas fed molten carbonate fuel cell. Through modification to the system design it is proposed, and indeed it has been demonstrated at a small scale, that it is possible to operate a molten carbonate fuel cell system on solid carbon fuels with electric efficiency as high as 80% with near 100% fuel utilisation [53−58,155−157]. Fig. 13 depicts one design proposed by Cooper et al. [155,157]. The carbon fuel in the form of fine particles is supplied mixed with molten carbonate electrolyte. The unconventional tilted design allows excess molten electrolyte to be drained (thus stopping the cathode from being flooded by the electrolyte as the fuel is consumed) and for the cell to be continually refuelled with a carbonate slurry [155]. Other designs that more closely resemble the Jacques design have also been tested [158−161]. These designs offer greater simplicity but are likely to have similar drawbacks to the designs being tested by Zecevic et al. [151]. Development of these systems would benefit from the greater understanding of corrosion of metals in carbonates vs hydroxides [162] and from the larger amount of information available on the long term operation of molten carbonate fuel cells [163,164].

The use of a molten carbonate as the electrolyte has a number of advantages; the electrolyte has good long term stability in CO_2 [163,164], can catalyse carbon oxidation [165] and has a high ionic conductivity [166] (although lower than that of sodium hydroxide [139]). However, due to the higher melting point of carbonates [142], the operating temperature is somewhat higher than for hydroxide based systems, typically between 600 and 850 °C [58,158−161]. Carbon can either be formed into a rod where it is used as the anode and current collector [158−161] or dispersed into the electrolyte with an inert metal current collector [58,167−169]. Mixed molten carbonates of (Li, K) are generally used as the
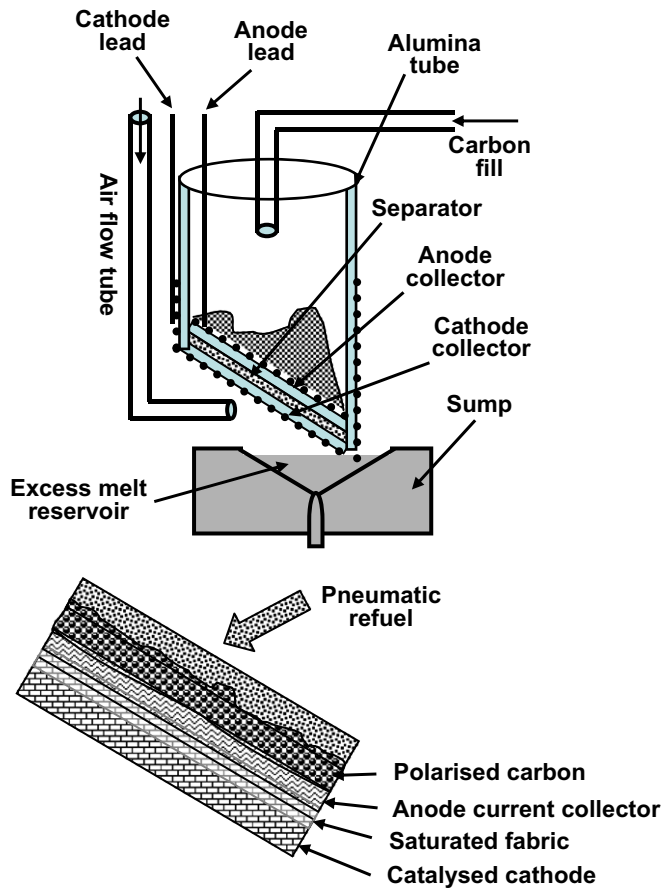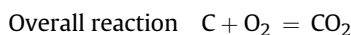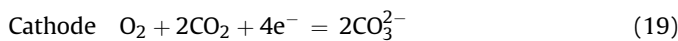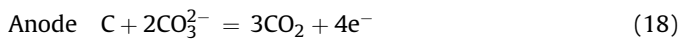
Fig. 13. A schematic drawing of a basic cell configuration of the tilted DCFC of LLNL. Figure redrawn based on References [156,157].

electrolyte. The anodic and cathodic reactions that occur in this type of fuel cell are as follows:
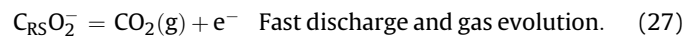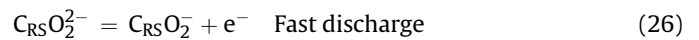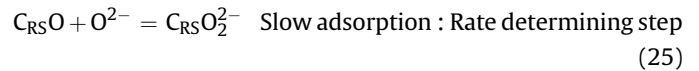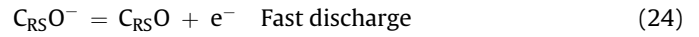
$$\text{Anode} \quad C + 2CO_3^{2-} = 3CO_2 + 4e^- \tag{18}$$

$$\text{Cathode} \quad O_2 + 2CO_2 + 4e^- = 2CO_3^{2-} \tag{19}$$
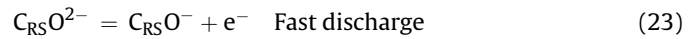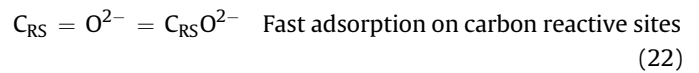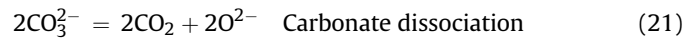
Overall reaction $C + O_2 = CO_2$

For mass balance, two molecules of CO_2 for every atom of carbon, consumed in the cell reaction, need to be cycled from the anode to the cathode compartment. The above electrochemical reactions show that CO_2 partial pressure at the anode and the cathode would affect the value of the open circuit voltage of the cell as given by the following equation [58]:

$$E = E^{\circ} + RT/4F \ln \left[pO_{2,\text{cath}} \right] \left[pCO_{2,\text{cath}} \right]^2 / \left[pCO_{2,\text{an}} \right]^3. \tag{20}$$

There have been a number of studies investigating the reaction mechanisms involved with electrochemical oxidation of carbon in carbonate melts [58,170,171]. However, similar to other DCFC systems, the mechanism of carbon reactions in the molten carbonate based DCFCs is not yet fully understood. Various electrochemical aspects such as the number of electrons transferred, role of reverse Boudouard reaction and possible intermediate chemical reactions between the anodic species are still under investigation. Cherepy et al. proposed the electrochemical mechanism parallel to the mechanism describing the Hall process which

is used in aluminium production [58,172]. The reaction sequence is as follows:

$$2CO_3^{2-} = 2CO_2 + 2O^{2-} \quad \text{Carbonate dissociation} \tag{21}$$

$$C_{RS} = O^{2-} = C_{RS}O^{2-} \quad \text{Fast adsorption on carbon reactive sites} \tag{22}$$

$$C_{RS}O^{2-} = C_{RS}O^- + e^- \quad \text{Fast discharge} \tag{23}$$

$$C_{RS}O^- = C_{RS}O + e^- \quad \text{Fast discharge} \tag{24}$$

$$C_{RS}O + O^{2-} = C_{RS}O_2^{2-} \quad \text{Slow adsorption : Rate determining step} \tag{25}$$

$$C_{RS}O_2^{2-} = C_{RS}O_2^- + e^- \quad \text{Fast discharge} \tag{26}$$

$$C_{RS}O_2^- = CO_2(g) + e^- \quad \text{Fast discharge and gas evolution}. \tag{27}$$

Reactions (21–27) describe sequences that occur in the overall anode reaction described in reaction (18). Key to the mechanism described by Cherepy et al. [58] is the adsorption of oxygen at the surface. They have concluded that surface adsorption is likely to be limited by the number of reactive sites (C_{RS}) which in turn is dependent on the surface area of the carbon and the concentration of reactive sites. With respect to limiting factors for fuel cell performance, there are a number of factors including resistive losses (such as current collectors and the electrolyte), gas diffusion losses (caused by gas/fuel transport through the electrodes), chemical diffusion losses (caused by transport of ionic species through the electrodes or along the electrode surface) and slow electrode reaction kinetics that can be rate limiting.

Significant work has been carried out by Li et al. on a number of carbon sources and they found that the reaction rates for carbon in molten carbonate slurries are largely dependent on surface area and the number oxygen surface groups [167,173–176]. Similarly, modelling studies have also shown the number of reactive sites to be the rate controlling parameter both of which would appear to support the mechanism proposed by Cherepy et al. [58]. In addition to the surface chemistry, the degree of carbon crystallinity and the crystallite size have all been determined to greatly affect the reactivity of carbon fuels used. This has largely been attributed to the increase in the number of active sites on the carbon surface [167,173–177]. The significance of this investigation is that it suggests that the electrochemical oxidation of carbon during cell operation is selective, producing CO_2 in preference to CO. However, for temperatures above 650 °C, CO concentration would predominate via the reverse Boudouard reaction [58] and is known to be catalysed by various molten salts [165,178], and can also proceed even when the cell is held at OCV. This is of interest as it would suggest that the use of molten carbonates may lead to higher fuel utilisations and ultimately higher efficiencies through favouring the formation of CO_2 during cell operation rather than CO. This experimental study is in good agreement with the more theoretical discussion by Cooper [54].

3.3.1. Systems investigated

Cooper et al. have been developing DCFC technology based on the molten carbonate electrolyte. They constructed a cell with tilted orientation design, which along with the basic cell configuration of cathode/electrolyte - separator/anode/fuel, is shown in Fig. 13 [155,157,179]. The operating temperature of the cell was between

750 and 850 °C. The cell consisted of a paste of particulate carbon fuel in a molten carbonate electrolyte (carbonates of 32% Li, 68% K eutectic) [56]. Open foam nickel was used as the anode and the current collector while a sintered frit of fine nickel particles was used as the cathode and current collector. The latter was given a thermal treatment in air to form a compact layer of nickel oxide and then lithiated by exposing to lithium salts to impart its catalytic properties for cathodic reaction. Zirconia felt was used as a separator between the anode and cathode. The cell was tilted at an angle of 5–45° to enhance electrolyte drainage from the cell and thus avoiding flooding of the cathode [155,157].

3.3.2. Technology status

Various types of fuels such as acetylene black, coal derived carbon, furnace oil carbon black (Aerosperse 3) graphite particles, heat treated petroleum coke, etc. were investigated using the tilted cell design [157]. Fig. 14 shows the performance of LLNL's tilted DCFC with carbon fuel from furnace black and petroleum coke. The peak current density achieved was 120 mA/cm^2 at 0. 8 V and 800 °C (96 mW/cm^2 power density, 80% efficiency) with furnace black. This power density is of the same order as gas fed molten carbonate fuel cells that generally operate around 120 mW/cm^2 [180], however, the efficiency of DCFC is significantly higher. The results also showed that nano-structured (crystallographic) disorder of the carbon particles, electrical conductivity and reactive site density control the rate of electrochemical oxidation and efficiency of the cell with the purity of carbon fuel being less critical. The angled cell was found to be effective at controlling electrolyte wetting of fuel whilst avoiding flooding the cathode as the fuel was consumed, confining the reaction zone to wetted carbon and enabling refuelling [157]. It has also been suggested that this angled cell design can be readily scaled-up to a demonstration prototype level [156,181,182]. Cherepy et al. [58] studied the performance of carbon derived from fuel oil, methane, coal, bio-char and petroleum coke. Power densities in the range 40–100 mW/cm^2 at 0.8 V were achieved with cells with active area up to 60 cm^2.

The presence of sulphur and ash in the carbon fuel was found to lower the achievable current densities and degrade the anode current collector over time. The power densities were less than half about 34 mW/cm^2 for Conoco coke with 2.86wt% sulphur and 0.28wt% ash as compared to 82 mW/cm^2 for purified coke with less than 1wt% sulphur and about 0.15wt% ash. Further the performance of cell with high sulphur containing Conoco coke degraded the power density to about 31 mW/cm^2 within 24 h of operation which was attributed to the degradation of Ni current collector by sulphur.
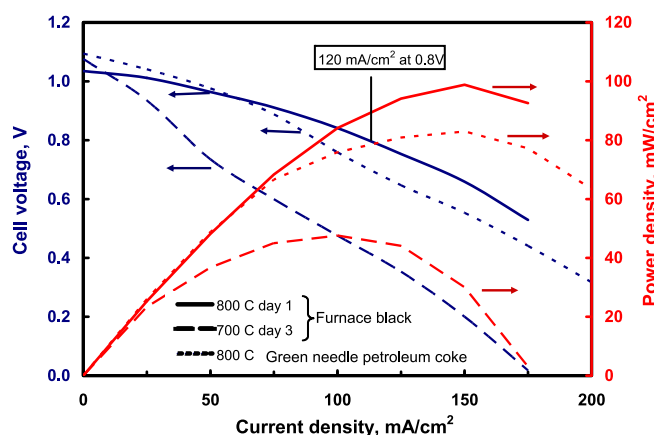
The surface area of carbon fuels studied in the 0.4–1225 m^2/g range and generally, was not found to have a strong effect on the discharge rate (current density). It was concluded that the carbon fuel properties that control the discharge rate, are the crystallographic disorder (the lower the crystallisation index, the higher the chemical and electrochemical reactivity), electrical conductivity (controls the reaction of carbon particles not in direct contact with the current collector and also facilitates current collection) and adequate reactive surface sites.

LLNL reported that repeated tests on cells produced power densities up to 100 mW/cm^2 with efficiencies of 80% (HHV) being routinely obtained with fossil chars, petroleum coke, bio-chars and carbon blacks [53,157,182]. These cells have been operated for nearly a week with periodic refuelling and with little drop in performance.

Cooper and his team have also designed a self-feeding cell that is refuelled pneumatically and incorporates internal pyrolysis of the coal as shown in Fig. 15. The pyrolysis of coal would produce hydrogen (that can be used for other fuel cells or as a reactant), and low molecular weight hydrocarbons and a non-agglomerating char, that is reactive and sufficiently conductive, for use as a fuel for DCFC [53]. The team at LLNL reported in 2005 that they intend to test a 75–150 W, 5-cell self-feeding bipolar stack (Fig. 16) using pure turbostratic carbon as the fuel [156]. However the technology was licensed to Contained Energy and there have been no further reports on the progress of the work.

Lee et al. reported the testing of coin type (button) cell with molten carbonate electrolyte [183]. They used LiAlO$_2$ as a matrix to hold the Li/K eutectic. Porous Ni–Al alloy was used as the anode and porous Ni is used as the cathode. Activated carbon was used as a fuel with N$_2$ as the anodic purge gas with a mixture of Air:CO$_2$ (70:30%) used as the cathode gas. They achieved current densities up to 140 mA/cm^2 at a voltage of about 0.6 V at 850 °C with carbon fuel. The performance of the carbon fuel cell was compared with H$_2$ fuel. H$_2$ delivered a higher power density (136 mW/cm^2) as compared to carbon (84 mW/cm^2), possibly due to slower reaction rates of the solid fuel as compared to H$_2$.

Predtechenskii et al. have also carried out various studies examining the performance of coal derived fuels in a cell similar to devices being tested with molten hydroxide systems. Despite the fact that this development work appears only to be in its early stages, the overall performance of their cells was good with a wide range of fuels being tested, producing peak power densities of between 60 and 120 mW/cm^2 [159–161].

3.3.3. Technical issues

The main cell related technical issues reported with molten carbonate DCFC [53,157] include high cathode polarisation, loss of

Fig. 14. Voltage − current density and Power density − current density characteristics of the cell showing current densities of >100 mA/cm^2 achieved with carbon black as the fuel. Figure redrawn based on Reference [157].
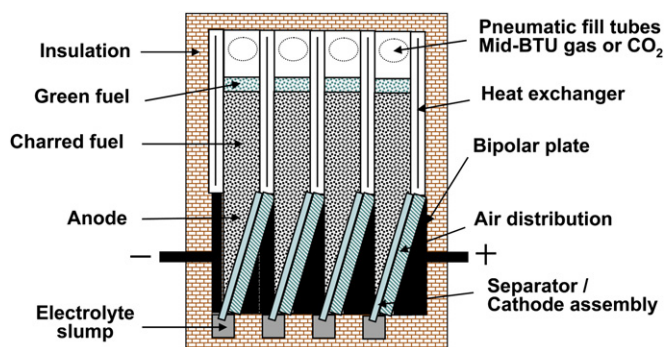

Fig. 15. Design of LLNL's self-feeding cell that is refuelled pneumatically and incorporates pyrolysis of cleaned coal. Figure redrawn based on Reference [156].
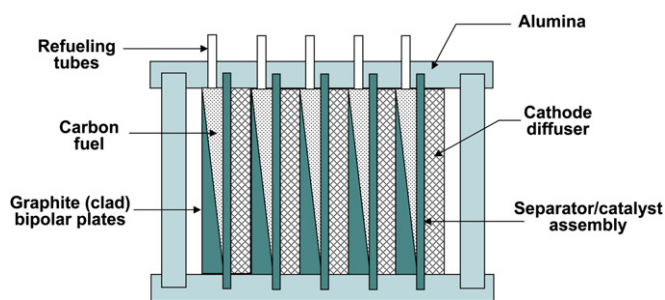
Fig. 16. Design of LLNL's self-feeding 5-cell bipolar stack that uses pure carbon as fuel. Figure redrawn based on Reference [156].

cathode performance with time, corrosion of metal bipolar plates, difficulties associated with fuel delivery, low power densities, short cell lifetimes and the need to keep the cell under constant polarisation to avoid the reverse Boudouard reaction. A number of materials degradation issues (which are a key to limiting cell lifetime) are common with more mature gas fed molten carbon fuel cells. A number of advances in this area over the past decade have lead to significant increases in cell lifetime. These have included modification of the electrolyte melt through the addition of sodium carbonate (amongst other additions) to improve electrolyte stability and reduce reactivity with metallic current collectors and improved gas flow, which avoids the loss of volatile electrolyte species especially in large systems [163,164,184]. Despite these improvements in power densities, even for gas fed molten carbonate systems, these are still typically around 120–160 mW/cm^2 (much lower than other higher temperature SOFC systems which typically operate at 300–400 mW/cm^2). Furthermore, lifetime for molten carbonate fuel cell stacks has been suggested to be around 5 years with significant degradation in performance being noted over that period [163,164,180,184].

Along with stack based issues there have also been a number of challenges that relate to fuel processing and fuel delivery system [57,58,155,157,168,169,179,181,185–187]. A lack of a suitable fuel delivery system has delayed long term testing with the majority of testing being carried out on small scale button cells that have to be manually refuelled. This will need to be resolved before long term testing of large (1 kW+) systems. Although there has been significant work in understanding the reaction mechanisms within molten carbonate salts (see section 5.1), a relationship between the carbon structure and its electrochemical activity is still to be fully established. This is essential because it will ultimately determine the required raw material parameters and pyrolysis conditions. Poisoning of the fuel cell from various fuel contaminants such as ash or sulphur needs further investigation in particular looking at long term durability under realistic operating conditions. Once the required structure and fuel composition is determined it will then be necessary to develop a series of low cost pre-treatment processes such as pyrolysis, hydro-pyrolysis, solvent extraction for obtaining the carbon fuel of desired properties in terms of ash content, sulphur content, structure (surface area, extent of disorder, etc.) and electrical conductivity.

Cooper has reported that de-ashing processes developed by organisations such as UCC Energy (Sydney, Australia), NEDO (Tokyo, Japan), and South African Synthetic Oil Limited (SASOL; Johannesburg, SA) can produce fuel for DCFCs at a competitive cost of about $2–3/MMBtu [53].

3.3.4. Technology outlook

LLNL has historically been the main group working in this technology domain and has made significant progress in demonstrating the technology both at cell and small stack level and understanding

the role of carbon structure and impurities on its electrochemical reactivity [156,168,169,179]. These developments have resulted in a number of suggested design variations for a commercial scale device (Figs. 12, 13, 15 and 16). In addition, LLNL have also developed a significant intellectual property portfolio within this area. In order to commercially exploit this technology, LLNL had engaged with a partner company Contained Energy based in Ohio. Despite continuing to licence this technology from LLNL, Contained Energy (now Logos Energy) does not appear to have a program currently ongoing in this area. Research, however, continues looking at the reactivity of carbon and processing of coal for use in devices of this design at a number of academic institutes most notably the University of Queensland and Curtin University of Technology both in Australia. Although arguably one of the most well understood DCFC fuel cell designs, it appears that there is little commercial interest in the further development of this technology at this stage.

3.4. Oxygen ion conducting electrolyte technology

This type of direct carbon fuel cell utilises an oxygen ion (O^{2-}) conducting ceramic as the electrolyte similar to that in the solid oxide fuel cell (SOFC). The temperature of operation is currently 800–1000 °C, although there is a strong technology push to lower this operating range. Fully stabilised zirconia (i. e. 8–10 mol% Y_2O_3 stabilised zirconia) is the most common electrolyte being investigated for direct carbon fuel cells. Other electrolytes such as 2–3 mol% $Y_2O_3 - ZrO_2$ compositions which are known to have high strength but lower ionic conductivity, scandia − zirconia compositions, which are known to have superior conductivity but somewhat higher cost of the dopant or doped ceria may also be used. The earliest work that can be cited where solid carbon was used as the anode and zirconia was used as the electrolyte is the work carried out by General Electric Company in 1965 [188]. The electrolyte used was ZrO_2-CaO which was formed into a tube of 0.62 mm wall thickness. A layer of porous ZrO_2 flooded with molten silver on the outer wall of the tube, saturated with oxygen, was used as the cathode. The anode was a continuously regenerated pyrolytic carbon formed by decomposition of methane (natural gas), which was mainly used as the fuel. Nickel wire screen or nickel dispersion in zirconia was used as the current collector at the anode.

Fig. 17 shows the schematic view of the General Electric cell. The OCV obtained was in the range 0.95–1.05 V and power densities of up to 125 mW/cm^2 were achieved over a short testing period [188]. The main issues with the cell were the evaporation loss of silver at the cathode and keeping the pyrolytic carbon deposition and consumption in equilibrium.

There are three sub-categories of DCFCs that use an oxygen ion conducting ceramic as the solid electrolyte. These differ only in the anode chamber design, and are discussed in the following sections (3.4.1, 3.4.2 and 3.4.3).

3.4.1. Fuel as solid carbon or in fluidised bed

It is possible for the fuel to react within a solid oxide fuel cell anode via a number of different reaction paths. Which reaction path dominates is largely dependent on the fuel composition and the anode design.

Direct electrochemical reaction between the carbon and oxygen ions at the anode has been reported by Hasegawa and Ihara [189]. The overall cell reaction would be the same as for all direct carbon fuel cells (reaction (5)) with the anode reaction being:

$$C + 2O^{2-} = CO_2 + 4e^- \tag{28}$$

This reaction would require a triple phase boundary (TPB) to be present between the reactant (carbon), oxygen ion conductor
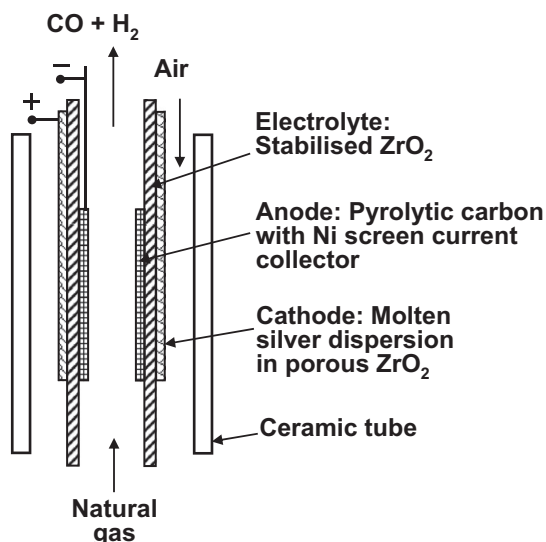
Fig. 17. General Electric Company's pyrolytic carbon − anode fuel cell with zirconia electrolyte tube. Figure redrawn based on Reference [188].

(electrolyte) and an electronically conducting material (current collector). The current collector may be the fuel if an electronically conducting form of carbon is used. A schematic of the triple phase boundary is shown in Fig. 18. Direct electrochemical reaction of carbon at carbon/anode or carbon/anode/electrolyte interface in this way may result in lower power being generated from the cell due to the small number of available reaction sites (i. e. triple phase boundaries) when compared to conventional porous SOFC anodes involving gaseous fuels. In addition, any carbon particles reacting at a triple phase boundary will be consumed creating a gap between the remaining solid fuel and the reaction sites unless there is a way for continuous contact between solid fuel and available reaction sites.

The carbon particles which do not make direct contact with the electrolyte can, however, be first gasified through the reverse Boudouard reaction (10) followed by the oxidation of CO by the reaction sequence:
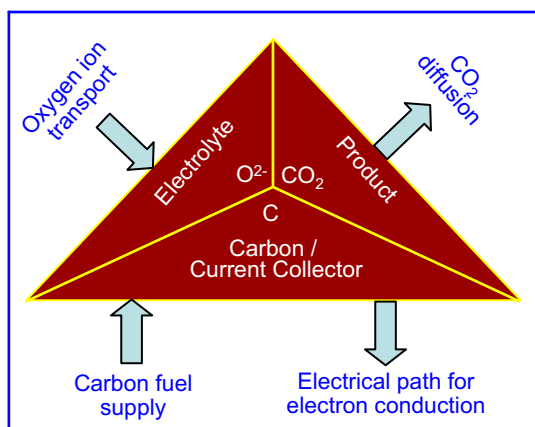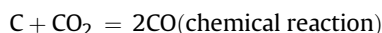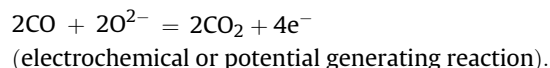
$$C + CO_2 = 2CO \text{(chemical reaction)}$$

Fig. 18. Schematic diagram of a triple phase boundary required for a DCFC using a solid oxygen ion conductor electrolyte and particulate carbon as fuel.

$$2CO + 2O^{2-} = 2CO_2 + 4e^-$$
(electrochemical or potential generating reaction).

This reaction path would initially require the presence of CO_2 produced electrochemically via reaction (28) if it is not used as the purge gas. The rate of formation of carbon monoxide and its subsequent reaction within the anode will be sensitive to temperature as the reverse Boudouard reaction is only likely to occur spontaneously for most carbon types at temperatures above 700 °C [190].

Considering another scenario, if CO_2 formed in reaction (28) is removed via constant purging with an inert gas such as helium or argon, it is possible that some oxygen would be liberated at the anode/electrolyte interface due to the partial pressure differential across the cell, which then could react with the carbon fuel via the following reaction sequence:

$$O^{2-} = 0.5\,O_2 + 2e^- \quad \text{(anode reaction)} \tag{29}$$

$$C + 0.5\,O_2 = CO \quad \text{(chemical reaction)}. \tag{30}$$
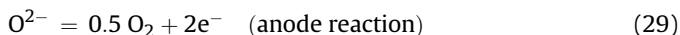
The reaction sequence described in reactions (29) and (30) is likely to occur on some scale, however, is unlikley to be able to generate significant power. This is because the overall reaction kinetics for oxygen recombination are slow when compared to other reactions (such as CO or hydrogen oxidation).

Overall the oxidation of solid carbon fuel is likely to involve a combination of the mechanisms described above with a number of different reaction paths being possible. As with other fuel cell systems, fuel oxidation would involve multiple reaction steps with contributions from surface diffusion, bulk diffusion, adsorption, desorption and charge transfer processes. CO formation and oxidation at the anode is likely to be the favoured mechanism in most systems (reactions (10) and (11)). This is due to the comparative ease (when compared to solid carbon) at which CO_2 and CO can travel between active sites within the anode and fuel. The higher potential and faster reaction kinetics of CO oxidation are also likely to make it more favourable than molecular oxygen formation and subsequent fuel reactions ((11) vs (29)). However, in systems where the formation of CO via reverse Boudouard reaction is inhibited via operation at a temperature below 700 °C, or through the flushing of the anode chamber with an inert gas, which reaction mechanism dominates will largely be dependent on the proximity of the solid carbon to the reaction sites within the anode. Overall DCFCs that operate directly with carbon within the anode chamber and which have been evaluated by various authors, can be further sub-divided into four families irrespective of their practicality or commercial viability:

1. Vapour deposited systems − hydrocarbon fuels are decomposed within the anode chamber, directly depositing carbon over a large area within the anode.
2. Consumable anodes pressed against the electrolyte − carbon is pressed directly to the electrolyte.
3. Carbon placed within the anode chamber but not necessarily in constant direct contact with the anode or the electrolyte and includes systems with fluidised or packed beds and systems where the fuel may simply be within the anode chamber either in direct contact or a small distance from the anode.
4. Use of an integrated external gasification − carbon gasified external to the fuel cell stack.

Within all of these families, the dominant reaction mechanism is affected enormously by the formation or absence of CO. Thus,

obtained power densities can be greatly affected by the use of a purge gas or the operating temperature of the cell.

3.4.1.1. Systems investigated

3.4.1.1.1. Carbon deposited systems. These systems generally comprise of a SOFC with a nickel based cermet anode. Nickel is well known to catalyse the thermal decomposition of dry hydrocarbon fuels into hydrogen and carbon [15]. Thus, it is possible to deposit carbon directly into the anode of the fuel cell by simply passing a dry gaseous hydrocarbon fuel over the fuel cell. Once the carbon has been deposited the flow of the hydrocarbon fuel can be replaced by an inert purge gas and the cell operated with carbon as the fuel.

Hasegawa and Ihara used methane or propane as the charging fuel which they thermally decomposed at 900 °C onto the anode [189,191]. Once 'charged' the fuel gas flow was stopped (replaced by flowing argon) and the fuel cell was then operated with the deposited carbon used as the fuel. The cell for the investigation consisted of a 0.3 mm thick 8 mol% $Y_2O_3 - ZrO_2$ disc with a nickel-gadolinia doped ceria (GDC) cermet as the anode and LSM as the cathode. The cell was operated at 900 °C at a constant current density with oxygen as the oxidant supplied to the cathode. The peak power density achieved was 55 mW/cm^2 at 80 mA/cm^2 current density (Fig. 19a). Through varying the flow rate of the purge gas (argon) and monitoring the effect on the flue gas composition and polarisation curves, Hasegawa and Ihara were able to propose a series of global carbon oxidation mechanisms. These included three electrochemical reactions at the triple phase boundary and one chemical reaction (Fig. 19 (b)). It was found that on reducing the flow rate of argon, the cell voltage decreased. This was attributed to the increased concentration of reaction products within the anode chamber that reduced the potential differential across the cell. However, the increased concentration of carbon dioxide within the anode increases the rate of CO formed via the reverse Boudouard reaction, which in turn reduces the anode overpotential due to the higher mobility and reactivity of CO when compared with carbon. This led to the cell having an optimal argon flow rate for maximum power density. This work also clearly illustrated the complexity of the balance between chemical and electrochemical reactions occurring at the anode. For fast argon flow rates, when direct electrochemical reaction of carbon to CO_2 occurs, the cell would produce the highest efficiency and the fuel utilisation would be the highest, however, at much lower power densities than when the cell is operated with lower argon flow rates.

3.4.1.1.2. Consumable anodes. The use of carbon as a sacrificial anode has a number of advantages. Carbon is relatively cheap when compared to other anode materials and gaseous fuels (e. g. H_2, CO, CH_4). It can be derived from a number of low grade, low cost sources such as coal, biomass, organic waste and it is also a by-product of petroleum refining. Carbon blacks have very low ash content and can be used directly in DCFCs. Cooper has given a cost estimate of between \$2−6/GJ for carbons derived from different sources including deep de-ashed coals [179]. These costs are quite competitive with the price of natural gas fuel. The carbon can have high electrical conductivity and when pressed directly onto the solid electrolyte offers the shortest distance possible for mass transport from the anode to the electrolyte of any of the SOFC based systems. However, using the fuel as the anode, makes refuelling technically challenging and restricts the choice of fuel to only conductive forms of carbon excluding the use of raw coal.

Nurnberger et al. studied the performance of solid electrolyte DCFC using carbon as the sacrificial anode [192]. The button cell consisted of 3 mol% Y_2O_3 stabilised zirconia (TZ3Y) electrolyte disc with LSM-YSZ composite cathode. A dry pressed carbon pellet was used as the fuel source and placed directly over a TZ3Y electrolyte disc. Two types of carbon namely graphite and carbon black (Vulcan XC-72) were compared as a fuel. Nitrogen was used as a purge gas for the anode chamber. An OCV of ∼0. 8 V and power densities up to 40 mW/cm^2 were achieved for Vulcan XC-72 fuel at 1000 °C (0. 4 V at 100 mA/cm^2). However, with graphite anode, the OCV was 0. 45 V and less than 1 mW/cm^2 power density was obtained. Despite the better electrical conductivity of the graphite, it delivered significantly lower power densities and lower open circuit voltage than the amorphous carbon black fuel. The authors attributed the better performance of carbon black to the non-crystalline structure and higher surface area. The current density was found to increase linearly with time which was attributed to a reduction in the thickness of the anode (pellet) as fuel was consumed thus reducing ohmic losses within the cell. In this experimental set-up, the carbon pellet was consumed via direct electrochemical oxidation of carbon at the anode/electrolyte interface and the reaction of CO_2 formed with carbon via the reverse Boudouard reaction to generate CO. Since the current densities were found to be independent of purge gas flow rate, the authors suggested that the current output was largely a function of direct electrochemical oxidation of carbon at the anode/electrolyte interface, with gases generated via the reverse Boudouard reaction playing a less significant role in the overall cell performance. From the measurement of current density-time transients, the amount of carbon consumed by electrochemical oxidation was calculated using the formula:
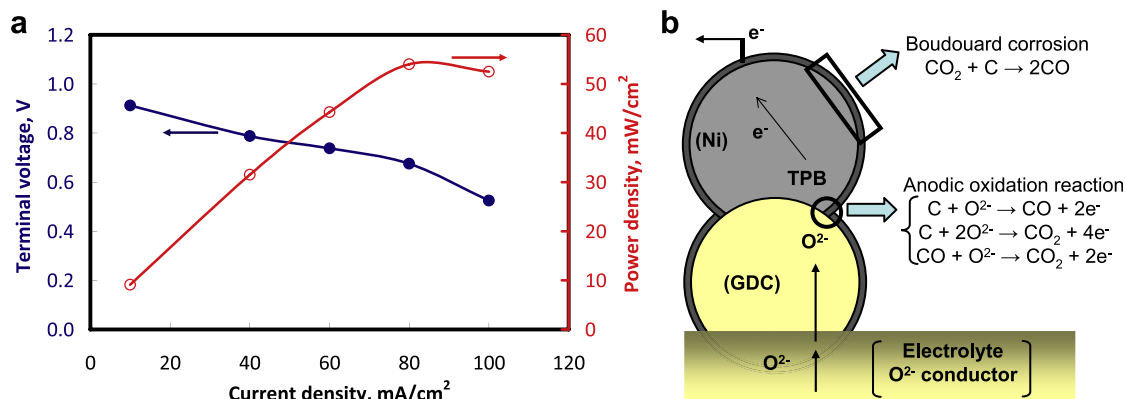

Fig. 19. (a) Voltage − current density and power density − current density characteristics of a rechargeable DCFC at 900 °C with methane as the charging gas. (b) A schematic drawing of the anode reaction mechanism proposed by Hasegawa and Ihara. Figures redrawn based on Reference [189].

$$x(t) = x_0 - \frac{Mb}{4FA\rho} \int\limits_0^t J(t)\, \mathrm{d}t \qquad (31)$$

where x is thickness of pellet, M is molar mass of carbon, A is area of cross section, ρ is density of carbon pellet, $J(t)$ is the value of current at an instant of time t during the experiment and b is the factor which determines the contribution to carbon consumption by the reverse Boudouard reaction. It was concluded that 60% of the fuel was consumed by the cell via direct electrochemical oxidation while the rest was consumed via the reverse Boudouard reaction. The CO generated from this latter process exited the chamber with the purge gas without taking part in electrochemical reaction.

It is also clear from Fig. 2 that CO, as an electrochemical reactant generated from carbon, produces lower theoretical efficiencies at higher temperatures. This low fuel utilisation and efficiency could be improved if the cell operating temperature was lowered to below 700 °C due to the fact that the reverse Boudouard gasification is significantly reduced at these temperatures [133,135,193]. However, reducing the operating temperature will result in a range of other technical issues including slow carbon oxidation and oxygen reduction kinetics, higher electrode polarisation and increased ohmic losses from the electrolyte. One strategy would be to reduce the electrolyte resistance by either using very thin films of electrolyte (∼10 μm) supported on anode or cathode material and/or employing materials that show sufficient ionic conductivities in the temperature range of 600–700 °C, such as gadolinia doped ceria (CGO). The development of electrodes that show sufficient catalytic properties for carbon oxidation and oxygen reduction in this lower temperature range would also significantly improve the fuel cell performance. Thus there will be compromise between system efficiency and maximum power that can be obtained from a DCFC. Taking various factors into consideration and availability of materials and fabrication technology, an operating temperature range of 600–700 °C appears reasonably promising.

3.4.1.1.3. Carbon placed within the anode chamber. The incorporation of carbon within the anode chamber of a fuel cell as a fluidised bed, packed bed or simply as static carbon a short distance from the anode is by far the most commonly reported way of oxidising carbon within a SOFC type fuel cell [109,132,134,194,195]. Due to the solid carbon fuel being further away from the anode and electrolyte than with other direct carbon solid electrolyte fuel cell designs, most of the systems of this type do not result in direct electrochemical oxidation of the carbon fuel, with most requiring formation of CO or perhaps molecular oxygen as an intermediate step within the overall reaction path.

Gür and Huggins [194] employed a two compartment carbon fuel cell arrangement as shown in Fig. 20 (a) for their investigations on electrochemical conversion of carbon to electrical energy at high temperatures. The set-up consisted of a tubular yttria-stabilised zirconia (YSZ) solid electrolyte cell (closed at one end) placed in one section and carbon pellets placed in another section of a quartz tube (Fig. 20 (a)). Platinum paste was used to make porous platinum electrodes inside and outside the YSZ tube. The YSZ tube was placed such that the open end of the tube was outside the quartz tube for supplying air to the inside of the YSZ tubular cell.

The carbon fuel section was operated at temperatures between 524 and 955 °C and fuel cell section above 800 °C. This design allows a separate control of temperature of the fuel and fuel cell. The OCV values measured were between 1.0 and 1.1 V. The power densities achieved with the cell at 932 °C and the fuel at 725 and 955 °C were approximately 1 and 5 mW/cm² respectively as shown in Fig. 20 (b). Gür and Huggins suggested that the driving force for the oxygen transport across the electrolyte membrane is the gradient of the oxygen activity across it. Poor observed power
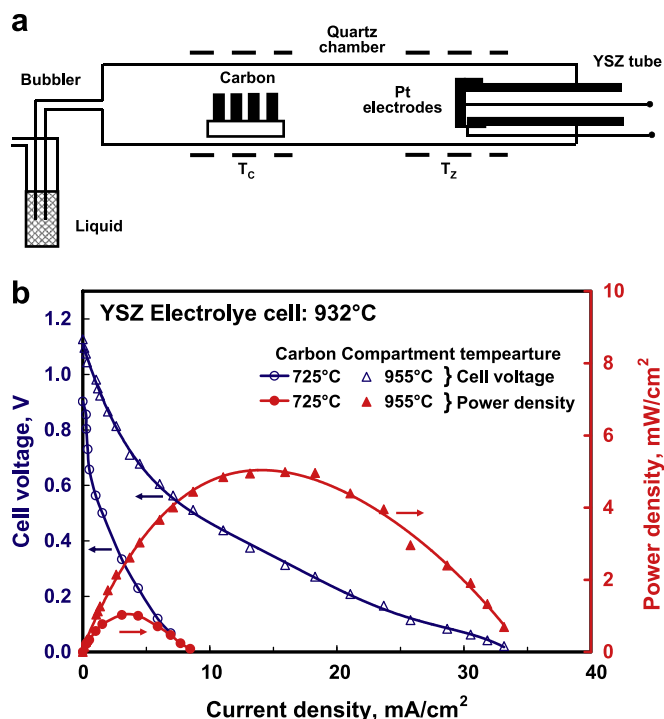

Fig. 20. (a) A schematic drawing of a two compartment DCFC set-up employed by Gür and Huggins for their investigations. (b) Voltage − current density and power density − current density characteristics of the cell under resistive load. The YSZ electrolyte temperature was maintained at 932 °C while the cell fuel compartment was kept at 725 and 955 °C. Figures redrawn based on Reference [194].

densities are likely to be due to the large distance that the gas molecules must travel between the carbon surface and fuel cell anode. Platinum electrodes are also known to have high polarisation losses due to only a restricted number of triple phase boundaries at the electrode/electrolyte interface. The oxygen activity (partial pressure inside the quartz chamber) was calculated from the open circuit voltage as a function of carbon fuel chamber temperature. At temperatures above 800 °C the experimentally measured values for oxygen activity agreed reasonably well with the theoretically calculated values. Gür and Huggins were granted a patent in 1994 based on the above concept [196]. This patent further includes concepts such as YSZ electrolyte tube in a fluidised bed of particulate carbon and recirculation of fuel reactant in the fuel chamber over the YSZ tube.

Nakagawa and Ishida [195] used button cells of 8 mol% Y_2O_3 stabilised zirconia with Pt electrodes on both sides to investigate the characteristics of direct oxidation of carbon. Platinum wire mesh connected to the electrodes was used for current collection. A YSZ disc separated the anode and cathode electrode chambers with the use of a glass ring seal. Fig. 21 shows the schematic diagram of the set-up. Charcoal pieces (∼4 mm blocks) placed in a perforated crucible located 5 mm away from the anode electrode were used as the fuel. Nitrogen and air were supplied to the anode and cathode chambers respectively. The cell was operated at 802°, 915° and 1002 °C. The fuel and air electrode potentials were measured with respect to the reference electrode (platinum wire connected to the periphery of the disc) and the product gas from the fuel chamber was analysed. It was observed that with increase in temperature from 802 to 1002 °C, the proportion CO in CO/CO₂ mixture in the fuel chamber increased from 70% to nearly 100%. The current density achieved was 8 mA/cm² with estimated polarisation losses of 0. 508 V at 802 °C. The proposed reactions in the fuel cell system
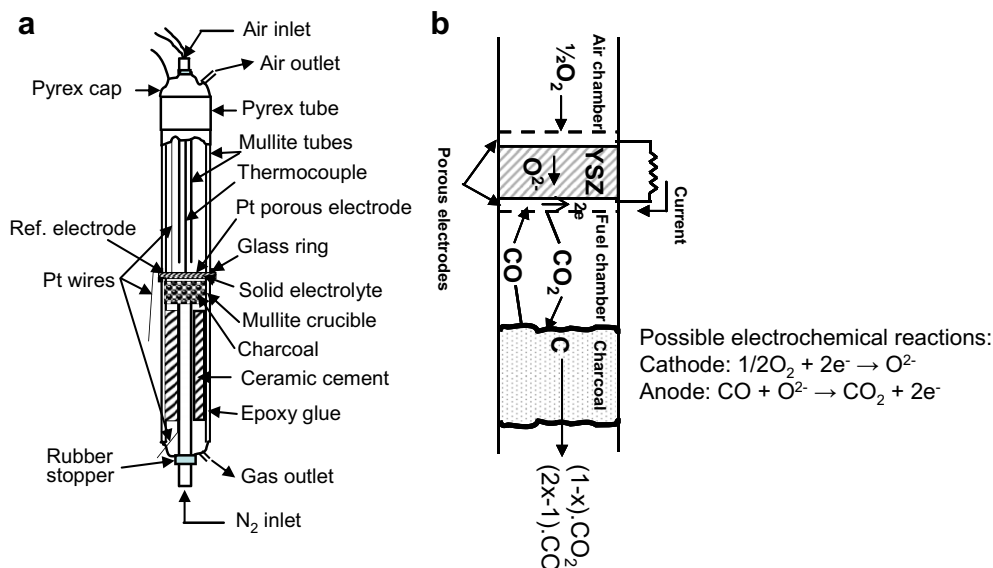
Fig. 21. A schematic view of a button cell apparatus used by Nakagawa and Ishida (a); and a representation of the fuel cell system and reactions occurring in the fuel chamber and at interfaces (b). Figure redrawn based on Reference [195].

are as shown in Fig. 21 and involve the gasification of charcoal to CO in the fuel chamber and its electrochemical reaction with oxygen ions (O^{2-}) at the electrode/electrolyte interface to produce CO_2.

Lee et al. [185,197] investigated the operation of a direct carbon fuel cell using button cells consisting of YSZ disc (0.2–0.3 mm thick) with screen printed LSM (lanthanum strontium manganate) cathode and Ni/ceria anode. The electrodes were 50–100 μm thick with about 40% porosity. Platinum wire mesh was used for current collection from both electrodes. Fuels investigated were synthetic carbon (81%C), bituminous coal (65.7%C) and almond shells (27.2% C), all in the pulverised (20–100 μm) form. The cell was operated at 900 °C in two configurations — fuel inside (placed on top of the Ni/ceria electrode inside the tube), air outside the tube and CO_2 as the fluidising/stirring gas for the fuel; and fuel and fuel electrode outside the tube, air and air electrode inside the tube, and helium as the fluidising/stirring gas for the fuel. In the cell configuration where fuel was fed inside the tube, power densities up to 140 mW/cm^2 and ~10 mW/cm^2 were respectively produced with synthetic carbon and almond shells. In the cell configuration where the fuel and fuel electrode was outside of the tube, the maximum power density produced with bituminous coal was 43 mW/cm^2 as shown in Fig. 22. Under identical fuel cell operating conditions, the power density of 56 mW/cm^2 was obtained with 3% H_2 (balance N_2) fuel. The variations in the performance of the cells in terms of power density can be attributed to different solid fuel characteristics (size, structure, carbon and ash content, etc.), cell configuration and fluidising gas employed in the investigations.

In their findings, Lee et al. [197] postulated that carbon reacts with the stirring gas CO_2 by the reverse Boudouard reaction (reaction (8)). The conversion of carbon to CO and CO_2 was confirmed by the analysis of flue gases by gas chromatography. The equilibrium value of CO/CO_2 ratio in the gas phase at 900 °C is 36, but actual values observed by Lee et al. [197] were lower than this probably due to insufficient contact between the CO_2 and carbon particles. However, there is sufficient CO formed to feed the anodic oxidation reaction (11). This would result in the overall oxidation of carbon to CO_2 (reaction (5)).

The University of Akron has been performing research on direct carbon fuel cells using YSZ electrolyte button cells and solid carbon as the fuel [55,56,198]. Most of the research is focused on anode and

cathode catalysts. Fig. 23 (a) shows the experimental set-up used for these investigations. Anode catalysts were based on nickel, copper and gold, while the cathode catalyst was based on LSM. Generally, raw coal or devolatilised coal was used as the fuel and placed in direct contact with the cell. The cells were operated in the temperature range of 750–850 °C. Power densities achieved over a short duration of few hours were in the range 50–150 mW/cm^2 [55]. It has been claimed that a build up of ash on the anode surface decreases the power density, however, on removal of ash, the power density is restored to previous values. Chuang, from his investigations on Ni composite anode/YSZ electrolyte/LSM composite cathode based button cells operated in the 800–900 °C temperature range, has reported that coal performed better than methane [198]. This is shown in Fig. 23 (b), where the voltage and power density versus current density curves for Ohio Coal no. 5 containing 83.99% carbon (from ultimate analysis) and methane (most likely dry as an entry gas) have been compared, for anode supported cells at 900 °C. In general, the power density trend for various fuels was as follows:
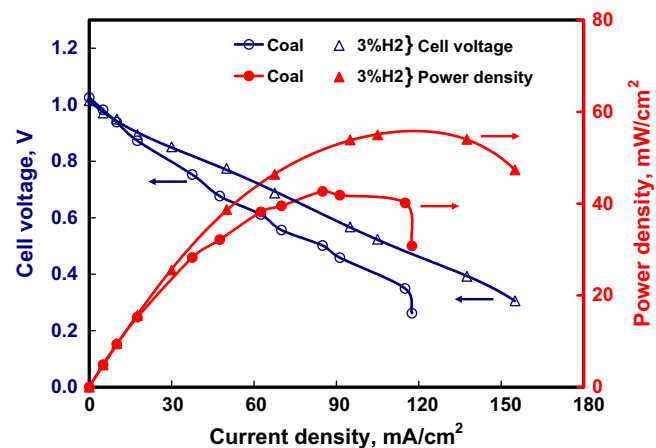

Fig. 22. Voltage − current density and power density − current density characteristics of the cell (Ni/ceria cermet as anode outside the tube facing fluidised bed and LSM as cathode inside the tube) at 900 °C operated on bituminous coal fluidised with helium, and 3% H_2 in N_2. Figure redrawn based on Reference [197].
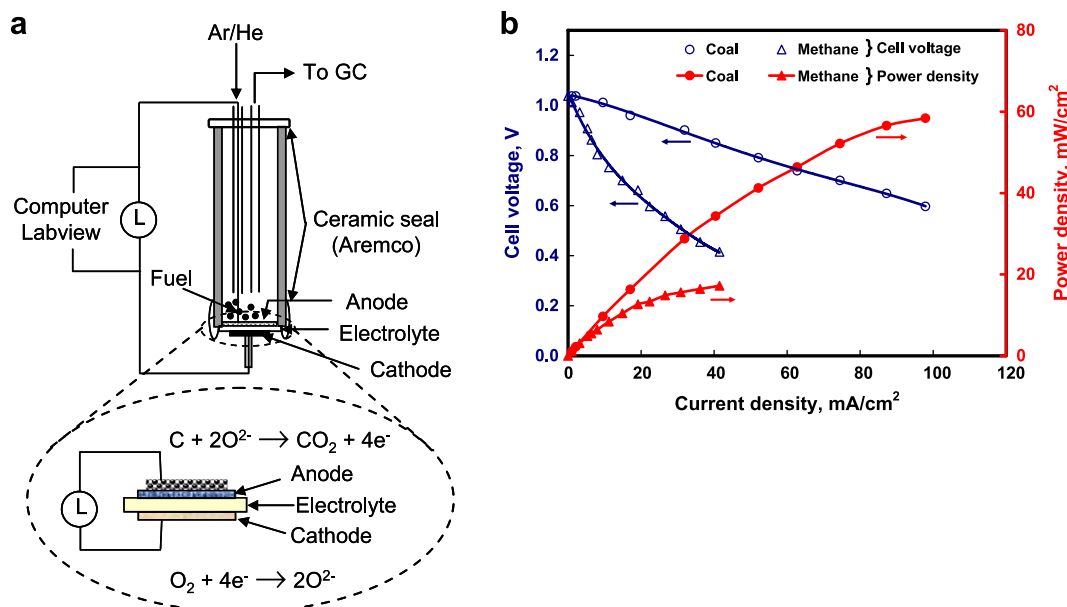
Fig. 23. (a) Experimental set-up employed by Chuang and his group at Akron University for their investigations on DCFC using solid carbon and YSZ electrolyte button cells. (b) Voltage − current density and power density − current density characteristics of the cell at 900 °C obtained with methane and coal as the fuels. Figures redrawn based on Reference [198].

petroleum coke > coal > coal gas > methane [198]. The major challenges reported were the limited oxygen ion diffusion across the electrolyte membrane and long term activity of anode catalyst which obviously degrades with time. Fig. 24 shows an envisioned design by Chuang at Akron University of a coal fuel cell stack for stationary power generation [198].

In addition to button cells, tubular SOFC designs are also being investigated for application in gas bed DCFCs. Recently, Lee et al. reported power densities up to 220 mW/cm^2 at 0. 68 V at 905 °C with anode supported tubular cells (manufactured by MSR Inc., USA) [133]. The cell consisted of a 800 μm thick anode (Ni/YSZ cermet) tube (12.7 mm OD), with a 10 μm thick electrolyte and 100 μm thick lanthanum strontium manganite (LSM) as the air electrode. The fuel was an activated carbon which was placed inside the cermet tube to form a packed bed reactor. The cell operation at 0.32 A/cm^2 delivered a stable voltage for 40 min. For an OCV of 1.1 V, the voltage efficiency of 62% was obtained for cell under load. Fuel utilisation was low at around 50% due mainly to only the partial electrochemical oxidation of carbon to CO. In a similar experiment, Liu et al. performed experiments on a closed end anode supported tube [199]. The cell consisted of a scandia-stabilised (ScSZ) electrolyte, NiO - ScSZ anode and LSM - ScSZ cathode, manufactured via dip coating and co-sintering. They achieved power densities up to

104 mW/cm^2 at 850 °C using commercial carbon black with a particle size between 2 and 10 μm (surface area 0.633 m^2/g) with pure oxygen as the oxidant. The electrochemical characterisation of the cell showed significant mass transport related losses at lower temperature under open circuit conditions as indicated by large low frequency arcs observed in impedance analysis. These arcs were found to reduce when the cell was placed under load at high operating temperatures.

The formation of gaseous species (more specifically CO) in such systems is essential to their operation. This inevitably leads to lower thermodynamic efficiencies and reduced fuel utilisation. However, due to the far greater reactivity and mobility of CO compared to carbon, these systems offer potentially higher power densities than most DCFC designs including those that use molten media for fuel delivery.

3.4.1.1.4. Use of an integrated external gasification. Although systems that use an integrated external (to the fuel cell stack) gasifier cannot be described as a direct carbon fuel cell, these systems do offer some advantage over systems that run on gas derived from coal. The main advantage of an integrated external gasifier and fuel cell system over a fuel cell system that simply operates on gas derived from coal is that the integrated system allows for the more efficient use of waste heat and gas streams which results in higher overall efficiency. The use of an integrated external gasifier also offers advantages over systems where the carbon fuel is directly injected into the anode chamber and include the removal of residual impurities in the fuel external to the fuel cell stack avoiding contamination of fuel cell components, and the fact that existing fuel cell modules developed for gas fed SOFC systems can be directly used with very little modification. As shown in reaction (8), carbon may be gasified to CO via the reverse Boudourad reaction. This CO can be utilized directly as a fuel in conventional solid oxide fuel cell. Gür et al. have reported power densities as high as 450 mW/cm^2 with the tubular SOFC operated on CO generated from an external Boudouard gasifier [119]. The 'Boudouard Gasifier' consisted of a steel chamber maintained at 750 °C fed with CO$_2$ preheated at 750 °C before entering the gasifier. Low sulphur Alaska coal with calorific value of 28. 208 MJ/kg (dry basis) was used as the fuel. An open-ended anode (Ni − YSZ
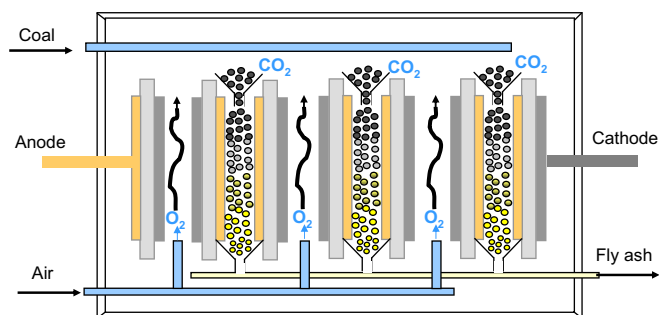

Fig. 24. A proposed design by Chuang at Akron University of a coal fuel cell stack for stationary power generation. Figure redrawn based on Reference [198].

cermet) supported tubular SOFC with thin 8 mol% $Y_2O_3 - ZrO_2$ electrolyte (8–10 μm) and perovskite cathode was used as the cell. Copper and silver meshes were used as current collectors on the anode and cathode side respectively. The highest power density (450 mW/cm^2) was achieved at 0.64 V and 720 mA/cm^2 current density at 850 °C for a fixed flow rate corresponding to 60% CO utilisation (Fig. 25 (a)). However, the electrical conversion efficiency at this power density was only 35.7%. These authors reported a higher electrical efficiency of 48.6% at 0. 7 V cell voltage corresponding to 80% fuel utilisation at 480 mA/cm^2 [119], the peak power density for these operating conditions was lower at 300 mW/cm^2 (Fig. 25 (b)). According to the data presented, the stability of the cell was monitored for over 30 h of operation at a current of 8A. The initial performance degradation of 1.3 mV/h was observed because of changes in the fuel composition but no significant performance degradation was observed due to carbon deposition or sulphur poisoning of the cell. These performances are quite good and on par with the best reported for SOFCs operating under these conditions. It should be noted that the data presented are for single cells and for a real fuel cell power generation system, there will be further stack and system based efficiency losses.

Lee et al. have performed thermodynamic analysis of three carbon fuel gasification systems based on oxygen-ion conducting solid electrolyte based fuel cells [133]. One involved autothermal

Fig. 25. Voltage, Power density and efficiency as a function of current density obtained for a Ni/YSZ cermet supported tubular cell at 850 °C on CO produced by a Boudouard gasifier at 930 °C. These characteristics were obtained at CO flow rates corresponding to 60% CO fuel utilisation (a) and 80% CO fuel utilisation (b). Figures redrawn based on Reference [119].

gasification consisting of a separate gasifier with oxygen input and a solid oxide fuel cell. The second system was similar but gasification step involved a physically separate CO_2 gasifier to give maximum CO/CO_2 ratio with heat being transferred to the gasifier to drive the endothermic reactions. In the third, in-situ or single step DCFC system, carbon fuel is in direct contact with the anode and CO is produced through the reaction of carbon with oxygen ion transported in the solid electrolyte with no separate air separation unit required. The operating temperature for the fuel cell was 900 °C with 20% and 85% air and fuel utilisation respectively and the cell operating voltage of 0.7 V under load.

The thermodynamic analysis of the three systems indicated that for a range of coals, biomass and waste, electric efficiencies above 50% and up to 58% can be achieved for the solid state in-situ gasification driven system. For additional constraints, such as the introduction of an external CO_2 gasification step, efficiencies can be somewhat lower. However, for the autothermal gasification process, efficiencies for fuel cell operation were significantly lower at about 35%. Although there are advantages in terms of exhaust stream consisting mainly of CO_2, for the scenarios offering high efficiency, additional carbon purification steps to remove sulphur and ash material need to be considered to avoid anode degradation and system clogging up over time with residual ash.

Li et al. reported the performance of an anode supported SOFC button cell fed with CO generated by catalysed gasification of carbon black with CO_2 [200]. The cell consisted of a Ni/YSZ anode with an interlayer of Ni/ScSZ, ScSZ electrolyte and LSM/ScSZ cathode. In their experiment carbon black fuel was oxidised to CO in the presence of Ca, Ni and K additives. The ratio of additives to carbon black used was 1:10 wt%. The fuel with additives was placed in a separate tubular chamber and was not in direct contact with the anode. The fuel gasification was performed at temperatures between 700 and 1000 °C and the gas was fed to the anode of the fuel cell operating at 750 °C. Power densities obtained were 147.7, 103.4 and 112.3 mW/cm^2 respectively for K, Ca and Ni additives as gasification catalysts at 0. 7 V and for gasification temperature of 750 °C. These values of power densities were well related to the molar fraction of CO in the gaseous mixture fed to the anode of the cell. It was concluded that the Boudouard gasification temperature can be reduced by up to 200 °C using K catalyst additive without any penalties on the achieved power densities.

Performances of external gasification driven fuel cells are impressive in terms of high power densities, however, the system efficiencies are low. Carbon conversion directly in the anode compartment is likely to lead to significantly higher overall system efficiencies due to the possibility of direct electrochemical oxidation of solid carbon.

3.4.1.2. Technology status. Various cell designs with YSZ as the electrolyte and solid carbon as a fuel in the form of pellets, pulverised carbon or carbon deposited by thermal decomposition of methane, have been investigated. Mostly the cells used were small button or tubular cells. The operating temperature range was 750–1002 °C. For cells where carbon was deposited in-situ by thermal decomposition of hydrocarbons, the power density achieved was ∼55 mW/cm^2 at 900 °C. Such cells were used only for fundamental studies of the carbon oxidation mechanism. For systems, where carbon was placed in close proximity to the anode, the power densities ranged between 40 and 220 mW/cm^2 for temperatures between 800 and 1000 °C [55,133,192]. However, when carbon was placed further away from the anode, power densities were only around 4–5 mW/cm^2 [194,195]. Li et al. by employing internal catalytic Boudouard gasifaction of carbon to CO obtained a power density of 148 mW/cm^2 [200], and Gür et al. obtained power densities of up to 450 mW/cm^2 by employing an
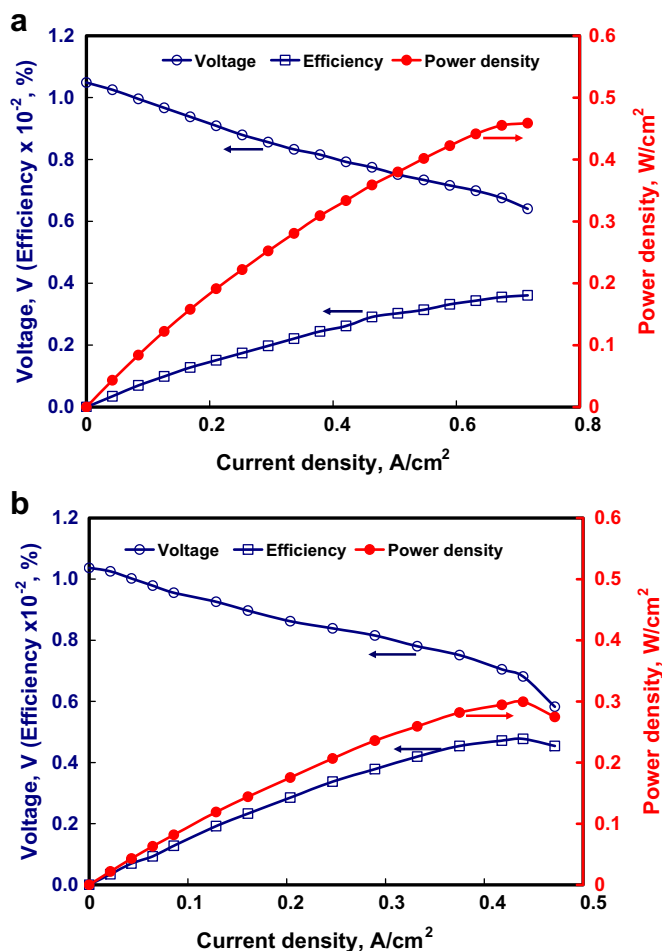
external Boudouard gasifier [119], though the latter may be classified as an integrated coal gasifier/solid oxide fuel cell system.

3.4.1.3. Technical issues. In addition to the technical issues associated with SOFC technology (availability of materials which are stable at high temperatures in fuel cell operating environments, electrode degradation especially that of anode in the presence of impurities such as sulphur, thermal cycling, thermal load management, sealing, etc.), there are a number of other challenges for the development of DCFCs. The effect of sulphur on the Ni based anode performance degradation is well known in solid oxide fuel cells [15]. Gür et al. for a tubular anode (Ni − YSZ cermet) supported SOFC with thin 8 mol% $Y_2O_3 − ZrO_2$ electrolyte (8−10 μm) and perovskite cathode investigated the role of sulphur on the performance degradation of anode by introducing increasing level of H_2S into a 50:50 mixture of CO and CO_2 [119]. They observed that at the cell operating temperature of 850 °C and at 330 mA/cm^2 current density, the cell voltage started decreasing above 4−5ppm level of H_2S and degradation accelerated once the H_2S content increased above 9−10ppm level. Based on these observations, it does appear that the presence of sulphur would be detrimental to the DCFC performance. It should, however, be noted that not much work has been performed on different anode materials and for different fuel feed systems, to establish tolerance limits for S, ash and other mineral matter in carbon derived from coal and biomass sources. The other major technical issues, in the case of DCFC are the solid fuel delivery to the electrode/electrolyte interface such that direct electrochemical oxidation of carbon fuel becomes possible, fuel processing requirements to produce low cost fuel, technology up-scaling and thermal and mechanical stresses. Understanding the fundamental mechanisms of carbon oxidation and their dependency on various cell designs and operating parameters is also crucial for its differentiation from the conventional SOFC technology. The limited oxygen ion diffusion through the electrolyte membrane, especially if the DCFCs are operated below 700 °C, the long term stability of the anode catalyst and kinetic performance of both anode and cathode materials are also of concern. So far no group has developed a working fuel cell stack that generates power solely from the direct electrochemical oxidation of carbon or high carbon fuels.

3.4.1.4. Technology outlook. Clean Coal Energy (or Direct Carbon Technology) and Akron University have separately proposed concept designs for large scale fuel cell stacks. However, the technology would need to be first consolidated at a single cell level [53,198]. Akron University's future R & D plan is to optimise the anode catalyst and electrolyte composition, develop fuel cell assemblies and designs that can operate at high temperatures (600−800 °C) and then to concentrate on the fabrication of stacks and accessories for coal loading and ash removal. A design of a coal fuel cell stack for stationary power generation has been proposed by Chuang of Akron University (Fig. 24).

Clean Coal Energy (CCE) has been developing the DCFC technology based on US patent 5, 376, 469 held by Stanford University and license granted to CCE [53,196]. A schematic drawing of the fuel cell concept envisioned by CCE is shown in Fig. 26 [53]. The technology previously based on solid carbon feed through fluidised bed type arrangement offered advantages such as easy fuel feed and easier separation of heavier ash component from carbon, but faced cell design challenges such as two dimensional configuration of solid fuel/solid electrolyte resulting in very small number of reactive sites and maintaining an effective electrical contact between the anode and the solid fuel particles [52]. However, more recently, higher power densities have been achieved in arrangements where either the solid fuel was placed in direct contact with the anode (on
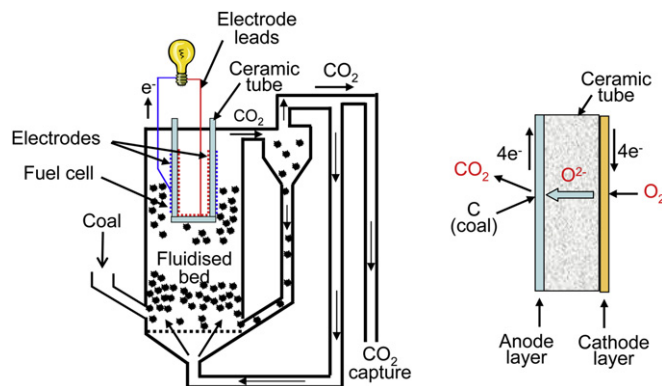

Fig. 26. A design proposed by CCE of a direct carbon fuel cell based on SOFC and fluidised bed technologies. Figure redrawn based on Reference [53].

top of button cell anode or packed inside a tubular cell) or through Boudouard gasification and not by fluidised bed type arrangement [55,119,185,197−200].

3.4.2. Fuel in molten metal

Molten metals have been tested as fuel cell electrodes on many occasions in early solid oxide fuel cells [109,201]. These metals can be inert (such as silver) which transport ionic species to and from the electrolyte in solution or reactive (such as tin or iron) which oxidise at the electrode surface and are then reduced by the fuel. It is the latter system that has been of most interest to the direct carbon fuel cell community as it offers the potential to rapidly shuttle oxygen from the electrolyte to a solid carbon fuel. One of the earliest systems was proposed by Yentekakis et al. who carried out a theoretical study investigating the feasibility of a hybrid system that could be used either as a coal gasifier or DCFC with molten metal anode [202]. In their work they analysed the steady state model for DCFC with a zirconia based electrolyte and iron as the liquid anode with carbon as the fuel. It was proposed that oxygen could be fed to either the cathode side of the electrolyte (as in a conventional fuel cell) or to the anode side to directly oxidise carbon in the molten bath to create CO, thereby combining the advantages of coal gasification with a high temperature fuel cell. No actual experimentation was reported, but as one would expect, the outcome of the theoretical analysis showed an increase in power density and current with temperature. More recently CellTech Power has lodged patents covering tin and many other metals [203,204] for use as a molten anode. Clean Coal Energy has also filed a patent based on molten metal (silver, bismuth) bath containing carbon as the anode [205].

3.4.2.1. Systems investigated. Although a number of other metals have been investigated for use in electrochemical cells, tin is the most studied system so far [206−213]. Tin has a low melting point (232 °C), and the boiling point of 2270 °C [142] is far in excess of the operating temperature of a fuel cell, making it suitable for use as a liquid anode. The chemical reaction of tin with oxygen is exothermic as given by the following reaction:

$$Sn(1) + O_2(g) = SnO_2. \qquad (32)$$

In the electrochemical cell based on a solid oxide electrolyte such as YSZ with a liquid tin anode, oxygen ions are transported through the electrolyte where they react with the tin to form tin oxide as per the following reaction:

$$Sn(1) + 2O^{2-} = SnO_2 + 4e^-. \qquad (33)$$

Based on the free energy of the reaction the OCV ($E_{OCV} = \Delta G$ [J/mol]/4F) of the cell would be 0.805 V with pure oxygen as the oxidant at the cathode (0.78 V for air). The tin oxide thus formed can be converted back to tin by chemical reaction between tin oxide and any fuel such as solid carbon, H_2 or CO. It is worth mentioning that the chemical reaction of tin oxide with any of these fuels under standard conditions, and at 1000 °C is exothermic as shown by the negative free energy values. Therefore, in a SOFC cell with molten tin as the anode in contact with carbon fuels, electricity is produced by direct oxidation of carbon.

Fig. 27 shows the basic operating principle of CellTech's liquid tin anode based direct carbon fuel cell. According to CellTech, this type of device can act as a primary or secondary battery or a fuel cell [214]. As with a battery, the CellTech cell can operate for significant amounts of time with no fuel being added to the system. Although literature reports the use of molten metals such as Sb, Pb, In, Sn and Bi in high temperature batteries, however, complete oxidation of the liquid metal does not occur due to the formation of an insulating oxide layer between the electrolyte and the remaining liquid metal [212,213], the exception being bismuth metal. This is most likely due to the high ionic conductivity of bismuth oxide [212,213]. The low oxidation potential of bismuth makes it unlikely that a liquid bismuth anode would be of practical use in either a fuel cell or a battery [212,213].

When compared to conventional SOFC anodes such as Ni/YSZ, liquid anodes appear to be much more resistant to coking and poisoning. In a conventional gas fed fuel cell, under certain conditions, carbon can be deposited from carbon containing fuel streams (CO, CO_2, CH_4) on to the anode. This causes rapid anode degradation due to physical damage to the microstructure of the anode (cracking) [215]. This becomes more of an issue when heavy fuels are used due to the fact that there is a higher carbon to hydrogen ratio within these materials. Within a liquid anode there are no hard surfaces for the carbon to deposit and no defined microstructure to block or crack thus eliminating this issue. In addition to carbon deposition, there are also a number for fuel impurities that can cause deactivation of a conventional anode [215]. The most damaging of which is sulphur which is used as an odourant in

pipeline gas [216]. The presence of sulphur in the fuel leads to rapid degradation of the anode due to the formation of nickel sulphide compounds (in the case of Ni/YSZ anodes) or cerium sulphide compounds (in the case of Cu/ceria anodes) [215]. Liquid tin anodes, however, have been operated on high sulphur fuels with little degradation [217], with such impurities being oxidised in the same way as the fuel [209,210,218]. CellTech have performed many tests with fuels such as JP-8 (liquid fuel) containing up to 1350ppm of sulphur and have not observed any significant degradation in the cell performance for periods of up to 200 h as shown in Fig. 28 (a). Sulphur in the molten tin oxidises to SO_2 and is vented into the anode exhaust [209,210,218].

CellTech have mainly used a tubular cell design for their single cells and stacks as shown in Fig. 28 (b) & (c). The cells were operated at 1000 °C with air as the oxidant at the cathode. In the case of a stack, a number of tubular cells share a common anode chamber. A porous ceramic separator is used to separate the tin melt from the fuel and helps in retaining a thin layer (few hundred microns thick) of tin melt in contact with the electrolyte. The separator allows the diffusion of the molecules of fuel (hydrocarbons, CO, H_2) into the tin and back diffusion of products formed (H_2O, CO_2, etc.) [217]. The main fuel tested was a liquid fuel, JP-8. The use of a porous separator in recent designs has the advantage of controlling the anode thickness and stopping liquid tin from migrating to areas of the cell where it is not required causing potentially short circuits, however, this would imply that the carbon based fuel cannot react directly with the anode having to first form a gaseous species that then diffuse through the porous separator to the anode. This will inevitably, as with other gas fed fuel cells result in a reduced fuel utilisation and a drop in system efficiency. CellTech have reported

Fig. 28. (a) Voltage, current and fuel efficiency as a function of time obtained from a single LTA-SOFC at 1000 °C, operated on JP-8 fuel containing 1350ppm sulphur, showing a stable performance up to 200 h of operation. (b) CellTech LTA-SOFC schematic of a single cell set-up. Figures (a) and (b) redrawn based on Reference [217]. (c) CAD drawing of a multi-cell stack for direct fuel conversion. Figure reproduced from Reference [217] with permission of the publisher.

Fig. 27. A schematic of the basic operating principle of an LTA-SOFC.

comparatively low efficiencies for their cells, about 32% for operation on JP-8. CellTech has suggested that their system would be approximately 60% efficient on a pure carbon fuel [209]. It is unclear if the reduced system efficiency is related to fuel utilisation or other factors. CellTech's main drive, however, seems to be to deliver a robust system that operates on a range of real world fuels for military applications and not to develop a highly efficient system. In this respect their system appears to be more advanced than many others currently under development with CellTech demonstrating small systems operating for 200 h on JP-8 [209].

Recently, Jayakumar et al. evaluated performance of Sb, Pb, In, Sn and Bi as molten anodes for SOFCs [212,213]. A YSZ wafer was prepared by co-sintering two laminated green tapes at 1500 °C – one pure YSZ and the other tape containing graphite as a pore former. The obtained porous YSZ side was impregnated with nitrate salts of La, Sr and Fe followed by calcination at 850 °C to produce an air electrode composite of 40 wt% $LaSrFeO_3$ (lanthanum strontium ferrite) - YSZ. A ceramic bar of lanthanum strontium titanate (LST) or chromite (LSCr) was used as the anode current collector. The cells were tested in "battery mode", i. e. the molten metal oxides of corresponding metal were reduced with H_2 and then the anode gas was switched to He. The electrochemical driving force was the oxidation of metal oxide by oxygen ions from the electrolyte. The OCVs of the cells matched well with thermodynamical data for the metal oxide formation reactions. After the oxidation reaction is complete the cells can be recharged by reduction with H_2. The thermodynamic oxidation potential and tendency of molten metal to form an oxide layer at the interface are decisive factors in the performance of these types of cell. The increase in polarisation losses during operation has been attributed to the formation of insulating oxide layers of Sn, Pb and In at the electrolyte surface. The polarisation losses in case of Bi were very low, most likely, because of high oxygen ion conductivity of Bi_2O_3. The main issue with Bi molten anodes is low open circuit voltage owing to lower free energy for the Bi oxidation reaction. According to the data presented by authors, Sb delivered the maximum power density of 26 mW/cm^2 at 973K [212]. The lower Nernst potential and diffusion of molten metal through the ceramic seals could be the issues for the practical operation. Although H_2 is used as a reducing agent in these studies, carbon can also be used as a fuel in these cells, to chemically reduce metal oxides formed in the electrochemical process at the molten metal anode/electrolyte interface.

3.4.2.2. Technical issues. The major technical hurdle reported by CellTech is the excessive anodic polarisation losses due to the design where a porous ceramic separator was used for separating the molten tin melt at the anode from the fuel [207,217]. The porous structure is required to allow only the gaseous fuel species to diffuse through the separator but prevent molten tin to flow through the pores. The introduction of a fuel such as JP-8 into the molten tin melt causes its pyrolysis resulting in the formation of gaseous components that have molecular weight 1-2 orders of magnitude higher than hydrogen. The diffusion of these gaseous components through the porous separator is much slower (3–10 times slower) than that for hydrogen, which results in high anodic polarisation.

3.4.2.3. Technology status. The use of a high porosity separator (70%) in the cell has been quoted to double the power densities achievable from tubular Liquid Tin Anode (LTA)–SOFC. The power densities achieved so far are 160 mW/cm^2 and 80 mW/cm^2 respectively from hydrogen and JP-8. Further improvements are possible by modifying the anode architecture, cell configuration and fuel side characteristics. Stand-alone kilowatt class prototypes of LTA-SOFC systems using hydrogen and natural gas were

demonstrated in 2004. CellTech has been developing LTA-SOFC systems with support from DARPA (US Defence Advanced Research Projects Agency) that can use waste plastics and military logistic fuels such as JP-8 [207,209,210,218]. Recently the cell has also been evaluated using biomass and coal as fuels. The company has demonstrated a Generation - 3 cell operating on JP-8 for 200 h with over 30% efficiency [210,217,218]. The technology has been demonstrated in single cells as well as in stacks with similar performances.

3.4.2.4. Technology outlook. CellTech is working with DARPA and the US Army to develop a field battery charger (portable power 20–100 W) that operates on JP-8, diesel and most other common fuels. The Company is also looking at other applications of LTA-SOFC technology including auxiliary (1–10 kW) and utility power (100 kW to >1 MW). CellTech has built and tested cells, small stacks and systems for tens to hundreds of hours. The Company has achieved an efficiency of just over 30% on JP-8 fuel and is projecting that with the carbon fuel and liquid tin anode the efficiency would increase to 60%.

3.4.3. Fuel in molten carbonate

This technology combines a solid oxide fuel cell with a molten carbonate fuel cell and is one of the most recent design concepts under development. Although there are some variations in the design proposed by different authors [135,219–221], essentially this type of system consists of a solid oxide fuel cell in which the anode has been flooded with a slurry of molten carbonate and carbon fuel. Balachov et al. at the SRI International in May 2005 had filed US and PCT patents on this technology [220]. Fig. 29 depicts the basic principle of the technology.

The anticipated mechanism of carbon oxidation in this arrangement has been proposed by Jain et al. as described below [222]. The carbon in the molten carbonate melt not only electrochemically oxidises to CO and CO_2 at the interface, but also reacts electrochemically with carbonate ions (CO_3^{2-}) as follows:

$$C + 2CO_3^{2-} = 3CO_2 + 4e^- \tag{34}$$

$$C + CO_3^{2-} = CO + CO_2 + 2e^-. \tag{35}$$

These reactions are followed by the regeneration of carbonate ions at the electrolyte interface by the following reaction to keep the molten carbonate electrically neutral:

$$CO_2 + O^{2-} = CO_3^{2-}. \tag{36}$$

As in other systems, the carbon can also be converted to CO chemically by the reverse Boudouard reaction and it can oxidise electrochemically at the anode/electrolyte interface to form CO_2.

This type of fuel cell system avoids the need for CO_2 circulation (as is the case with molten carbonate fuel cells) and protects the cathode from molten carbonate, allowing the use of advanced cathode compositions already developed for SOFCs [135,219,222,223]. It also avoids cathode flooding and corrosion issues associated with the closely related molten carbonate direct carbon fuel cell.

3.4.3.1. Systems investigated. Fig. 30 shows a schematic drawing of a single cell DCFC construction proposed by Balachov et al. from SRI International [221]. The cell employs a cathode supported tubular cell geometry. Air is supplied via a concentric tube to the cathode consisting of metal mesh or coil as a current collector and lanthanum strontium manganate (LSM) as the catalyst layer. The electrolyte is yttria-stabilised zirconia (YSZ). The circulating molten
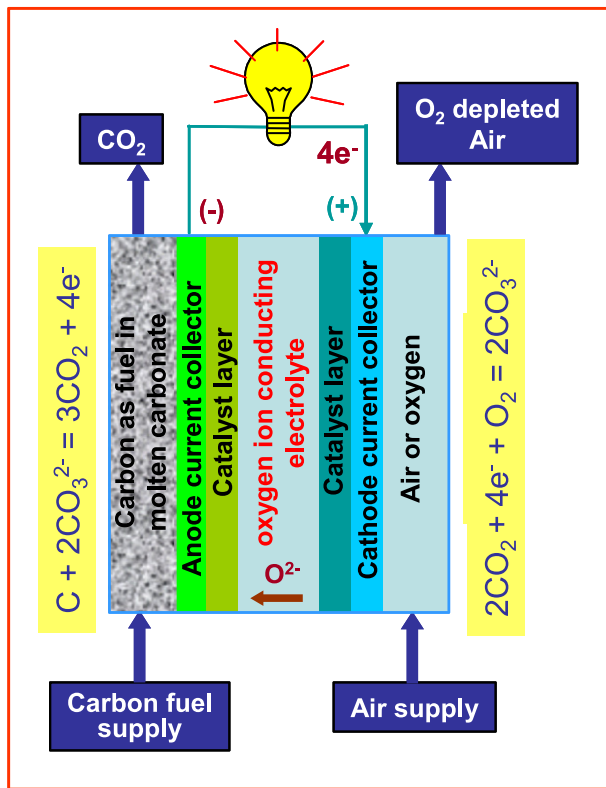
Fig. 29. A schematic of the basic operating principle of a DCFC based on carbon fuel mixed with molten salt on the anode side and oxygen ion conducting electrolyte.

Fig. 31. Peak power densities achieved using the cell design in Fig. 30 and performance with different types of fuels as a function of temperature. Figure redrawn based on Reference [221].

SRI International had been quite active for this type of technology and has tested solid carbon fuels mixed with salt powders [224]. It has been reported that power densities of approximately 300 mW/cm^2 have been obtained, and a lifetime of more than 1200 h has been demonstrated [55]. Fig. 32 shows an SRI multiple tubular DCFC stack (eight YSZ electrolyte tubes inserted into a common anode chamber containing carbon fuel in molten salt) prototype.

St. Andrews University is also working on a similar concept [219,223,225]. Both tubular geometry (Fig. 33) as well as button cells (Fig. 34) have been used in their investigations. The tubular cell utilises platinum paste applied to the inside of YSZ tube as the cathode and nickel mesh as the anode [219]. The YSZ tube is immersed in carbon black mixed with molten carbonate (lithium/potassium carbonate eutectic mixture) bath held in a nickel container. The total power produced with this arrangement at 700 °C was 10 mW, and the cell produced an area specific resistance of around 17 Ω cm^2. This is significantly higher than that observed with SOFCs operated with gaseous fuels such as CO and H$_2$ (typically below 1 Ωcm^2). The major materials issues reported are the corrosion of the nickel anode and the stability of YSZ in molten

salt mixed with fuel particles (more than 30% by volume) is supplied to the anode side of the electrolyte which has an anode current collector. The anode current collector is a corrosion resistant metal/alloy coil or a mesh.

Balachov et al. have achieved power densities of up to 120 mW/cm^2 using acetylene black as the fuel [221]. The operating performance of this design was also tested on real fuels such as biomass, coal, tar and mixed plastic waste. Power densities achieved with these fuels were 70, 110, 80 and 40 mW/cm^2 respectively (Fig. 31).
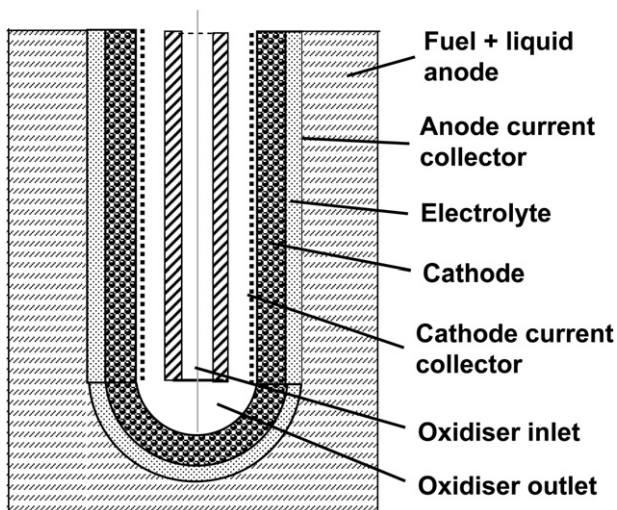

Fig. 30. A schematic drawing of a single cell DCFC based on a cathode supported tubular cell with fuel in molten salt as the anode and YSZ as the electrolyte. Figure redrawn based on Reference [221].
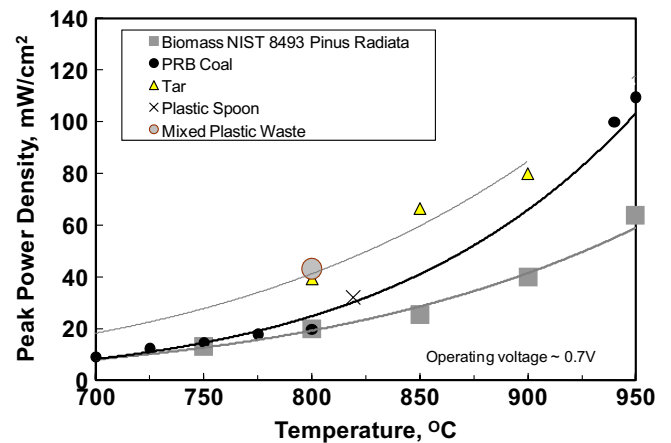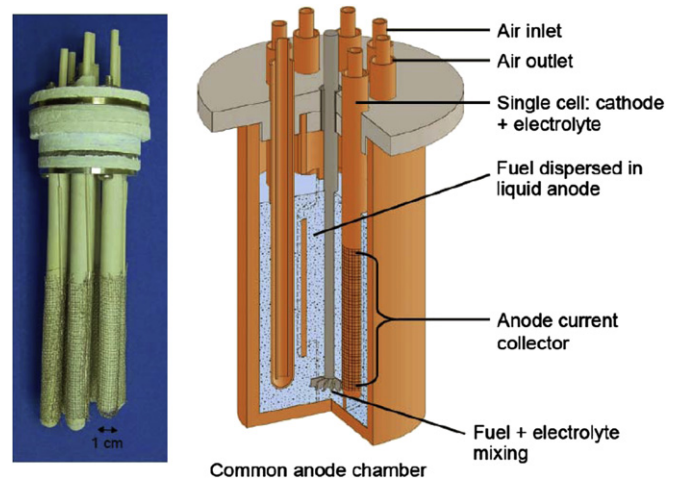

Fig. 32. Cutaway drawing of an SRI designed eight cell stack with eight YSZ electrolyte tubes inserted into a common anode (carbon fuel in molten salt) chamber. Figure reproduced from Reference [55] with permission of the publisher.
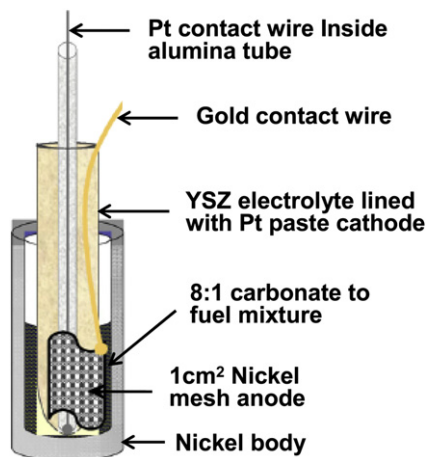
Fig. 33. A schematic of a tubular cell used by St. Andrews University for their DCFC investigations. Figure reproduced from Reference [219] with permission of the publisher.

carbonate. The latter is due to the formation of lithium zirconate in the presence of Li/K carbonate eutectic mixture at 700 °C. Preliminary studies have shown that sodium (instead of lithium) compositions to be significantly less reactive and that ceria appears less reactive than zirconia based materials [219].

The button cells use a NiO – YSZ anode, YSZ electrolyte and LSM – YSZ cathode. The cathode consisted of 2–3 layers [135]. The layer adjacent to the electrolyte has 50 wt% LSM mixed with YSZ and the farthest layer has 100% LSM and is used for current collection. The molten carbonate has composition of 62 mol% Li_2CO_3 and 38 mol% K_2CO_3 forming a eutectic carbonate mixture. Two types of carbon namely Super-S (surface area (SA) 45 m^2/g) and XC-72R (SA 250 m^2/g) dispersed in the molten carbonate (1:1 mol) were investigated as the fuel. The cells were operated between 550 and 900 °C. The lowest values of area specific resistance calculated from the voltage – current curves obtained for Super-S carbon fuel were approximately 23 Ωcm^2 at 900 °C and 98 Ωcm^2 at 700 °C. The peak power densities obtained for Super-S carbon were 13 mW/cm^2 at 900 °C and 3.6 mW/cm^2 at 700 °C, and for XC-72R carbon were 12.6 mW/cm^2 at 900 °C and 6.4 mW/cm^2 at 700 °C. Electrochemical impedance measurements on cells confirmed that the low cell performance can be attributed to the high anodic polarisation losses caused possibly by low reactivity of the carbon fuel. The polarisation resistance due to LSM cathode was determined separately using symmetrical cells and was found to be only 0.07 Ω cm^2 at 900 °C and 1.06 Ω cm^2 at 700 °C. The open circuit voltage from the button cells was reported to be 1.24 V at 900 °C which is high, indicating the incomplete oxidation of carbon to CO [135]. The influence of temperature on the OCV was studied which suggested that the electrochemical oxidation of carbon to CO was the dominant reaction occurring within the anode chamber [135].

As with most DCFC designs, the formation of CO at high temperature is an issue. One strategy that has been adopted to try and eliminate CO formation via the reverse Boudouard reaction is to reduce the operating temperature of the cell. This has lead a number of researchers to trial a wide range of cell concepts and designs that may offer lower temperature operation. Zhu et al. have examined ceria–molten carbonate electrolytes for use within SOFCs. According to these authors, the composites demonstrate enhanced ionic conductivity possibly via a synergistic multi-ion conduction mechanism [226]. Jia et al. have built on these initial studies and have reported results from a cell with a composite samarium doped ceria (SDC)/molten carbonate (Li/Na eutectic) electrolyte which the operated on solid carbon [227]. A mixture of molten carbonate and carbon was fed to the anode chamber and a mixture of CO_2 and O_2 as a cathode gas. They obtained a power density of 100 mW/cm^2 at 700 °C. The significantly higher ionic conductivity for ceria molten carbonate composite electrolyte was not reflected in the DCFC performance due to higher anodic over-potentials possibly caused by oxygen dissolution within the molten carbonate. Although 100 mW/cm^2 is significantly less than gas fed solid oxide fuel cells this is of similar magnitude to other DCFC designs and gas fed molten carbonate systems [180,228].

3.4.3.2. Technology status. This technology provides a simple way of feeding carbon directly to the electrolyte surface by using molten carbonate as the media. This also allows for a simple design of the anode current collector. The power densities achieved from single cells have been as high as 120 and 110 mW/cm^2 respectively from acetylene black and coal as fuels [221]. The technology has been tested on other fuels such as biomass, tar and mixed plastics, producing reasonable power densities (40–70 mW/cm^2). It has been reported in literature that SRI has been able to achieve power densities of up to 300 mW/cm^2 [55]. Further, lifetimes of more than 1200 h have been demonstrated, but no data has been provided on the degradation rates [55]. A 6-cell stack with six YSZ electrolyte tubes/electrodes in a single molten carbonate bath containing carbon fuel has been built by SRI. Power densities from the stack averaged at 83 mW/cm^2 (minimum 38 mW/cm^2 and maximum 110 mW/cm^2) at 940 °C [52].

3.4.3.3. Technical issues. The major materials related issues are similar to those for MCFC and SOFC technologies. However, specific materials issues related to this technology as experienced by investigators are the corrosion of nickel anode and stability of YSZ electrolyte in molten carbonate, with the formation of lithium zirconate and other lithium based compounds in the presence of Li/K carbonate eutectic mixture being observed within 24 h [135]. Other technical issues reported on this technology are low power densities, very short lifetime, slow electrode kinetics, circulation of the melt for continuous delivery of the fuel to the anode and scale-up [52,53,55,219,221].

3.4.3.4. Technology outlook. SRI International has made significant advances in this technology area including the development of small stacks and the operation of the fuel cells on a number of
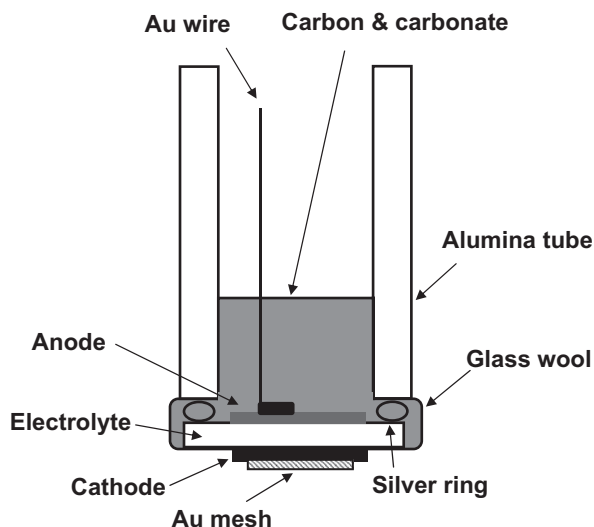

Fig. 34. A schematic diagrams of the test button cell used by St. Andrews University in their DCFC investigations. Figure redrawn based on Reference [222].

commercially available fuels [221,224]. Despite the advances made there is currently no ongoing program developing this technology at SRI international although they continue to monitor the area and are actively seeking partners for future developments. St. Andrews University continues to investigate the fundamental science underpinning this technology and is investigating alternative solid oxide electrolytes for better ionic conductivity and stability of molten carbonates, developing anode materials and optimising cell design for higher power densities. Their work is at an early stage although it does involve partners who would be interested in the development of a device for military applications [219]. Most of the early work is directed at batch type cell and stack testing. The design and operation of a continuously fuel fed operating stack has not been demonstrated thus far.

3.5. Fuels for DCFC

A DCFC utilises solid carbon as a fuel, the structural and chemical characteristics of which play a vital role in performance of the fuel cell. In particular when coal is used as the fuel, its characteristics and properties can vary greatly depending on the source and pre-treatment. Direct carbon fuel cells have been operated on a wide range of fuels including coal [58,161,179,197,221], liquid hydrocarbon fuels [209,210], biomass [208] and organic waste [229]. Some of these fuels have been used directly within the fuel cell with very little pre-treatment [197,209,210] whilst others have been heavily processed and purified to produce a fuel that is almost pure carbon [57,154,174,182,193,229].

Although the detailed mechanism of carbon electrochemical oxidation is not fully understood in most DCFC designs, there is a general agreement in the research community that the characteristics of a fuel such as crystal structure (degree of graphitisation), particle size and impurity content play an important role in the DCFC performance. Since the oxidation mechanism varies from one type of DCFC system to the other, the degree of the effect of the particular property of carbon on DCFC performance, is subject to the type of DCFC. For example, the electrical conductivity is of significant importance when carbon is used as a fuel and a current collector (anode) but may not play a significant role in gasification driven systems.

Carbon exists in several allotropic forms, the chemical and physical properties of which can vary greatly. The thermal oxidation of carbon has been studied over decades to understand the correlation between crystal structure and oxidation reaction mechanism. It is evident from classical studies that the oxygen reactivity in graphitic or partially graphitic carbons is highly anisotropic [190,230,231]. The carbon oxidation rate was found to be significantly faster at crystal edges as compared to the basal planes by Kinoshita [190]. The author has reported that for the oxidation of oriented pyrolytic carbon, the reaction rate is directly proportional to edge area and independent of basal plane area. Recent studies, however, have indicated that basal planes may not be completely inert with respect of oxidation reactions [230,231]. Besides crystallographic anisotropy, the rate of carbon oxidation is also affected by structural defects, dislocations, lattice vacancies and grain boundaries and as expected, highly disordered structures, such as amorphous carbon have much higher oxidation rates than highly ordered structures [190,230,231].

Work on electrochemical oxidation of carbon is less developed. For electrochemical applications such as Li-ion batteries and electrolytic capacitors it has been well established that the crystal structure of carbon has a profound effect on its electrochemical properties. The crystallite size and lattice spacing are considered useful parameters for electrode characterisation in these applications. Furthermore, it has also been demonstrated (as within classic

combustion studies) that the electrochemical reactivity of carbon differs significantly at the edge of basal planes when compared to the centre of these closely packed planes. Studies of the reactivity of carbon in molten salts have also shown that these factors play a critical role in DCFCs. The effect of these parameters on DCFC performance has been demonstrated in various molten carbonate direct carbon fuel cells via a number of studies that correlate the crystal structure of carbon to its electrochemical reactivity [58,190,232,233]. In general, structures with a greater degree of crystal disorder have higher electrochemical reactivity due to the greater availability of reaction sites. The electrochemical oxidation of carbon in non-carbonate melts, such as molten metals, is not as well studied but it is expected that similar trends will be observed.

In the late 1980s, Vutetakis et al. studied the electrochemical oxidation of different types of carbon (source) fuels in molten carbonate slurries using gold electrodes in the presence of CO_2 (Fig. 35) [232]. Carbon fuels such as bituminous (black coal) and lignite coals (brown coal) were dispersed in a Li/K carbonate eutectic and I−V measurements were carried out at 700 °C. It was found that observed trends in chemical reactivity generally correlated well with trends in electrochemical reactivity. Black coal delivered the highest current densities among all the types of fuels examined and carbon with diamond structure delivered the lowest power as expected [232]. It was also observed that the direct chemical consumption of carbon by CO_2 results in low carbon utilisation efficiencies. More recently, Cherepy et al. have studied performance of various types of fuels in MCFC and correlated the performance with crystallinity data obtained from X-ray diffraction [58]. They determined the degree of crystallinity by measurement
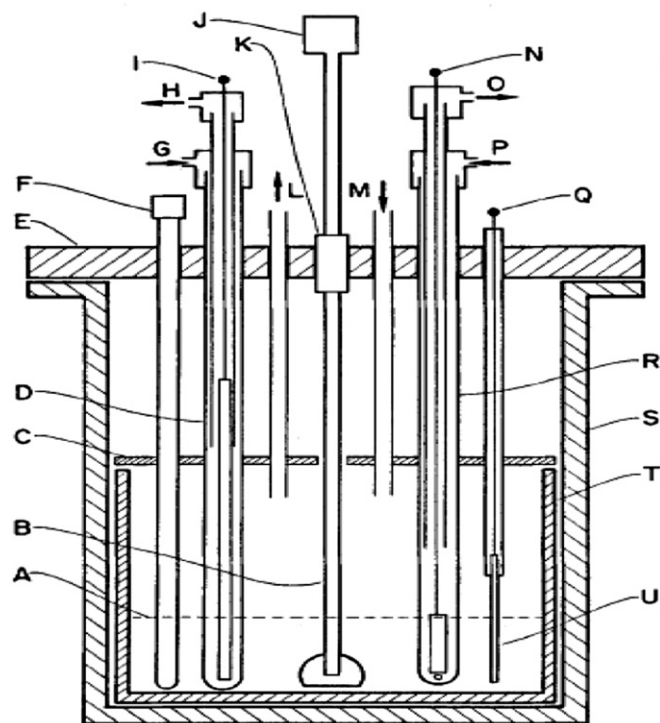
Fig. 35. Experimental set-up used by Vutetakis et al. for electrochemical oxidation of carbons of various types in molten carbonate electrolyte. Figure reproduced from Reference [232] with permission of the publisher. A: melt level; B: alumina stirring shaft; C: crucible cover; D: counter electrode assembly; E: water cooled lid; F: thermocouple; G: CE purge inlet; H: CE purge outlet; I: CE terminal; J: stirring motor; K: water cooled rotary seal; L: cell purge outlet; M: cell purge inlet; N: RE terminal; O: RE purge outlet; P: RE purge inlet; Q: WE terminal; R: RE assembly; inconel canister; T: alumina crucible; U: gold WE.

of lattice parameters and d-spacing in various carbons and ranked carbon fuels according to the degree of crystallanity or 'crystallization index'. Fig. 36 shows the graphical representation of the data obtained by Cherepy et al. Highest current densities were obtained with 'amorphous' peach pit coke as a fuel which has the highest crystallisation index. The unusually high performance of graphite in this study was attributed to its superior electrical conductivity which resulted in lower ohmic losses within the cell. This artificially inflated the performance of the cell when operated on this fuel. The chemical activation energy of a carbon fuel can be calculated from I−V data obtained at different temperatures as suggested by Vutetakis et al. [232]. Using the experimental set-up similar to as shown in Fig. 35, Li et al. calculated the chemical activation energy of various carbon fuels in molten carbonate slurries [167]. The chemical activation energy for granular activated carbon, carbon black and graphite was calculated. As expected, the data indicates that activation energy is a function of crystallinity with graphite giving the highest activation energy of 183 kJ/mol and the non-crystalline activated carbon having only 48 kJ/mol. It is noteworthy that the chemical activation energy is a global parameter and is a function of a number of processes and not crystallinity alone [167].

Similar to the observations in molten media, the effect of carbon crystal structure is also seen in solid oxide electrolyte type DCFC, where the less graphitic carbon black delivers significantly enhanced power density as compared to well ordered graphite [193]. More comprehensive studies are required to quantify these observations, although they are in broad agreement with classical combustion studies described above in this section.

In addition to the crystal structure, electrical properties of the fuel such as ohmic resistance and double layer capacitance may have a large impact on the performance of a DCFC, especially, when the fuel is used as a consumable anode. Using a molten hydroxide fuel cell, similar in design to those developed by SARA Inc. (Fig. 9), Hackett et al. reported that the graphitic anode performs better than coal derived anodes because of the higher electrical conductivity of the graphite [154]. They achieved power density up to 84 mW/cm^2 with a graphite rod (ASR = 2 Ωcm^2) while coal based rod delivered 33 mW/cm^2 (ASR = 6 Ωcm^2) at 675 $^\circ$C. This improvement suggests that the overall reactivity of the fuel is less critical than the conductivity of the anode in this design. Thus, if a design is chosen where the electrical conductivity of the fuel is important, the overall system performance may be a trade-off between the material reactivity and its electrical conductivity.
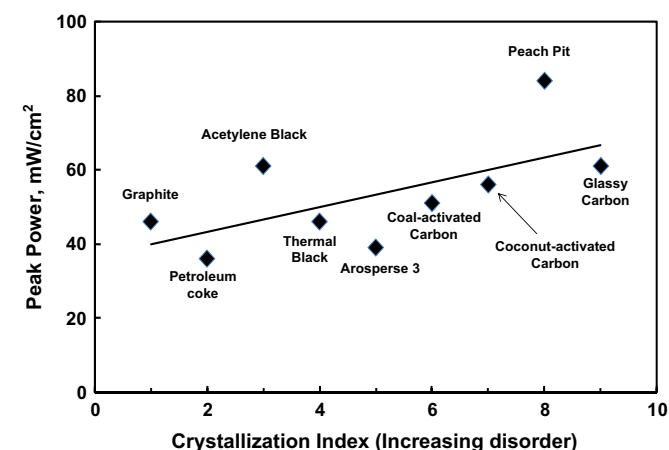
Other physical properties such as particle size, surface area and texture are thought to have a significant impact on DCFC performance, although results reported in the literature are often somewhat contradictory. Data obtained by Vutetakis et al. showed a 60% increase in current density when carbon particle size was decreased from 20 to 40 mesh to 200−325 mesh (tested in stirred bath of molten carbonate [232]), while Cherepy et al. reported no significant cumulative impact of particle size, surface area and micro-morphology on current discharge for particulate carbon samples obtained from different sources [58]. Although the effect of the specific surface area is reported to be insignificant in some reports, in recent work, Li et al. reported that the power density increased linearly with mesoporous surface area, while it was relatively insensitive to mircroporous surface area, perhaps because of only partial access of carbonate melt to the mircopores [173]. In order to fully understand the effects of the physical dimensions on the reactivity of carbon fuels, a more extensive systematic study trialling a variety of carbon materials with different crystal structures and surface areas would be required for a given system design.

The wettability of carbon by molten carbonate is another factor which determines the DCFC performance. It is well known from wetting angle studies that in carbon-water systems, the degree of wetting varies greatly for different types of carbon. For carbon-molten media DCFCs, Chen et al. reported a 30% enhancement in power density when the carbon anode was pre-soaked in a carbonate melt for few hours before operation [233]. The better performance was attributed to improved wetting of the carbon providing enhanced reaction interface. Recently, Cooper and Selman have reported a gradual change in OCV in MC-DCFC as the graphite anode is wetted by the carbonate melt [57]. The transition from non-wetting to wetting meniscus at carbon−carbonate interface is found to be complete after 2−3 h of operation and is accompanied by an initial OCV reduction, which is followed by a gradual wetting of the entire anode surface leading to the OCV increasing until a quasi-steady state OCV is reached.

Cherepy et al. have reported an investigation of various types of carbon blacks (turbostatic or disordered to different degrees) and have tried to correlate their electrochemical reactivity in a molten carbonate electrolyte based DCFC with micro- and nanostructures of carbons [58]. The observations on three samples of carbon black showed a large variation in peak power densities (8−100 mW/cm^2) (Fig. 37) [234]. It was suggested that this variation was largely due

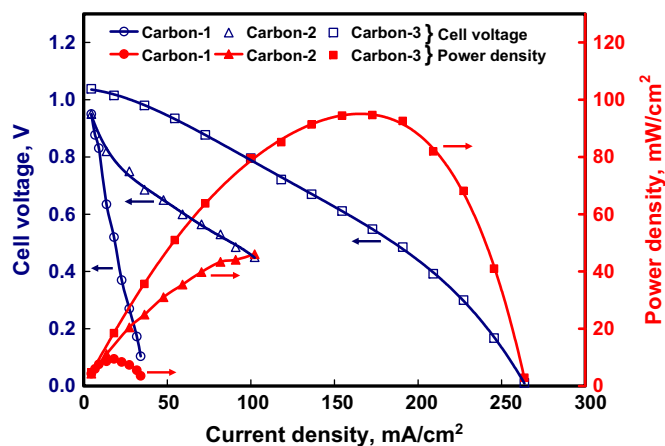**Fig. 36.** Performance of different carbon fuels in MCFC. Graph plotted from the data in Reference [58].

Fig. 37. Voltage − current density and power density − current density characteristics of a molten carbonate electrolyte based DCFC at 850 $^\circ$C, operated on three carbon blacks made by pyrolysis, but with different structure on a nanometer scale. Figure redrawn based on Reference [234].

to a significant differences in micro and nanostructures of the three types of carbon black samples. XRD measurements showed that all samples of carbon had much larger spacing between layers of carbon atoms, and only a small area of crystallinity when compared with graphite. Cherepy et al. concluded that carbons with high degree of disorder and defects and low degree of crystallinity were more accessible for chemical reactions and produced high power densities in comparison to carbons with ordered structures such as graphite which is significantly less reactive [58].

Kulkarni et al. have shown that for a solid electrolyte (ceria – gadolinia) based DCFC, somewhat similar behaviour is observed [193]. They found that amorphous carbon fuel was more reactive electrochemically and produced higher power density in comparison with micronised graphitic fuel when tested under identical fuel cell operating conditions (Fig. 38). It should be noted that most coal derived carbons are generally amorphous and have disordered structure.

It has been known that surface functional groups of heteroatoms such as oxides and nitrates play an important role in physical and chemical properties of carbon [190,200]. Properties of carbon such as electrical properties, wettability, zeta potential, catalytic activity and adsorption capability can all be altered by appropriate surface treatments such as nitradation and oxidation. In the carbon electrode materials in Li-ion batteries, the presence of oxygen groups on the surface results in increased capacitance and wettability by the electrolyte. The surface chemistry is considered to play a vital role in such applications and hence the modification of surface chemistry by various treatments is seen as a promising way for improved performance of carbon materials in catalysis, adsorbent and energy storage applications. In the case of DCFC as well, the modification of the surface functional group or surface activation of carbon fuel is thought to influence the performance. Several researchers have investigated the effects of pH, electrolyte composition and current density on the properties and composition of surface oxides. It has been reported that the custom tailored surface functional groups can be obtained via electrochemical oxidation of carbon in aqueous mediums by choosing suitable current input profiles and electrolytes [235]. This implies that the current generation using the carbon fuel can be improved by tuning the surface functional groups. Recently Li. et al. reported the effect of surface treatments on carbon fuels [175] in a DCFC. In their experiments, activated carbon and carbon black fuels were treated with 4 M HNO₃, 4 M HCL or microwave air plasma surface treatments. It was found that the treatment with HNO₃ resulted in an increased number of oxygen functional groups on the surface of the

carbon which doubled the current at 0.6 V at 600 °C. The surface treatment with HCl and plasma was found to be not as effective as that with HNO₃. This was related to the number of oxygen surface groups which were found to be greatly reduced within the fuel treated with HCl and plasma compared to HNO₃ treated materials. Cao et al. reported similar results for activated carbon fuels treated with HF, HNO₃ and NaOH [236]. Carbon treated with acid delivered better current densities than those subjected to an alkali treatment. However, in all cases surface treatments appeared to have a positive effect on the performance of carbon. This was attributed to increased specific surface area and micropore volume of carbon because of the removal of inorganic impurities in addition to surface chemistry modifications [236]. However, it is unclear if the enhancement in electrochemical reactivity of carbon by surface treatments is merely a surface phenomenon or it progresses to bulk of the carbon fuel. If the enhancement is restricted to the surface, the effect of surface treatments may not be significant in long term operation of DCFCs. Li et al. [175] have speculated that once the active surface layer is reacted, a large number of active sites are further exposed for subsequent chemisorptions of oxygen (ions). To clarify this, further investigations including long term evaluation of such fuels in DCFCs are warranted.

Understanding the effect of impurity content on fuel cell performance is a key point, especially when low grade fuels such as coal are considered. Depending on the source, location and pre-treatment, the impurity content of coal varies greatly. From a purely thermodynamic perspective, coal with a high carbon content would deliver higher efficiencies than coal with higher ash or hydrocarbon components. High ash content may lower the output by restricting mass flow to and from the fuel and reactive species such as silicon may attack the electrolyte thus lowering its ionic conductivity. Some metal oxide impurities, however, may act as catalysts for carbon oxidation. Recently, Li et al. have reported that the impurities such as CaO, MgO and Fe₂O₃ deliver slight improvements in current densities by acting as a catalyst in molten carbonate type DCFCs [167]. Other mineral impurities such as oxides of Na, Cr, Cu, Ni, Co may also act as catalysts for electrochemical reactions and Boudouard type reactions within the anode chamber, especially in gasification driven DCFCs. Al₂O₃ and SiO₂, are the major constituents in coal ashes and increasing amounts of these impurities have been shown to lower the performance of MC-DCFCs by impeding mass transport within the anode chamber [167]. The role of hydrocarbon impurities, often associated with high carbon fuels, has not been clearly understood to date. The presence of short alkyl side chains may increase the electrochemical reactivity of the carbon fuel by providing active sites for oxidation [167], however, other components may be detrimental, in particular with lower temperature systems as some heavy hydrocarbon materials are particularly stable at lower temperatures (around 500 °C).

The studies on SOFC technology with fuels such as natural gas indicate that sulphur based impurities degrade the anode performance especially for a Ni/YSZ cermet anode. However, in a recent study on coal gasification driven SOFC, Lee et al. reported that the sulphur content in coal did not degrade the Ni based anode performance significantly, possibly because of reactions of sulphur with coal impurities such as hydrogen and moisture during the charring process [133]. This effect may be lost in systems where the coal is directly introduced into the anode chamber and physical contact of the anode with fuel particles occurs.

Although there are similarities between classic oxidation models and the electrochemical oxidation of carbon, there are also a number of factors that require further investigation. The oxidation of carbon appears to be the rate limiting step in all direct carbon fuel cell designs with the exception of systems based on
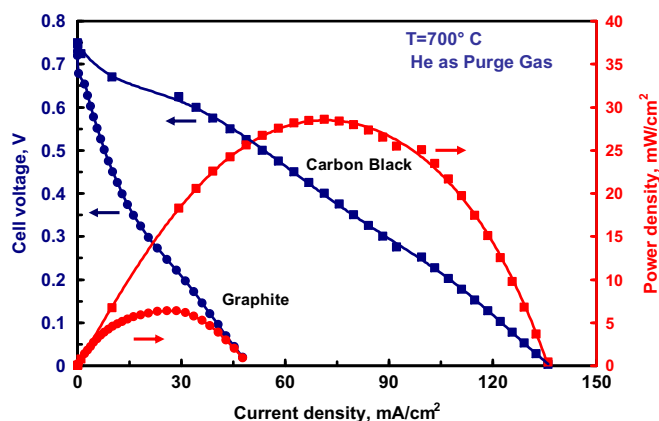

Fig. 38. Voltage – current density and power density – current density characteristics of a solid electrolyte based DCFC at 700 °C, operated on carbon black and graphite as fuels, and helium as a purge gas. Figure redrawn based on Reference [193].

gasification and, potentially, systems with molten metal anodes (where charge transfer between the ceramic electrolyte and the metal anode may be rate limiting). Therefore, it is essential to gain a good understanding of the carbon oxidation mechanisms within each fuel cell design in order to improve performance and select appropriate fuels and establish fuel processing requirements. Although, this work has already commenced, results are still somewhat fragmented and systematic studies on the impact of various fuel properties over a wide range of direct carbon fuel cell operating conditions are required. Initial data presented by various authors suggest that the following broad factors are likely to be critical to the fuel cell performance:

- Carbon structure and the degree of crystallinity of carbon.
- Wettability of carbon fuel in the case of molten media based DCFC.
- Electrical conductivity of carbon.
- Particle size, pore size distribution and surface area.
- Surface functional groups (nature and degree of functionalisation).
- Type of impurities and their concentration.

If a detailed understanding of these factors could be gained and results used to design and develop low cost fuel pre-processing techniques to produce a range of high performance fuels specifically tailored for the type of direct carbon fuel cell, it is likely that overall system performance would be greatly improved. This would also accelerate the development and commercialisation of direct carbon fuel cells.

4. Competing technologies, significant issues and future direction for DCFC

As discussed in section 3, DCFCs offer many advantages over other types of fuel cells and power generation technologies including the high net efficiency approaching 70%, almost sequestration ready CO_2 without the substantial extra cost and energy losses associated with its capture and the use of low cost fuel. Fuel Cell energy offer fuel cell systems based on a molten carbonate electrolyte operating on natural gas with an electrical efficiency of 47%, which can be scaled from 300 kW up to 50 MW [35]. These systems could be operated on cleaned gasified solid fuels such as gasified coal. System modelling by Yoshiba et al. have suggested that an integrated MCFC, steam turbine and autothermal gasification system could attain an efficiency of around 47% [237]. This is similar to the overall system efficiency of a state of the art IGCC power plant which is typically taken to be 45% [238], however, with the clear advantage of a fuel cell/gasifier system could be designed to produce an almost pure CO_2 exhaust stream which can be easily captured for sequestration. In the case for advanced IGCC plants, for capture of over 90% of the CO_2, the overall efficiency would fall to around 40% [238].

In a similar manner to MCFCs, solid oxide fuel cells such as those being marketed by Bloom energy, operating with natural gas fuel, offer electrical efficiencies (around 50%) and can be scaled from 100 kW systems to around 1 MW [46]. Also as part of the SECA program, there has been significant effort in the USA, developing an integrated coal gasification solid oxide fuel cell system [239]. A number of detailed system modelling studies have shown that, in principle, it is possible to achieve an overall system efficiency of over 45% for an atmospheric pressure coal gasification fuel cell system and around 60% for a pressurised system both without CO_2 capture [238,240]. With CO_2 capture the efficiency would drop to 43 and 57% respectively for atmospheric and pressurised systems. In contrast, the efficiency of a molten carbonate DCFC system has

been predicted to be over 70% [179] with CO_2 being the main product gas which can be easily captured for storage. A system of this type would become cost competitive with IGCC and NGCC plants with CO_2 sequestration at around US$2000/kW installed cost [136]. However, as discussed before DCFC systems are at an early stage of development compared to the conventional SOFC systems used in the SECA program and there are still a significant number of technical materials stability and fuel reactivity challenges that need to be overcome before solid carbon can be directly used in a commercial fuel cell.

The development of direct carbon fuel cells to commercialisation stage is largely prohibited by the following key technical issues:

1. Poor power densities.
2. High degradation rates − corrosion of cell components.
3. Fuel feed system − getting the fuel to the anode.
4. Up-scaling of the technology to kW and larger size systems
5. Establishing fuel processing requirements to produce low cost fuel.

There is no one area within the overall research field, where a concerted and coordinated effort from the research and development sector would result in a breakthrough that would lead to the rapid commercialisation of this technology. A number of technology challenges need to be tackled simultaneously. As alluded to earlier in the article, the major limit to DCFC performance is related to the state of the fuel, because the fuel is solid it cannot diffuse to the active sites within a porous electrode this greatly reduces the number of accessible active sites where chemical oxidation can occur. This combined with the sensitivity of conventional anodes (Ni-YSZ) to poisoning and carbon deposition, makes conventional fuel cell designs and materials impractical. The use of molten metal's and salts that flow into the fuel cell show promise as these systems coat the surface of the fuel greatly increasing the surface area available for reaction. However, the use of molten materials also greatly increases the degradation of any system either via chemical attack on other system components, as with molten salts, or through rapid reaction with fuel impurities as with molten metals which will alloy with even small quantities of metal within the fuel. Gasification of the carbon is an appealing option as it greatly increases the power density by allowing the fuel to fully access the anode, allows for the use of far better understood 'traditional' SOFC materials and eliminates the requirement for molten media. However, this approach does reduce the thermodynamic efficiency and, if a system of higher efficiency than a standard thermal power plant is to be developed, greatly increases system complexity. Directly introducing the carbon to the anode chamber as opposed to the thermal integration of an external gasifier may reduce the system complexity and improve efficiency by allowing some direct oxidation of carbon in contact with the anode, however, it will increase the material reactivity issues and increase fuel processing requirements.

The other major areas requiring effort to improve the DCFC performance and take the technology to commercialisation stage are: development of anode materials that can extend TPBs to increase solid fuel reactive sites for example the use of mixed ion conductors or partly utilise gaseous by-products of solid carbon fuel; investigations on carbon fuel characteristics and required level of fuel processing (de-ashing, purification, surface treatments, micronisation, etc.) that maximises its reactivity at the fuel/electrode or electrode/electrolyte interface and reduce anode degradation and prolong fuel cell life; development of electrode supported cell designs preferably cathode supported to minimise the electrolyte and anode thickness to reduce resistive losses across

electrolyte and enhance fuel transport/diffusion through anode; and development of cell materials for low temperature operation to minimise materials degradation issues. General programs looking generically at 'performance' or 'degradation' across the whole field, rather than focusing on one or two specific system concepts, are unlikely to result in the driving of this technology towards a commercial product.

Despite the early stage of most development programs, there are already examples of single lab scale fuel cells of various designs that offer sufficient performance ($>150 \text{ mW/cm}^2$). What is required is significant increase in the scale of fuel cells trialled both in terms of the size of the fuel cells tested and the length of time of each test to demonstrate sustained power densities and low degradation rates. If direct carbon fuel cells are to follow a similar commercialisation path as of other fuel cell types such as PEM, MCFC, SOFC or PAFC, the solutions found during the development and long term testing (1000's of hours) of a system at roughly kW scale will greatly catalyse the commercialisation of the technology.

Stack, system and flow sheet modelling also need to be performed to address issues such as thermal and mechanical stresses, energy and mass balance, fuel utilisation, system efficiencies.

5. Conclusions

There are currently five distinct types of DCFCs under development by various groups globally. These include one based on molten hydroxide electrolyte, one based on molten carbonate electrolyte and three based on solid oxide electrolytes. For the three based on solid oxide electrolytes, there are different methods of fuel delivery (solid carbon as a fluidised bed of carbon particles, carbon mixed with a molten metal and carbon mixed with molten carbonates). For each type of DCFC, there are a number of design variations, different technical issues and performance outcomes (power density, lifetime, etc.). In addition, there is the complication whether DCFC involves total direct carbon oxidation or partial direct carbon oxidation in electrochemical reactions or indirect conversion, first to CO and then electrochemical reaction of CO in a conventional SOFC. There are significant implications for overall electrical efficiency depending on the reaction mechanism.

The international effort towards developing DCFC technology is relatively small in comparison to MCFC, SOFC and PEMFC technologies with only a few major key players. Most of the R & D is performed in universities and at research organisations. A part from SARA, there is no other major well established company working in the area. A number of small companies (e. g. CellTech, Contained Energy (now Logos Energy) and Direct Carbon) have been formed exclusively to research, develop and commercialise the DCFC technology. Most groups are testing small cells or stacks over short time periods (few hundred hours at the most). Typical power densities achieved from DCFCs are in the $5-150 \text{ mW/cm}^2$ range, although somewhat higher values have been reported especially for systems operating on Boudouard gasification of carbon.

There are very clear advantages of the DCFC technology – high projected electric system efficiencies of about 70%, almost 50% reduction in emission of greenhouse gases and fuel consumption compared to current coal fired power plants thus substantially reducing the amount of CO_2 for sequestration and extending the life of fuel reserves, near 100% fuel utilisation, CO_2 produced is in pure form thus no gas separation required leading to cost and energy savings and low operating costs (use of very low cost and easily available fuels such as biomass, coal, tar, plastics, etc.). For conventional coal fired thermal power plants, about 20–25% of the power generated is lost in post-combustion capture of CO_2. All these factors point to a favourable power generation option with

a direct carbon fuel cell. However, at the same time, there are substantial technical challenges in terms of delivery of solid fuel to the electrode/electrolyte interface, long term effect of residual impurities in the carbon based fuels, technology scale-up, corrosion of components due to higher operating temperatures, lifetime and degradation. Thus, a substantial R & D effort is required. It is hoped that the integration of real world fuels at an early stage of system development programme will reduce overall R & D costs, by reducing the overall development time and produce a system that will be more applicable to a wider range of established markets avoiding the need for large investment in infrastructure. Due to the modular nature of fuel cells this technology once developed, DCFCs would be suitable for a wide range of applications from small domestic kilowatt systems to large centralised multi-megawatt facilities. An EPRI report [52] has indicated that the eventual capital system costs would be in the vicinity of US$1350 to $1600 per kW. This would make this technology competitive with a wide range of other technologies including current coal fired power plants [179]. Typical cost targets for a mature technology of around US$2000 per kW for the complete system are quite attractive and competitive although higher costs are tolerable due to the high efficiency and low cost for CO_2 capture.

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