Progress and challenges in the direct carbon fuel cell technology

Junjie Chen*, Xuhui Gao, Longfei Yan, Deguang Xu
School of Mechanical and Power Engineering, Henan Polytechnic University, Jiaozuo, Henan, China

*E-mail address: comcj@163.com, comcj@yahoo.com

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Abstract

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. Direct Carbon Fuel Cells (DCFC) utilize 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 study community. A DCFC converts the chemical energy in solid carbon directly into electricity through its direct electrochemical oxidation. The fuel utilization 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 utilization 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 commercialization. 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.

1. Introduction

Direct Carbon Fuel Cells (DCFCs) are still at the very preliminary stage of development with only a few authors or industrial organizations 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. 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 oxidized 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 [1]. The fuel and products are distinct separate phases (solid and gas), so their separation is easy and the fuel utilization 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 [2].

There are three basic types of direct carbon fuel cells: molten hydroxide; molten carbonate and oxygen ion conducting ceramic. In addition to the use of different electrolytes, there are further sub-categories 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.

Overall effort in the development of DCFC technology has been relatively small in comparison with other major fuel cell technologies [3]. The theoretical or thermodynamic efficiency in DCFC is close to 100%. Actual stack efficiencies are projected to be 80% with total system efficiencies estimated to be above 60% - almost twice those of current generation coal fired plants and significantly higher than other fuel cell types. The projected cost, including balance-of-plant (BOP) is lower than most other fuel cell types with substantially lower operating costs due to the availability of cheap fuel sources [4].

The DCFC technology has many obvious benefits, however, it is still at an early stage of development with considerable effort required to take it to the commercialization stage [5]. Some major challenges that need to be resolved before commercialization include: mode of solid fuel delivery to electrode electrolyte interface; fuel processing and fuel quality requirements; 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; degradation rates and causes; improvement in materials performance and power densities; overall systems design; and technology up-scaling [6].

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 shown in Fig. 1 is an electrochemical device that converts chemical energy directly into electrical and heat energy when supplied with a fuel and an oxidant. It consists of an electrolyte, anode and a cathode. 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 generation of power in the fuel cell. The cathodic reaction involves consumption of electrons, and either reaction between oxygen and ionic species transported through the electrolyte or the formation of oxygen anions which are transported through the electrolyte from the cathode to the anode.
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 [7]. 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 [8]. 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 thermodynamic (maximum) fuel efficiency ($\phi_{F_{th}}$) of a fuel cell is defined as the ratio of free energy ($\Delta G$) and enthalpy ($\Delta H$) of the fuel oxidation reaction.

Fig. 2 shows how the maximum or theoretical efficiency could vary with operating temperature of the fuel cell.
2.2. Different types of fuel cells.

Fuel cells are generally named based on the type of electrolyte or fuel used. Fig. 3 shows various types of fuel cells and their characteristics, i.e., fuel and oxidant, anodic and cathodic reactions, electrolytes and operating temperature range [9]. For detailed descriptions of other main fuel cell types see references [10].

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, kerosene, diesel, naphtha, hydrogen and coal. 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 [11]. Essentially, with the exception of direct alcohol and direct borohydride fuel cells, all 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 [12].

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, transport and portable power etc. [13]. The application of fuel cells vary depending on their operating characteristics, efficiency, cost, lifetime, fuel availability and processing requirements, requirements for the quality of heat in combined heat and power etc. However, despite some major environmental advantages, most market segments are looking for high degree of reliability and costs which are competitive with existing technologies [14].

3. DIRECT CARBON FUEL CELL

The only difference between direct carbon fuel cell and others 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. Key features of a DCFC, as distinct from other fuel cells and power generation technologies are as follows [15]:

- 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%.

The by-product is pure CO2 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 as described in Fig. 4. 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:

- Aqueous hydroxide - temperature <250 °C.
- Molten hydroxide (KOH, NaOH) - temperature 500-600 °C.
- Molten carbonate (Li, Na, K) - temperature 750-800 °C.
- Oxygen ion conducting ceramic (doped zirconia or ceria) - temperature 500-1000 °C.

Fig. 4. Main types of direct carbon fuel cells and fuel cell reactions.
A tree diagram of various DCFC technologies under development. Many 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 [16]:

- Reduction in operating temperature reduces both the thermodynamic driving force and kinetics of chemical reactions that form CO.
- Continuous operation of a direct carbon fuel cell is advantageous as it avoids formation of CO within the anode.
- Exposure of the carbon fuel to CO₂ in an unloaded fuel cell at the operating temperature should be minimized.

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 in order to maintain the electrolyte as a liquid. Early work was carried out within autoclaves at 200 °C and 30 bar pressure with raw brown coal as the fuel [17]. 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 it was related to reaction of the fuel with the cathode [18].
3.2. Molten hydroxide electrolyte technology.

![Diagram of a DCFC](Image)

**Fig. 6.** A schematic drawing of a DCFC used by SARA in most of their investigations.

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. SARA has continued to develop the technology with emphasis on solving problems and development and optimization of cell/stack materials and designs. Fig. 9 shows a schematic view of the hydroxide based direct carbon fuel cell design used by Xu et al. in most of their investigations [19]. 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).
3.3. Molten carbonate electrolyte technology.

![Diagram of a basic cell configuration of the tilted DCFC of LLNL]

Fig. 7. A schematic drawing of a basic cell configuration of the tilted DCFC of LLNL.

Gas fed molten carbonate fuel cells are one of the most commercially mature types of fuel cell systems. Essentially the direct carbon version of the cell 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. Fig. 7 depicts one design proposed by Li et al. [20]. 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 and for the cell to be continually refuelled with a carbonate slurry. Other designs that more closely resemble the Jacques design have also been tested [21].
Kacprzak et al. [21] have also designed a self-feeding cell that is refuelled pneumatically and incorporates internal pyrolysis of the coal as shown in Fig. 8. The pyrolysis of coal would produce hydrogen, and low molecular weight hydrocarbons and a non-agglomerating char, and that is reactive and sufficiently conductive, for use as a fuel for DCFC. The team at LLNL reported that they intend to test a 75-150 W, 5-cell self-feeding bipolar stack using pure turbostratic carbon as the fuel. However the technology was licensed to Contained Energy and there have been no further reports on the progress of the work.

3.4. Oxygen ion conducting electrolyte technology

This type of direct carbon fuel cell utilizes an oxygen ion conducting ceramic as the electrolyte similar to that in the solid oxide fuel cell (SOFC) [22]. 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 as following.

Fig. 9. Schematic diagram of a triple phase boundary required for a DCFC using a solid oxygen ion conductor electrolyte and particulate carbon as fuel.

**Fuel as solid carbon or in fluidized 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 [23]. A schematic of the triple phase boundary is shown in Fig. 9. 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 when compared to conventional porous SOFC anodes involving gaseous fuels [24].

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 [25]:

- Vapor deposited systems - hydrocarbon fuels are decomposed within the anode chamber, directly depositing carbon over a large area within the anode.
- Consumable anodes pressed against the electrolyte - carbon is pressed directly to the electrolyte.
- Carbon placed within the anode chamber but not necessarily in constant direct contact with the anode or the electrolyte and includes systems with fluidized 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.
- Use of an integrated external gasification - carbon gasified external to the fuel cell stack.

Ju et al. [26] employed a two compartment carbon fuel cell arrangement as shown in Fig. 10 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 placed in one section and carbon pellets placed in another section of a quartz tube. 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 as supplying air to the inside of the YSZ tubular cell.

**Fig. 10.** (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.

**Fuel in molten metal.** Molten metals have been tested as fuel cell electrodes on many occasions in early solid oxide fuel cells. These metals can be inert which transport ionic species to and from the electrolyte in solution or reactive which oxidise at the electrode surface and are then reduced by the fuel [27].
Fig. 11 shows the basic operating principle of CellTech's liquid tin anode based direct carbon fuel cell. This type of device can act as a primary or secondary battery or a fuel cell. As with a battery, the CellTech cell can operate for significant amounts of time with no fuel being added to the system [28]. 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, the exception being bismuth metal. This is most likely due to the high ionic conductivity of bismuth oxide. 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.

**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 [29]. Although there are some variations in the design, 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. Fig. 12 depicts the basic principle of the technology. This type of fuel cell system avoids the need for CO₂ circulation and protects the cathode from molten carbonate, allowing the use of advanced cathode compositions already developed for SOFCs. It also avoids cathode flooding and corrosion issues associated with the closely related molten carbonate direct carbon fuel cell.
**Fig. 12.** 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. 13 shows a schematic drawing of a single cell DCFC construction proposed by Lee et al. [30] from SRI International. 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 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. Li et al. [31] have achieved power densities of up to 120 mW/cm² using acetylene black as the fuel. 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/cm² respectively.
SRI International had been quite active for this type of technology and has tested solid carbon fuels mixed with salt powders [32]. Fig. 14 shows an SRI multiple tube DCFC stack prototype. 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 investigators to trial a wide range of cell concepts and designs that may offer lower temperature operation [33].

A DCFC utilizes 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, liquid hydrocarbon fuels, biomass and organic waste. Some of these fuels have been used directly within the fuel cell with very little pre-treatment whilst others have been heavily processed and purified to produce a fuel that is almost pure carbon [34].

Dudek et al. [35] have reported an investigation of various types of carbon blacks and have tried to correlate their electrochemical reactivity in a molten carbonate electrolyte based DCFC with micro- and nanostructures of carbons, which shows in Fig. 15. The observations on three samples of carbon black showed a large variation in peak power densities. It was suggested that this variation was largely due 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.

Kim et al. [36] have shown that for a solid electrolyte based DCFC, somewhat similar behavior is observed. They found that amorphous carbon fuel was more reactive electrochemically and produced higher power density in comparison with micronized graphitic fuel when tested under identical fuel cell operating conditions, which shows in Fig. 16. 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. 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 nitration 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 [37].

There are also many factors that require further investigation [38]. 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 gasification and, potentially, systems with molten metal anodes. Therefore, it is essential to gain a good understanding of the carbon oxidation mechanisms within direct 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 [39]. Initial data suggests 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 functionalization).
- Type of impurities and their concentration.

If a detailed understanding of these factors can 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 commercialization of direct carbon fuel cells.

4. COMPETING TECHNOLOGIES, SIGNIFICANT ISSUES AND FUTURE DIRECTION FOR DCFC

DCFCs offer many advantages over other types of fuel cells and power generation technologies including the high net efficiency approaching 70%, almost sequestration ready CO₂ without the substantial extra cost and energy losses associated with its capture and the use of low cost fuels. 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. These systems could be operated on cleaned gasified solid fuels such as gasified coal. System modelling by Eom et al. [40] have suggested that an integrated MCFC, steam turbine and autothermal gasification system could attain an efficiency of around 47%. This is similar to the overall system efficiency of a state of the art IGCC power plant which is typically taken to be 45%, however, with the clear advantage of a fuel cell/gasifier system could be designed to produce an almost pure CO₂ exhaust stream which can be easily captured for sequestration. In the case for advanced IGCC plants, for capture of over 90% of the CO₂, the overall efficiency would fall to around 40%.

As part of the SECA program, there has been significant effort in the USA, developing an integrated coal gasification solid oxide fuel cell system [41]. 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 pressurized system both without CO₂ capture [42]. With CO₂ capture the efficiency
would drop to 43 and 57% respectively for atmospheric and pressurized systems. In contrast, the efficiency of a molten carbonate DCFC system has been predicted to be over 70% with CO\textsubscript{2} being the main product gas which can be easily captured for storage [43]. A system of this type would become cost competitive with IGCC and NGCC plants with CO\textsubscript{2} sequestration at around US$2000/kW installed cost [44]. 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 commercialization stage is largely prohibited by the following key technical issues [45]:

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

There is no one area within the overall study field, where a concerted and coordinated effort from the development sector would result in a breakthrough that would lead to the rapid commercialization of this technology. A number of technology challenges need to be tackled simultaneously [46]. 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 the porous electrode this greatly reduces the number of accessible active sites where chemical oxidation can occur [47]. This combined with the sensitivity of conventional anodes (Ni-YSZ) to poisoning and carbon deposition, makes conventional fuel cell designs and materials impractical [48]. 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 [49]. 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 standard thermal power plant is to be developed, greatly increases system complexity [50]. Directly introducing the carbon to the anode chamber as opposed to the thermal integration of an internal 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 commercialization 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 utilize gaseous by-products of solid carbon fuel [51]; investigations on carbon fuel characteristics and required level of fuel processing that maximizes its reactivity at the fuel/electrode or electrode/electrolyte interface and reduce anode degradation and prolong fuel cell life [52]; development of electrode supported cell designs preferably cathode supported to minimize the electrolyte and anode thickness to reduce resistive losses across electrolyte and enhance fuel transport/diffusion through anode [53]; and development of cell materials for low temperature operation to minimize materials degradation issues [54]. 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 [55]. What is required is significant increase in the scale of fuel cells trialed 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 [56]. If direct carbon fuel cells are to follow a similar commercialization path as other fuel cell types such as PEM, MCFC, SOFC or PAFC, the solutions found during the development and long term testing of a system at roughly kW scale will greatly catalyze the commercialization of the technology [57]. 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 utilization, system efficiencies [58].

5. CONCLUSION

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. For each type of DCFC there are a number of design variations, different technical issues and performance outcomes. 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 at study organizations. Apart from SARA, there are no other major well established company working in the area. A number of small companies have been formed exclusively to study, develop and commercialize the DCFC technology. Most groups are testing small cells or stacks over short time periods. Typical power densities achieved from DCFCs are in the 5-150 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 utilization, CO$_2$ produced is in pure form thus no gas separation required leading to cost and energy savings and low operating costs. 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 favorable 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 program will reduce overall R & D costs, by reducing the overall development time and provide 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 centralized multi-megawatt facilities.
References

[1] Cooper J.F., Selman J.R., Analysis of the carbon anode in direct carbon conversion fuel cells. *International Journal of Hydrogen Energy* 37(24) (2012) 19319-19328.

[2] Elleuch A., Boussetta A., Halouani K., Analytical modeling of electrochemical mechanisms in CO\textsubscript{2} and CO/CO\textsubscript{2} producing Direct Carbon Fuel Cell. *Journal of Electroanalytical Chemistry* 668 (2012) 99-106.

[3] Zhang L., Xiao J., Xie Y., Tang Y., Liu J., Liu M., Behavior of strontium- and magnesium-doped gallate electrolyte in direct carbon solid oxide fuel cells. *Journal of Alloys and Compounds* 608 (2014) 272-277.

[4] Munnings C., Kulkarni A., Giddey S., Badwal S.P.S., Biomass to power conversion in a direct carbon fuel cell. *International Journal of Hydrogen Energy* 39(23) (2014) 12377-12385.

[5] Stähler M., Burdzik A., Calibration method for carbon dioxide sensors to investigate direct methanol fuel cell efficiency. *Journal of Power Sources* 262 (2014) 147-151.

[6] Qi J., Benipal N., Chadderdon D.J., Huo J., Jiang Y., Qiu Y., Tian X., Y.H. Shanks B.H., Li W., Carbon nanotubes as catalysts for direct carbohydrate fuel cells. *Carbon* 89 (2015) 142-147.

[7] Bruno M.M., Viva F.A., Petruccelli M.A., Corti A.K., Platinum supported on mesoporous carbon as cathode catalyst for direct methanol fuel cells. *Journal of Power Sources* 278 (2015) 458-463.

[8] Antunes R., Skrzypkiewicz M., Chronoamperometric investigations of electro-oxidation of lignite in direct carbon bed solid oxide fuel cell. *International Journal of Hydrogen Energy* 40(12) (2015) 4357-4369.

[9] Giddey S., Kulkarni A., Munnings C., Badwal S.P.S., Composite anodes for improved performance of a direct carbon fuel cell. *Journal of Power Sources* 284 (2015) 122-129.

[10] Lee J.-Y., Song R.-H., Lee S.-B., Park S.-J., Shul Y.G., Lee J.-W., A performance study of hybrid direct carbon fuel cells: Impact of anode microstructure. *International Journal of Hydrogen Energy* 39(22) (2014) 11749-11755.

[11] Rady A.C., Giddey S., Kulkarni A., Badwal S.P.S., Bhattacharya S., Degradation Mechanism in a Direct Carbon Fuel Cell operated with Demineralised Brown Coal. *Electrochimica Acta* 143 (2015) 378-292.

[12] Bonaccorso O., Irvine J.T.S., Development of tubular hybrid direct carbon fuel cell. *International Journal of Hydrogen Energy* 37(24) (2012) 19337-19344.

[13] Irvine J.T.S., Corte G., Antunes R., Irvine J.T.S., Scaling up of the hybrid direct carbon fuel cell technology. *International Journal of Hydrogen Energy* 38(20) (2013) 8497-8502.

[14] Ruffin I., Perwich Li A.D., Brett C., Berner J.K., Lux S.M., Direct carbon fuel cell: A proposed hybrid design to improve commercialization potential. *Journal of Power Sources* 213 (2012) 275-286.

[15] Liu J., Wang H., Wu C., Zhao Q., Wang X., Yi L., Preparation and characterization of nanoporous carbon-supported platinum as anode electrocatalyst for direct borohydride fuel cell. *International Journal of Hydrogen Energy* 39(12) (2014) 6729-6736.

[16] Cao T., Wang H., Shi Y., Cai N., Direct carbon fuel conversion in a liquid antimony anode solid oxide fuel cell. *Fuel* 135 (2014) 223-227.
[17] Yu X., Shi Y., Wang H., Cai N., Li C., Ghoniem A.F., Using potassium catalytic gasification to improve the performance of solid oxide direct carbon fuel cells: Experimental characterization and elementary reaction modeling. *Journal of Power Sources* 252 (2014) 130-137.

[18] Salernitano E., Giorgi L., Dikonimos Makris T., Direct growth of carbon nanofibers on carbon-based substrates as integrated gas diffusion and catalyst layer for polymer electrolyte fuel cells. *International Journal of Hydrogen Energy* 39(27) (2014) 15005-15016.

[19] Xu K., Chen C., Liu H., Tian Y., Li X., Yao H., Effect of coal based pyrolysis gases on the performance of solid oxide direct carbon fuel cells. *International Journal of Hydrogen Energy* 39(31) (2014) 17845-17851.

[20] Li C., Shi Y., Cai N., Effect of contact type between anode and carbonaceous fuel on direct carbon fuel cell reaction characteristics. *Journal of Power Sources* 196(10) (2011) 4588-4593.

[21] Kaczprzak A., Kobylecki R., Włodarczyk R., Bis Z., The effect of fuel type on the performance of a direct carbon fuel cell with molten alkaline electrolyte. *Journal of Power Sources* 255 (2014) 179-186.

[22] Zhang J., Jiang X., Piao G., Yang H., Zhong Z., Simulation of fluidized bed electrode direct carbon fuel cell. *International Journal of Hydrogen Energy* 39(8) (2015) 121-3331.

[23] Yu J., Yu B., Li Y., Electrochemical oxidation of catalytic grown carbon fiber in a direct carbon fuel cell using Ce$_0.8$Sm$_{0.2}$O$_{1.9}$-carbonate electrolyte. *International Journal of Hydrogen Energy* 38(36) (2013) 16615-16622.

[24] Elleuch A., Yu J., Boussetta A., Halouani K., Li Y., Electrochemical oxidation of graphite in an intermediate temperature direct carbon fuel cell based on two-phases electrolyte. *International Journal of Hydrogen Energy* 38(20) (2013) 8514-8523.

[25] Kulkarni A., Giddey S., Badwal S.P.S., Paul G., Electrochemical performance of direct carbon fuel cells with titanate anodes. *Electrochimica Acta* 121 (2014) 34-43.

[26] Ju H., Uhm S., Kim J.W., Song K.H., Choi H., Lee S.-H., Lee J., Enhanced anode interface for electrochemical oxidation of solid fuel in direct carbon fuel cells: The role of liquid Sn in mixed state. *Journal of Power Sources* 210 (2012) 36-41.

[27] Borghei M., Scotti S., Nanninen F., Hiekkanen T., Anoshkin I.V., Nasibulin A.G., Franssila S., Kauppinen E.I., Palli P., Ruiz V., Enhanced performance of a silicon microfabricated direct methanol fuel cell with PtRu catalysts supported on few-walled carbon nanotubes. *Energy* 65 (2014) 612-620.

[28] Huang Y., Huang H., Li Y., Xie Y., Liang Z., Liu C., Facile synthesis of poly(amidoamine)-modified carbon nanospheres supported Pt nanoparticles for direct methanol fuel cells. *Journal of Power Sources* 201(0) (2012) 81-87.

[29] Lee E.-K., Rapporto D., Hansen K.K., Enhancing Hybrid Direct Carbon Fuel Cell anode performance using Ag$_2$O. *Electrochimica Acta* 152 (2015) 222-239.

[30] Lee E.-K., Chun H.H., Kim Y.-T., Enhancing Ni anode performance via Gd$_2$O$_3$ addition in molten carbonate-type direct carbon fuel cell. *International Journal of Hydrogen Energy* 39(29) (2014) 16541-16547.

[31] Li C., Lee E.K., Kim Y.-T., Lee D., Enhancing triple-phase boundary at fuel electrode of direct carbon fuel cell using a fuel-filled ceria-coated porous anode. *International Journal of Hydrogen Energy* 39(30) (2014) 17314-17321.

[32] Lee C.-G., Kim W.-K., Oxidation of ash-free coal in a direct carbon fuel cell. *International Journal of Hydrogen Energy* 40(15) (2015) 5475-5481.
[33] Yu J., Zhao Y., Li Y., Utilization of corn cob biochar in a direct carbon fuel cell. *Journal of Power Sources* 270 (2014) 312-317.

[34] Yu X., Shi Y., Wang H., Cai N., Li C., Tomov R.I., Hanna J., Glowacki B.A., Ghoniem A.F., Experimental characterization and elementary reaction modeling of solid oxide electrolyte direct carbon fuel cell. *Journal of Power Sources* 243 (2013) 159-171.

[35] Dudek M., Tomov R.I., Wang C., Glowacki B.A., Tomczyk P., Socha R.P., Mosialek M., Feasibility of direct carbon solid oxide fuels cell (DC-SOFC) fabrication by inkjet printing technology. *Electrochimica Acta* 105 (2013) 412-418.

[36] Kim J.-P., Choi H.-K., Chang Y.-J., Jeon C.-H., Feasibility of using ash-free coal in a solid-oxide-electrolyte direct carbon fuel cell. *International Journal of Hydrogen Energy* 37(15) (2012) 11401-11408.

[37] Dudek M., Tomczyk P., Socha R., Hamaguchi M., Use of ash-free “Hyper-coals” as a fuel for a direct carbon fuel cell with solid oxide electrolyte. *International Journal of Hydrogen Energy* 39(23) (2014) 12386-12394.

[38] Deleebeeck L., Arenillas A., Menéndez J.A., Kammer Hansen T., Solid and direct carbon fuel cell anode processes investigated using a 3-electrode half-cell setup. *International Journal of Hydrogen Energy* 40(4) (2015) 1945-1958.

[39] Choi S.H., Park D.-n., Yoon C.W., Yoon S.-P., Nam S., Hong S.-J., Shul Y.-G., Ham H.C., Han J., A study on the electrochemical performance of 100-cm²-class direct carbon-molten carbonate fuel cell (DC-MCFC). *International Journal of Hydrogen Energy* 40(15) (2015) 5144-5149.

[40] Eom S., Ahn S., Rhie Y., Kang K., Sung Y., Min H.S., Choi G., Kim D., Influence of devolatilized gas composition from raw coal fuel in the lab scale DCFC (direct carbon fuel cell) system. *Energy* 74 (2014) 734-740.

[41] Li X., Zhu Z., Chen J., De Marco R., Dick A., Bradley J., Lu G., Surface modification of carbon fuels for direct carbon fuel cells. *Journal of Power Sources* 186(1) (2009) 1-9.

[42] Zhang H., Chen L., Zhou J., Chen Y., Performance analysis of a direct carbon fuel cell with molten carbonate electrolyte. *Energy* 68 (2014) 292-300.

[43] Yuan W., Zhou B., Hu J., Dang J., Zhang Z., Tang Y., Passive direct methanol fuel cell using woven carbon fiber fabrics as mass transfer control medium. *International Journal of Hydrogen Energy* 40(5) (2015) 2326-2333.

[44] Cinti G., Hingwe K., Integration of direct carbon fuel cells with concentrated solar power. *International Journal of Hydrogen Energy* 36(16) (2011) 10198-10208.

[45] Gharibi H., Amani M., Pahlavanzadeh H., Kazemeini M., Investigation of carbon monoxide tolerance of platinum nanoparticles in the presence of optimum ratio of doped polyaniline with p-toluene sulfonic acid and their utilization in a real passive direct methanol fuel cell. *Electrochimica Acta* 97 (2013) 216-225.

[46] Elleuch A., Halouani K., Li Y., Investigation of chemical and electrochemical reactions mechanisms in a direct carbon fuel cell using olive wood charcoal as sustainable fuel. *Journal of Power Sources* 281 (2015) 350-361.

[47] Jewulski J., Skrzypkiewicz M., Struzik M., Lubarska-Radziejewska I., Lignite as a fuel for direct carbon fuel cell system. *International Journal of Hydrogen Energy* 39(36) (2014) 21778-21785.

[48] Wang H., Cao T., Shi Y., Cai N., Yuan W., Liquid antimony anode direct carbon fuel cell fueled with mass-produced de-ash coal. *Energy* 75 (2014) 555-559.
[49] Li C., Shi Y., Cai N., Mechanism for carbon direct electrochemical reactions in a solid oxide electrolyte direct carbon fuel cell. *Journal of Power Sources* 196(2) (2011) 754-763.

[50] Zhou J., Ye X.F., Shao L., Zhang X.P., Qian J.Q., Wang S.R., A promising direct carbon fuel cell based on the cathode-supported tubular solid oxide fuel cell technology. *Electrochimica Acta* 74 (2012) 267-270.

[51] Javadekar A., Jayakumar A., Pujara R., Vohs J.M., Gorte R.J., Molten silver as a direct carbon fuel cell anode. *Journal of Power Sources* 214 (2012) 239-243.

[52] Cao J., Wang L., Song L., Xu J., Wang H., Chen Z., Huang Q., Yang H., Novel cathodal diffusion layer with mesoporous carbon for the passive direct methanol fuel cell. *Electrochimica Acta* 118 (2014) 163-168.

[53] Dudek M., On the utilization of coal samples in direct carbon solid oxide fuel cell technology. *Solid State Ionics* 271 (2015) 121-127.

[54] Xu X., Zhou W., Liang F., Zhu Z., Optimization of a direct carbon fuel cell for operation below 700 °C. *International Journal of Hydrogen Energy* 38(13) (2013) 5262-5274.

[55] Zhao M., Zhang H., Hu Z., Zhang Z., Zhang J., Performance characteristics of a direct carbon fuel cell/thermoelectric generator hybrid system. *Energy Conversion and Management* 89 (2015) 683-689.

[56] Giddey S., Kulkarni A., Munnings C., Badwal S.P.S., Performance evaluation of a tubular direct carbon fuel cell operating in a packed bed of carbon. *Energy* 18 (2014) 538-547.

[57] Kouchachvili L., Ikura M., Performance of direct carbon fuel cell. *International Journal of Hydrogen Energy* 36(16) (2011) 10263-10268.

[58] Li X., Zhu Z., De Marco R., Bradley J., Dicks A., Evaluation of raw coals as fuels for direct carbon fuel cells. *Journal of Power Sources* 196 (2010) 4051-4058.