

THE HOLY GRAIL OF CARBON COMBUSTION – THE DIRECT CARBON FUEL CELL TECHNOLOGY

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ABSTRACT

Fuel cells are under development for a range of transport, stationary and portable power applications and invariably utilise either a gaseous or a liquid fuel with most using hydrogen or syn gas ($\text{CO} + \text{H}_2$). Another type of fuel cell, namely the Direct Carbon Fuel Cell, converts the chemical energy in solid carbon directly into electricity through its electrochemical combustion in the 600 to 900°C temperature range. It has a number of advantages over other types of fuel cells or coal combustion technologies in terms of high efficiency and low greenhouse gas emissions. This paper will provide an overview of this exciting new technology which offers maximum achievable electrical efficiency and CO_2 reduction potential of all coal combustion processes.

1 INTRODUCTION

Fuel cell technology is under development for a range of applications including large scale power generation (MW range), distributed generation of heat and electricity at load centres (eg. remote areas, residential and commercial dwellings), transport (cars, buses, locomotives, scooters, auto rickshaws, small transporters) and portable power (electronic appliances, portable power packs, emergency power, etc.). Fuel cells can be divided into low temperature (polymer electrolyte membrane (PEMFC), alkaline (AFC) or direct (DMFC) or indirect methanol (IMFC), operating temperature below 80°C), intermediate temperature (phosphoric acid (PAFC) with operating temperature around 200-215°C) and high temperature (molten carbonate (MCFC), solid oxide (SOFC) and direct carbon (DCFC), operating temperature above 500°C) fuel cells.

The low operating temperature fuel cells such as those based on polymer electrolyte membrane (PEMFC) have rapid start-up and shut-down cycles, excellent load following capability and are ideal for small stationary, portable power and transport applications. The high operating temperature (>500°C) of some fuel cells allows co-generation of both electricity and high grade heat and are not subject to performance degradation due to CO poisoning (non-use of precious metal catalyst and high operating temperature) and therefore have less stringent fuel processing and cleaning requirements. However, the downside is the stringent requirements on construction materials, the slow start-up / shut-down time (several hours), limited capability for thermal cycling, significant thermal shielding to avoid heat losses, dissipation of heat if not required, and electrical / thermal load demand management versus operating temperature control.

Most fuel cells invariably use gaseous or liquid fuels. A fuel cell technology which has attracted attention only recently (the direct carbon fuel cell) uses solid fuel (carbon) and converts the chemical energy in the carbon

to electricity through its direct participation in the fuel cell reactions and electrochemical oxidation. The fuel utilisation can be almost 100% compared with around 85% for most other fuel cells. The electrical efficiency is expected to be above 70% - almost twice those of current generation coal fired plants leading to 50% reduction in greenhouse gas emissions. The amount of CO_2 for storage/sequestration is also halved. Moreover, the exit gas is almost pure carbon dioxide stream, requiring no or minimal gas separation and processing for sequestration. Therefore, the energy and cost penalties to capture the CO_2 will be significantly less than for other technologies. However, the technology is at an early stage of development requiring many complex challenges to be overcome, related to materials, fuel delivery mechanism and system development, before it can be commercialised. This paper gives an overview of this technology and the current development status.

2. DIRECT CARBON FUEL CELLS

2.1 Operating Principle

DCFCs convert the chemical energy in carbon directly into electricity without the need for gasification. It is the direct oxidation of fine (submicron) carbon particles in an electrochemical cell at high temperatures (600 – 900°C) with the overall fuel cell reactions being:



The reactions in DCFC produce almost pure carbon dioxide, 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.

2.2 Efficiency

In a fuel cell, the stack efficiency is determined by a

product of the thermodynamic efficiency, fuel utilisation factor and the voltage efficiency.

The fuel cell open circuit voltage, E_{ocv} , is determined by the free energy (ΔG) of the fuel oxidation reaction ($E_{ocv} = -\Delta G/nF$, where n is number of electrons transferred in the fuel cell electrochemical reaction and F is the Faraday constant). Figure 1 shows the thermodynamic efficiency as a function of temperature for different fuel types. With increasing temperature the free energy available for many fuel oxidation reactions decreases due to the entropy term. For example for hydrogen and carbon monoxide it is 83 and 91% at 25°C and 69% and 61% respectively at 980°C. However, for carbon oxidation reaction the entropy term (ΔS) is near zero and the thermodynamic efficiency is independent of temperature and remains close to 100%.

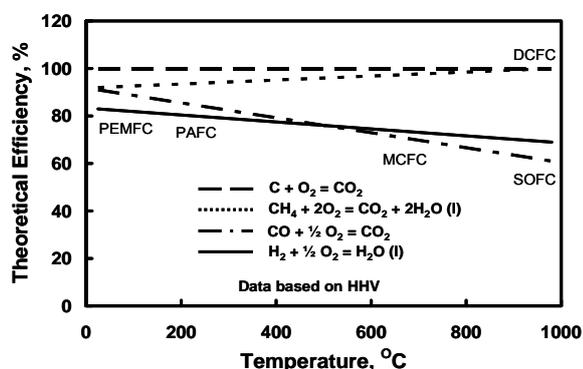


Figure 1: The maximum or theoretical efficiency for different fuels as a function of the operating temperature of the fuel cell.

In the case of DCFC, the fuel and products are distinct separate phases (solid and gas) making their separation and recycling of unspent fuel easier. Thus the fuel utilisation can be almost 100%. For most other type of fuel cells for which the fuel cell reaction products are gases mixed with un-combusted fuel, the fuel utilisation is typically 80-85%.

Allowing for 20-25% voltage efficiency losses the stack efficiency for DCFC is predicted to be around 75-80% with system electrical efficiencies in the 65-70% range taking into consideration system related losses. With heat recovery, overall system efficiency is expected to be well above 80%-85%. However, the fuel processing requirements for DCFC are somewhat unclear at this stage and there will be some losses associated with coal purification and processing which may reduce the overall efficiency. The system electric efficiency alone is 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 about 50% reduction in greenhouse gas emissions and significantly less quantity of CO_2 that would need to be sequestered.

2.3 Fuels for Direct carbon Fuel Cell

A variety of fuels including coal (both brown and

black), coke, tar, biomass and organic waste can be used as the raw fuel. To avoid down stream processing of exit effluent and to avoid degradation of fuel cell components, some processing of fuel is required to remove impurities and to turn the fuel in to submicron size carbon particles for easy combustion at the electrode / electrolyte interface. The quality of carbon and its structure appear to influence the electrode kinetics for its direct oxidation and thus have an effect on the fuel cell performance and power densities. For example, Cherepy et al.¹ have reported that nano-structured (crystallographic) disorder of the lattice, conductivity and the surface area play an important part in getting good performance in molten carbonate electrolyte based direct carbon fuel cell. However, the relationship between fuel quality and power density and long term fuel cell performance is not well understood. Major issues to be taken in to consideration, for future developments of DCFC technology, are the cost of fuel processing versus fuel cell power output and performance (both short and long term).

2.4 Types of Direct Carbon Fuel Cells

There are three basic types of direct carbon fuel cells distinguished by the type of electrolyte used as described below²⁻⁹:

1. Molten salt (KOH, NaOH) – operating temperature 500-600°C.
2. Molten carbonate (Li, Na, K) – operating temperature 750-800°C.
3. Oxygen ion conducting ceramic (doped zirconia, ceria) – operating temperature 800 - 1000°C (at temperatures higher than about 800 - 850°C, CO is likely to be produced as by-product).

In addition to the use of different electrolytes, there are further subcategories of DCFCs differing in materials and design of the anode and the method of fuel delivery to the electrode / electrolyte interface especially for the DCFC based on O^{2-} conducting ceramic electrolyte:

- Solid carbon – fluidised bed
- Carbon mixed with a molten metal
- Carbon mixed with a molten salt.

The basic DCFC technologies under development are summarised in Table 1.

There is another (less explored) DCFC technology based on aqueous-alkaline electrolyte, which uses an aqueous hydroxide solution of potassium, lithium, sodium, cesium and magnesium, and is operated at temperatures $<250^\circ C$ ³. However, there is very little effort on this type of fuel cell and the performance is very poor.

2.4.1 Molten salt (KOH, NaOH as the electrolyte)

This type of fuel cell uses molten hydroxide (NaOH or KOH) as the electrolyte contained in a metallic container, which also acts as a cathode⁴. Fuel is fed to the cell in the form of a rod made from graphite or coal

Table 1: Different types of direct carbon fuel cells.

Fuel / Anode	Electrolyte	Cathode	T, °C
Solid graphite rod as fuel & anode $C + 4OH^- = 2H_2O + CO_2 + 4e^-$	Molten Hydroxides $OH^- \leftarrow$	Air as oxidant $O_2 + 2H_2O + 4e^- = 4OH^-$	~ 600
Carbon particles as fuel in molten carbonate & anode $C + 2CO_3^{2-} = 3CO_2 + 4e^-$	Molten Carbonates $CO_3^{2-} \leftarrow$	Air as oxidant $O_2 + 2CO_2 + 4e^- = 2CO_3^{2-}$	~ 800
Carbon particles in a fluidised bed $C + 2O^{2-} = CO_2 + 4e^-$	Oxygen ion conducting ceramic electrolyte $O^{2-} \leftarrow$	Air as oxidant $O_2 + 4e^- = 2O^{2-}$	800 to 950
Fuel in contact with molten tin $Sn + 2O^{2-} = SnO_2 + 4e^-$			
Carbon particles as fuel in molten carbonate & anode $C + 2O^{2-} = CO_2 + 4e^-$			

derived carbon dipped into the electrolyte. This fuel rod also acts as an anode of the cell. Air is purged into the molten salt at the bottom of the container to supply oxygen at the cathode. Typical operating temperatures are in the range 500-650°C. The electrochemical reactions that occur in the cell are as follows.

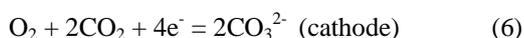
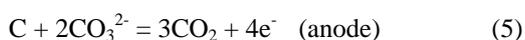


Although the use of molten hydroxide offers number of advantages such as high ionic conductivity, higher electrochemical activity of carbon that results in lower operating temperatures, but it suffers due to the formation of carbonates in the melt. The carbonates are formed by the product CO_2 and / or carbon reacting with hydroxide ions in the melt.

William Jacques was the first person to build a direct carbon fuel cell of this type in 1896². The major technical issues for the commercialisation of this type of cells are high corrosion rates of metals used in the cell and technology up-scaling.

2.4.2 Molten carbonate (Li, Na, K) as electrolyte

This type of fuel cell uses molten carbonate as the electrolyte and fine particles of carbon dispersed into the electrolyte as the fuel⁵. The ionic species that carry the charge between the electrodes are the carbonate ions (CO_3^{2-}). Mixed molten carbonates of lithium, potassium and sodium are used as the electrolyte due to high carbonate conductivity and good stability in the presence of carbon dioxide. The typical operating temperature of this type of fuel cell is in the range of 750-800°C. The electrochemical reactions that occur in the cell are as follows.



The cell consists of a paste of particulate carbon fuel mixed with an eutectic mixture of lithium and potassium carbonates. An open foam nickel is used as the anode current collector and a sintered frit of fine nickel

particles as the cathode current collector. Zirconia felt is used as a separator between electrodes. The cell orientation can be adjusted between 5 to 45° to enhance the electrolyte drainage from the cell and hence avoid cathode flooding.

The major technical issues related to this type of fuel cell are high cathode polarisation losses, corrosion of metal clad bipolar plates and up-scaling. Further, the fuel related issues include lack of a suitable fuel delivery system for a long term and continuous operation, poor understanding of relationship between carbon structure and its chemical and electrochemical activity, and electrolyte tolerance to high percentages of contaminants such as sulphur, ash, etc.

2.4.3 Oxygen ion conducting ceramic (doped zirconia, doped ceria) as electrolyte

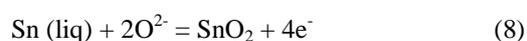
This type of fuel cell uses oxygen ion (O^{2-}) conducting ceramic as the electrolyte similar to that in solid oxide fuel cells. The most common electrolyte being investigated for direct carbon fuel cells is stabilised zirconia (8 - 10 mol % Y_2O_3 , balance ZrO_2). The operating temperature range for this type of cell is in the 800 – 1000°C range. There are three subcategories that use oxygen-ion conducting solid electrolyte but differ in the anode design and how the fuel is delivered to the anode / electrolyte interface as discussed below.

Solid carbon or fluidised bed as fuel: This technology is based on direct electrochemical reaction between the solid carbon at the anode and oxygen anions (O^{2-}) being transported through the ceramic electrolyte membrane from the cathode to the anode as per the following reaction.



The anode side is in direct contact with the carbon particles (typically a fluidised bed arrangement with, for example, CO_2 as the fluidising gas for continuous fuel feed to the anode/electrolyte interface)⁶⁻⁷. Mostly the developmental work on this technology has so far been concentrated on button cells consisting of ceramic electrolyte disk with nickel based anode and lanthanum strontium manganate (LSM) based cathode¹⁰⁻¹¹. The major technical issues apart from those associated with SOFC are the solid fuel delivery to anode / electrolyte interface, lack of understanding of carbon oxidation reaction mechanisms at the interface.

Solid carbon in molten metal as a fuel: In this technology molten metal (such as tin) is used as the anode and solid carbon fuel carrier⁸. The oxygen anions transported through the solid oxide electrolyte react with tin as per the following reaction.



The OCV of the cell based on above anodic reaction and oxygen (from air) as the oxidant at cathode would be 0.78 V. The tin oxide thus formed can be converted

back to tin by chemical reaction between tin oxide and a fuel such as carbon, hydrogen or CO. The latter reaction is exothermic. Such a cell with molten tin as the anode in contact with carbon fuel produces electricity by direct oxidation of carbon. The operating temperature is around 1000°C. A porous ceramic separator is used to separate the tin melt from the fuel and helps in retaining a thin layer of tin in contact with the electrolyte. The major technical hurdle reported is the excessive anodic polarisation losses due to the use of porous ceramic separator⁸.

Solid carbon in molten carbonate: This technology utilises circulating molten carbonates containing carbon fuel as the anode and oxygen-ion conducting ceramic as the electrolyte⁹. In one configuration, the cell employs a cathode supported tubular cell geometry. Air is supplied via a concentric tube to the cathode consisting of a metal current collector and LSM as the catalyst layer. The circulating molten carbonates mixed with carbon fuel particles are supplied to the anode, which also has a metal mesh / coil current collector. Various types of fuels such as biomass, coal, tar etc. have been tested on this cell. This type of fuel cell is a hybrid between molten carbonate and solid oxide fuel cells with similar materials issues (corrosion of nickel anode and other cell components, and stability of YSZ electrolyte in molten carbonate environments - for example, formation of lithium zirconate in presence of Li / K carbonate eutectic mixture at 700°C)¹².

There is a further class of carbon based fuel cells in which carbon is first oxidised either inside the cell as a part of the system design or externally to CO according to the following reaction:



The CO thus formed then reacts at the electrode/electrolyte interface with O²⁻ to form CO₂.

A dual reaction mechanism is also possible. The carbon particles which make direct contact with the electrolyte react with O²⁻ and are converted to CO₂ as in DCFC and the carbon particles which do not make direct contact with the electrolyte are oxidised first to CO and then in an electrochemical reaction to CO₂.

2.5 Technology Status, challenges and Developers

The main groups working on DCFC include: SARA (molten hydroxide electrolyte); Lawrence Livermore National Laboratory (LLNL) and Contained Energy (molten carbonate electrolyte); CellTech Power LLC (carbon mixed with molten tin, solid electrolyte), SRI International, Clean Coal Energy, Direct Carbon Technologies, St Andrews University, CSIRO Energy Technology, Tokyo Institute of Technology and the University of Akron (solid carbon or carbon mixed with a molten media, solid oxide electrolyte).

The DCFC technology is at an early stage of development with considerable effort required to take it

to the pre-commercialisation stage. Most groups are testing single cells or small stacks. The power densities are low typically in the 100-120mWcm⁻² range compared with 300-600mWcm⁻² for many other fuel cell types and strongly dependant on the fuel delivery system and the anode catalyst or current collector used. Table 2 below summarises the technology status.

DCFC Technology	Status
Molten hydroxide	Average power densities of 40 mWcm ⁻² for over 540h of operation with peak power density of 180 mWcm ⁻² . The maximum efficiency achieved is 60% ⁴ .
Molten carbonate	Power densities to 100-120 mWcm ⁻² , and 80 % efficiency with fuels such as fossil chars, petroleum coke, carbon blacks ^{1,5} .
Solid Oxide - Solid carbon feed	The peak power density achieved is reported to be 140 mWcm ⁻² at 900°C with synthetic carbon agitated with CO ₂ ¹⁰ .
- Carbon mixed with molten metal	The peak power density achieved so far is about 160mWcm ⁻² and 80 mWcm ⁻² respectively from hydrogen and liquid fuel JP-8. The company has built and tested cells, small stacks and systems for short periods of time ⁸ .
- Carbon mixed with molten carbonate	The peak power density achieved is 120mWcm ⁻² using acetylene black as the fuel. SRI International has tested a 6W 6-cell (6 cathode / electrolyte tubes in a single molten salt bath) demonstration stack using different fuels ⁹ .

Table 2 Technology status of various types of direct carbon fuel cells.

Some major technical challenging issues for DCFC are:

- Mode of solid fuel delivery to anode (solid or in molten salt or metal) to maximise interaction at the electrode and electrolyte interface.
- Fuel processing and fuel quality requirements, for example the effect of contaminants in coal, carbon structure and surface area on the DCFC performance.
- Understanding the electrochemical reaction kinetics and mechanism for carbon oxidation (direct and indirect) at the anode / electrolyte interface.
- Stacking of single cell or multi-cell construction to build reasonable size modules for technology comfort.
- Reducing corrosion of cell components especially where molten salts are used either as the electrolyte

or fuel carrier by suitable choice and development of materials and protective coatings.

- Scale-up from laboratory tests (few watts) to prototypes in the several hundred watts to kW range using with continuous fuel feed rather than the batch mode.
- Increasing life time which is currently too short even for reasonable demonstration of the technology), reducing degradation rates and understanding fuel cell and component degradation mechanisms.
- Demonstration of the technology with acceptable power densities at predicted efficiency.

3. CONCLUSIONS

The DCFC technology has some major benefits in terms of potentially highest electrical efficiency of any coal based power generation system, substantial reduction in the amount of CO₂ generated and minimal requirement for post combustion processing to capture CO₂. The projected cost, including balance-of-plant (BOP) of around US\$1000/kW is lower than most other fuel cell types with substantially lower operating costs due to availability of a cheap fuel source. At this stage, the overall investment in DCFC technology is relatively small in comparison with other major fuel cell technologies. Most of the research in universities is directed at individual components of the fuel cell system using small button cells: fuel quality and processing, anode materials and electrochemistry, fuel delivery system, optimisation of cathode and electrolyte, cell design, and understanding the reaction mechanisms. Some research organisations (SARA, Contained Energy and SRI International) are investigating complete systems and have started to build small stacks. The power densities obtained from single cells are typically below 150 mWcm⁻². For comparison power densities of 150-200 mWcm⁻² and 400-500 mWcm⁻² respectively have been reported for molten carbonate and solid oxide fuel cell stacks. A substantial effort is required to demonstrate DCFC technology in the kW range with reasonable life time (several thousand hours) with acceptable degradation rates.

4. ACKNOWLEDGEMENT

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