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Feasibility study for direct carbon fuel cells on Victorian brown coal

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Project “Feasibility of operation of direct carbon fuel cell on Victorian Brown Coal”

Final report

Contents

1 Executive summary

The objective of this project was to undertake a feasibility study investigating the use of Victorian brown coal for power generation in direct carbon fuel cells (DCFC). This project builds on a significant program that has been funded internally at CSIRO to develop DCFC and on an earlier PhD scholarship co-funded by BCIA, Monash University and CSIRO looking specifically at the use of Victorian Brown coal in DCFCs. Previous programs focused on development of a specific type of DCFC with the objective of maximising efficiency. This project, at the request of BCIA, had two parts both related to power generation from Victorian brown coal:

1. A broad examination of fuel cell concepts including near commercial concepts using currently available high temperature fuel cells that can operate on cleaned syngas, low temperature fuel cell systems that operate on pure hydrogen and more advanced blue sky options.
2. A more detailed study of the suitability of Victorian brown coal as a fuel for the high temperature fuel cell concept being developed at CSIRO including an assessment of if this fuel cell could be used in a “gasification” mode where the fuel does not have to be in direct contact with the fuel cell

The objective was to scope out the landscape for using Victorian brown coal in fuel cells for power generation and to provide insight into the technical challenges that need to be overcome to make this a reality. There are a wide range of different system concepts that could be considered. The most commercially mature of which rely on conventional gasification and gas cleaning processes either to produce a clean syngas stream or a high purity hydrogen stream. Detailed techno-economic modelling of specific technologies was not covered in this study. Similarly, the maturity and efficiency of the gasification and gas cleaning aspects of these concepts was out of scope of this study. Literature values and manufacture specifications used to give a high level assessment of a wide range of different concepts and their relative advantages and disadvantages.

The most commercially mature concepts, from a fuel cell perspective, would operate on high purity hydrogen produced via gasification and gas cleaning process. High purity hydrogen can be used directly in commercial polymer electrolyte or phosphoric acid fuel cells. The overall efficiency of this process will be poor. The fuel cell efficiency could be as high as 50% but when combined with the gasification and gas processing efficiency losses the overall efficiency is likely to be below 30%. The waste heat produced from these fuel cells is also too low to be of significant value (50-150°C) so there is little scope for improvement in this efficiency. The low overall efficiency of this concept leads to the use of low temperature fuel cells in combination with coal gasification being seldom considered in isolation. However, if a high purity hydrogen production facility were established in Victoria, as proposed by Kawasaki Heavy Industries and Toyota, then this concept could be realised with no further development of the fuel cells as there are a number of companies that produce commercial fuel cell units that could be deployed in the 1–100 MW range.

The next most mature fuel cell concepts would use existing high temperature fuel cells. These fuel cells are almost exclusively operated on natural gas and are highly thermally integrated with the fuel processor and reformer. These systems could be redesigned to operate in combination with a gasification process as the waste heat from these fuel cells is around 600-800°C. The level of integration strongly affects the system efficiency, level of development work required to produce a MW class prototype and the overall system cost. Overall the nearest term concepts have the lowest efficiency (around 30%) and least integration. Higher efficiency, more integrated concepts would require significant investment to realise a commercial scale prototype. The highest attainable efficiencies possible is likely to be in the order of 60–70% for a fully integrated system. To attain these high efficiencies would require the development of an entirely new fuel cell stack and system rather than modification of existing devices. There is significant uncertainty in these efficiency numbers as no complete system at any scale has been demonstrated operating on Victorian brown coal, however, it is likely that the highest efficiency system for conversion of Victorian brown coal to power would use a fuel cell as opposed to any other combustion based technology.

The CSIRO-developed high temperature fuel cell technology was found to operate equally well in both direct contact mode, where the fuel is fed directly to the surface of the fuel cell, or in gasification mode, where the fuel is separate from the fuel cell but still within the same reactor. A series of tube cell test were performed including a fuel cell operating on a char derived from Morwell coal in a gasification mode. This work builds on previous work carried out by Monash University and CSIRO co-funded by the BCIA (Phd. Scholarship – A. Rady) which focused on direct contact of fuel to the electrode surface in fuel cell of less than 1 cm^2. The cells used in this study represent an order of magnitude increase in the scale of previously funded work and also show the performance of the fuel cell in a gasification mode. Combined this work shows Victorian brown coal to be an attractive fuel for use in direct carbon fuel cells with coals from the Morwell and Yallourn regions being the most promising. Initial cell testing has been restricted to Morwell coals but further work is currently underway via an alternative funding mechanism investigating the performance of coals from the Yallourn region. Results on studies of Yallourn derived fuels will be published in the open literature once the work has been completed.

There continues to be significant effort and interest in DCFC's globally with groups in the EU, China and South Korea becoming increasingly established in the area. CSIRO continues to engage with international groups in this area and has signed an MOU with KIER (Korean Institute of Energy Research) covering DCFC amongst other technologies. A senior delegation from CSIRO visited KIER in 2015 in order to explore joint programs but a suitable funding source is yet to be identified. CSIRO is also actively pursuing joint funding opportunities with Monash University and Imperial College London in the DCFC area via the ARC.

2 Types of DCFC and the advantages of each design

2.1 Operation of a fuel cell and factors that affect efficiency

A fuel cell is an electrochemical device that converts fuel directly into electricity via electrochemical oxidation [**1**]. **Figure 2-1** shows the 3 main components of the anode, electrolyte and cathode. In terms of operation, oxygen molecules are ionised at the surface of the cathode to form oxide ions (O^{2-}). These ions are transferred to the anode via the electrolyte. At the anode they react with the fuel to produce CO_2 and H_2O molecules. The cathode process results in the consumption of electrons and the anode processes result in the release of electrons. Ions can pass through the electrolyte but not electrons. This results in the electrodes becoming polarised with the concentration of electrons on the anode increasing and the concentration on the cathode decreasing. If there is no electrical connection of the cathode to the anode the cell reaches equilibrium and the electrochemical reactions stop. If the electrodes are connected electrically, electrons flow from the anode to the cathode producing electrical current and discharging the electrodes. This process allows further electrochemical reactions to occur which lead to the fuel cell continuously producing electricity. Provided fuel is present at the anode and air is continuously fed to the cathode this process will occur indefinitely.

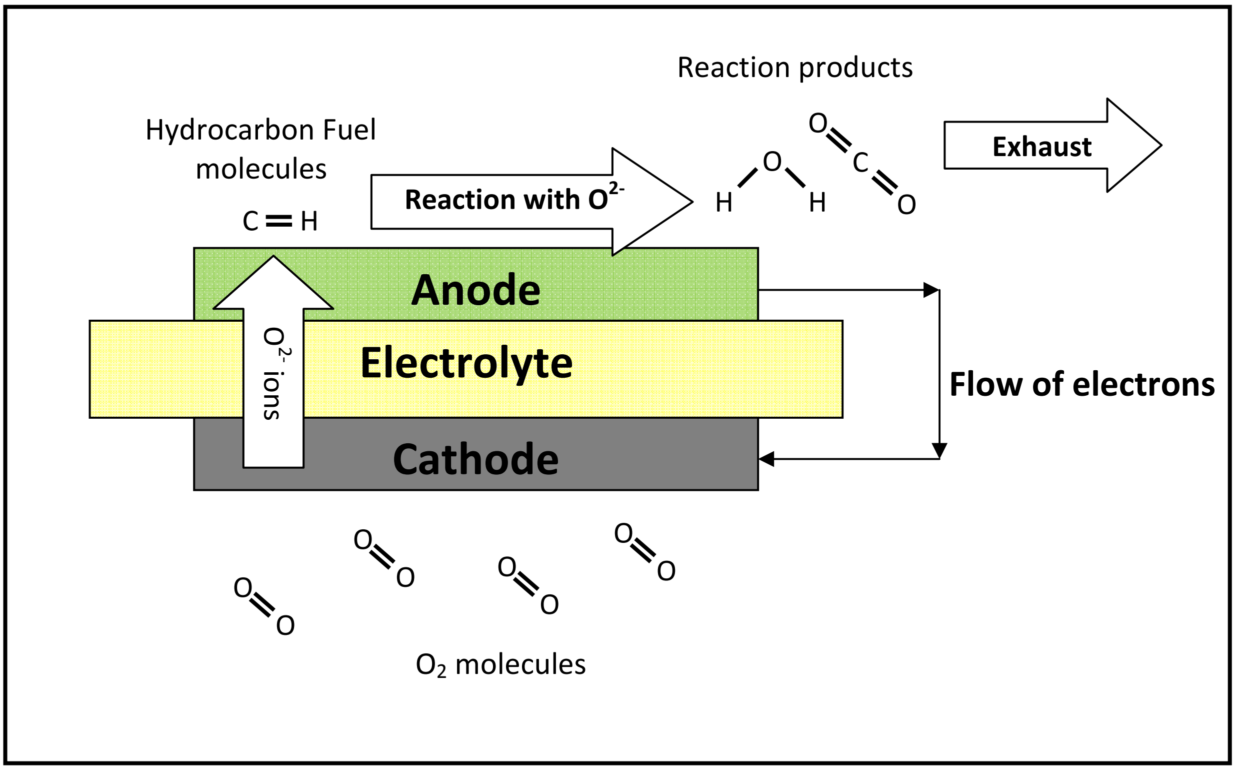


Figure 2-1 **Diagram showing operation of a high temperature oxide ion conducting fuel cell**

During operation the fuel cell will produce both heat and electrical power. The maximum theoretical electrical output of a fuel cell is determined by the Gibbs free energy of the reaction (1) with only the Gibbs free energy being available for the generation of electrical power [**1**].

$\Delta G = \Delta H - T\Delta S$ (1)

Where ΔG = Gibbs free energy

ΔH = enthalpy of the fuel oxidation reaction

ΔS = entropy term

T = temperature

With the total maximum theoretical efficiency (ϕF_{th}) being the ratio of the free energy (ΔG) to the enthalpy (ΔH):

ϕF_{th} (%) = $(1-(T\Delta S/\Delta H)) \times 100 = (\Delta G/\Delta H) \times 100$ (2)

This is essentially the ratio of heat to electric power produced for any given reaction. Direct reaction at the electrodes in a single step is not possible with even oxidation of very simple molecules such as hydrogen happening in multiple adsorption, decomposition and desorption steps. However, if all of these steps involve the electrode and are electrochemical in nature then the sum of the reaction steps can be used to calculate the theoretical efficiency. **Table 1** presents some of the typical reactions that occur within a DCFC and their potential efficiency at 980°C. Reactions with greater than 100% efficiency absorb heat energy from the system and those with less than 100% efficiency produce heat.

Reaction	n	-ΔH (kcal/mol)	-ΔG (kcal/mol)	E_{OCV} (V)	$øF_{th}$ (%)
$H_{2(g)} + ½O_{2(g)} \rightarrow H_2O_{(g)}$	2	57.8	54.64	0.97	72
$C_{(s)} + ½O_{2(g)} \rightarrow CO_{(g)}$	2	26.4	32.8	1.16	197
$CO_{(g)} + ½O_{2(g)} \rightarrow CO_{2(g)}$	2	67.6	61.5	0.9	61
$C_{(s)} + O_{2(g)} \rightarrow CO_{2(g)}$	4	94.1	94.3	1.03	100

Table 1 Thermodynamic efficiency of different cell reactions

In reality, when oxidising a complex fuel such as carbon or coal, there are multiple reaction pathways involving a number of intermediate steps. Some of the reactions are electrochemical in nature involving the electrode with others being chemical (i.e. not interacting with the electrodes). Chemical reactions absorb or create heat but do not contribute to the fuel cell operating voltage and hence do not directly produce electricity. If the fuel is not in contact with the electrode then the fuel must be first gasified before it can react with the electrode and will need to consume heat for these reactions to occur. If the fuel is in contact with the electrode then it can be, at least in part, directly oxidised/gasified by ionic species in the electrode. These reactions are electrochemical in nature and will therefore contribute to the overall cell voltage. The overall maximum theoretical efficiency of operating on these fuels is essentially the ratio of the sum of all of the electrical power generating reactions (i.e. the total Gibbs free energy terms) to the sum of all of the heat produced by those reactions (i.e. the total enthalpy terms) plus the sum of any exothermic or endothermic chemical reactions (i.e. the total enthalpy term for the chemical reactions) or:

$$øF_{th} = (\Sigma_{\Delta G}/(\Sigma_{\Delta H\text{-electrochemical}} + \Sigma_{\Delta H\text{-chemical}}) \times 100 \qquad (3)$$

Where $\Sigma_{\Delta G}$ = Sum of the Gibb's free energy terms for the electrochemical reactions

$\Sigma_{\Delta H\text{-electrochemical}}$ = Sum of the enthalpy terms for the electrochemical reactions

$\Sigma_{\Delta H\text{-chemical}}$ = Sum of the enthalpy terms for the chemical reactions

Clearly no system ever operates at 100% of its theoretical efficiency. Losses include the polarisation losses at the electrodes, the concentration polarisation losses, the ionic transfer losses, electrical conductivity losses and fuel utilisation losses. All of these result in the generation of additional heat within the system with the exception of fuel utilisation which is related to the amount of unreacted fuel in the exhaust stream.

Within the majority of fuel cell systems the fuel exhaust stream is mixed with air and combusted in an off gas burner to produce additional heat. The waste heat of high temperature fuel cells is around 800°C and can be boosted to 900–1000°C if combined with an exhaust off gas burner. When all of the losses are taken into account a fuel cell stack operating on hydrocarbon fuels (such as reformed methane) will have a cell efficiency of around 40–50%. The methane is not directly oxidised within the fuel cell stack and must first reformed to hydrogen and carbon monoxide. This process is highly endothermic with the waste heat from the fuel cell used to reform the fuel.

Once reformed to syngas the thermal content of the fuel increases by up to 25%. This higher energy content fuel is then consumed within the fuel cell stack producing more heat which is then further recycled via reforming of more fuel entering the system. This thermal recycling within the system leads to realistic total system efficiencies of high temperature fuel cell systems being in between 50–60% [**2**]. In a similar way waste heat from a high temperature fuel cell can be used within a heat engine to recover some of the waste heat. This is normally done via the production of high pressure steam which is fed to a steam turbine. Recovery of waste heat in this manner can add up a further 5-10% on the overall system efficiency [**3**].

In addition to high grade (600°C+) waste heat from a fuel cell there is also a significant amount of medium (300–600°C) and low grade (300°C) heat produced that can be used for any number of processes such as hot water heating, process heating, drying and cooling (if used within an absorption chiller) [**1-3**]. If both the high and low grade heat can be used then it is quite possible to achieve efficiencies in excess of 80% CHP [**1-3**]. The flexibility and availability of waste heat from a fuel cell provides many design options that can potentially lead to very high efficiency in a number of different applications [**3**].

2.2 Design considerations for operation of a fuel cell system operated on Victorian Brown coal.

Victorian brown coal is a low cost and abundant resource [**4**]. Its chemical makeup is varied as are the forms that it can be used for power generation. How brown coal is used within a fuel cell, what type of fuel cell is used and what level of processing the coal has been through before use will all affect the efficiency and technical challenges associated with using brown coal within a fuel cell. In this report we discuss a number of different scenarios for the use of the waste heat produced by a fuel cell for the processing of brown coal prior to its use within a fuel cell. Although low temperature polymer electrolyte membrane (PEM) fuel cells are discussed none of the scenarios discussed here involve the production of hydrogen from brown coal and its consumption in a low temperature fuel cell. This is because the use of a low temperature system would not allow for any thermal recycle within a system and thus would lead to round trip efficiencies lower than all of the systems considered here. CSIRO has significant capability in low temperature fuel cells and in the production of hydrogen from coal (including gasification, water gas shift reactors, gas separation, carbon capture and gas clean up). This capability could be used to assess the feasibility of this indirect route to power but the focus of this report is the direct production of power from coal within high temperature fuel cells.

Figure 2-2 gives an overview of the 6 stages that must occur to allow the consumption of brown coal within a fuel cell to produce electrical power and the energy flows for each stage.

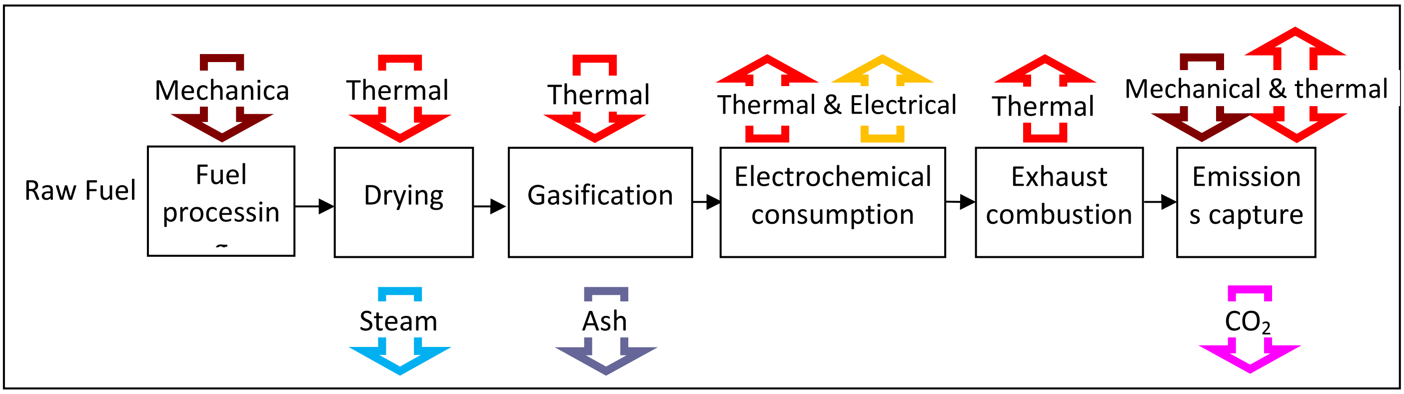


Figure 2-2 **Stages and energy flows that would allow for the consumption of brown coal within a fuel cell**

The ultimate aim of any power conversion process is to extract the maximum amount of useful energy from the fuel at the lowest possible cost. In the case of direct carbon fuel cells operated on Victorian brown coal, the useful energy is electrical energy with the thermal energy produced by the system being of limited value unless utilised within the system to produce more electrical power. As with other high temperature devices the waste thermal energy from a high temperature fuel cell can be used to dry, preheat or gasify the coal and other solid fuels. How effectively this can be done within a fuel cell system is largely determined by 2 factors:

1. The physical distance between the fuel cell and the fuel,
2. The quality (temperature) of the thermal energy

These 2 factors essentially determine the efficiency of the heat transfer and what the waste heat can be used for (i.e. drying can be done at below 100°C but high temperature process such as producing steam for a steam turbine or gasification would need temperatures in excess of 600°C). The waste heat from the exhaust stream of a fuel cell is can be access either as a hot gas stream (inert, oxidising or slightly reducing) or used to heat water or a separate gas stream via a heat exchanger. Within this report we will only consider coal to electrical power options although there are clearly opportunities for the use of fuel cells for the processing of brown coal where significant thermal energy is required for a process.

The energy content in Victorian brown coal ranges from 6 MJ/kg for wet coal to around 30 MJ/kg for dried coal [**4**]. The high moisture content is the main driver for the reduction in thermal energy with typical raw freshly mined coal having around 60% water content [**4**]. This high water content makes Victorian Brown coal less attractive for heat engines but provides a ready source of steam for any gasification process provided sufficient heat can be supplied to decompose the coal to syngas (note. Conventional high temperature fuel cell stacks consume syngas, CO and H_2, typically produce via the reforming of hydrocarbon fuels internally within the fuel cell system). The low level of ash content is also attractive quality for a fuel feedstock for a high temperature fuel cell system.

A wide number of system concepts have been suggested which use coal of various types for use with high temperature fuel cells. This has included concepts specifically looking at Victorian Brown coal [**5**]. In this report we shall consider the following 4 broad scenarios for the use of Victorian brown coal as a feedstock for use within high temperature fuel cells:

- A simple autothermal system
- A thermally integrated but separate gasification system
- A direct gasification system (where the fuel is fed to the anode)
- A direct reaction system (where the fuel directly reacts with the fuel cell electrodes)

These scenarios represent 4 families of system types and cover the majority of systems under consideration for the production of power from solid fuels within a high temperature fuel cell. We provide a broad overview of each system and then a discussion around the advantaged and disadvantages of each technical path for power generation. None of the system concepts proposed involve the production of hydrogen for the consumption in low temperature fuel cells or for export with all systems essentially operating on brown coal with the objective being to produce electrical power at high efficiency. In addition to the 4 high temperature scenarios a final scenario has been added which includes the use of low temperature fuel cells for power generation attached to a plant where the main output is hydrogen for an alternative use with power generation being of secondary importance. This is discussed separately as the primary focus of this report is the use of Victorian brown coal for power generation only.

2.2.1 Autothermal system

The most mature system concept for utilising brown coal within a fuel cell comprises of an initial autothermal gasification system followed by a completely separate fuel cell step (**Figure 2-3**). Below is a schematic of a system proposed by Lee et al [**6**]. In this system the air separation unit, gasifier and fuel cell unit are all separate with no recycle of the thermal energy at any stage. Some efficiency gain is possible if hot gas clean up is used as the gas leaving the gasifier can then be used directly in the fuel cell without first pre-cooling and then reheating but essentially this is the least integrated of all systems discussed here.

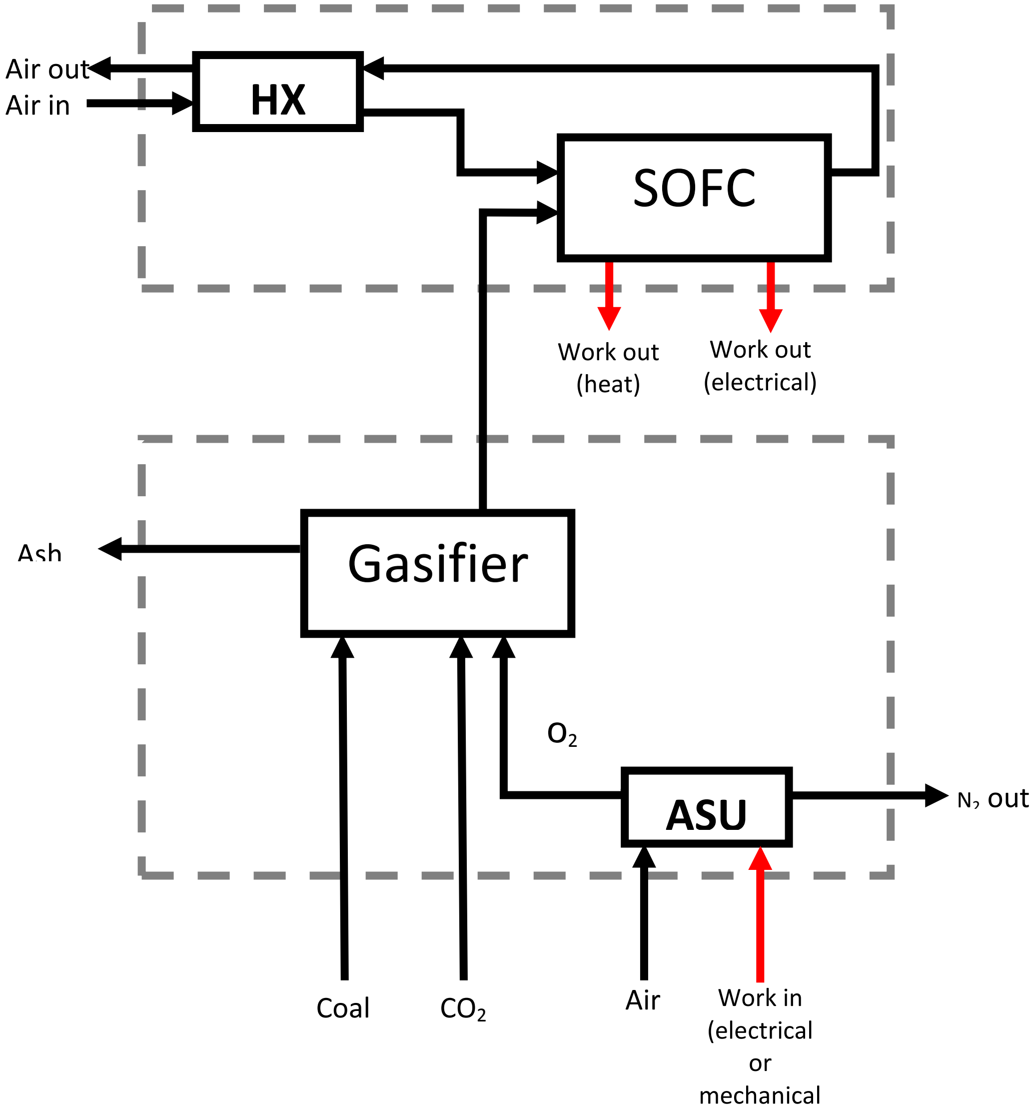


Figure 2-3 System configuration of and autothermal gasifier. Abbreviations used in figure - HX – heat exchanger, SOFC – solid oxide fuel cell and ASU – air separation unit. Figure adapted from [6].

2.2.2 Thermally integrated physically separate gasification system

The next stage in complexity in terms of system design is to thermally integrate the gasifier with the fuel cell stack. **Figure 2-4** shows a schematic of how this could be potentially achieved and is based on a system proposed by Lee et al [**6**].

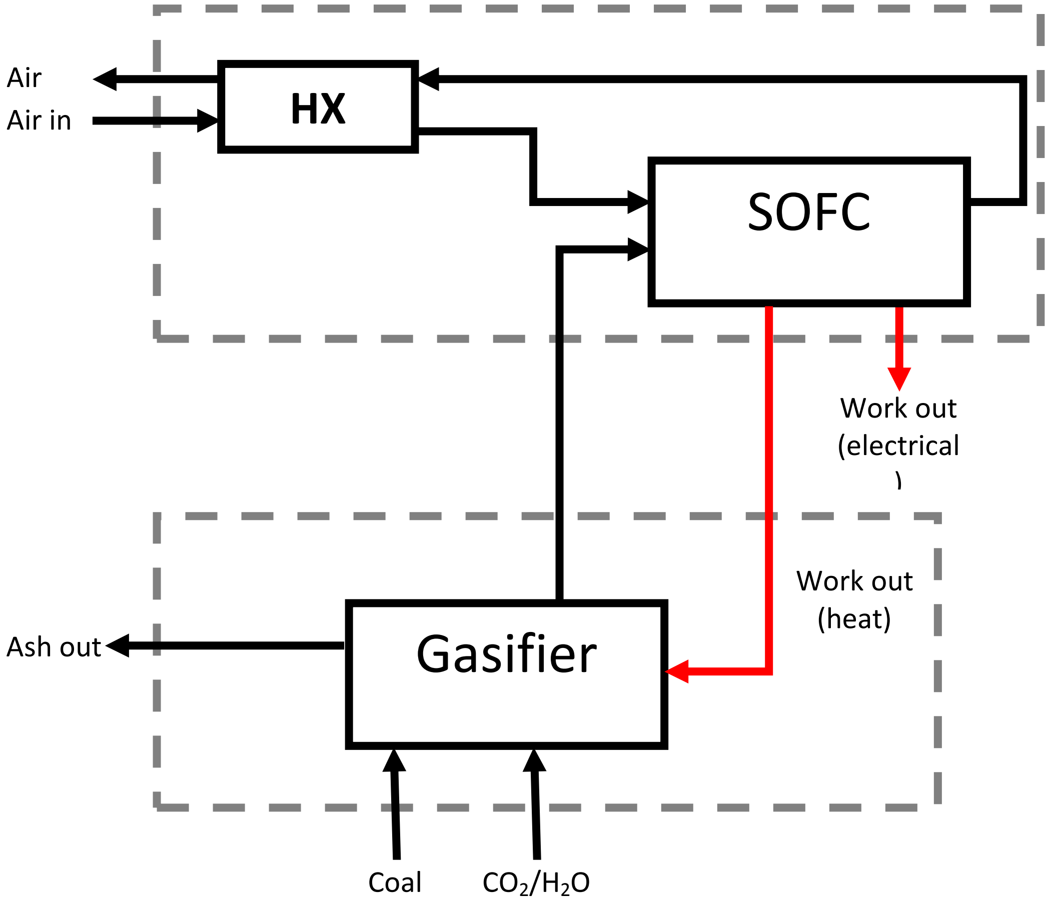


Figure 2-4 System configuration thermally integrated gasifier and fuel cell. Figure adapted from [6].

In this system design, the gasifier is fed thermal energy from the solid oxide fuel cell (SOFC) plant. This can be achieved through the supply of the exhaust gas from the SOFC to the gasifier. In this way the SOFC acts as the ASU. If this is to be a self sufficient system where the only input is coal and the only output is electrical power then it is necessary to only recycle a small percentage of the exhaust directly to the gasifier. The remainder of the exhaust gas can be used to pre-dry the coal before it enters the gasifier. The exhaust temperature of a typical SOFC can be in the range 600–950°C with around 800°C being typical. It is possible to use other types of high temperature fuel cell such as molten carbonate fuel cells (MCFC) although these typically have lower operating temperatures and hence lower temperature exhaust streams. High temperature fuel cell stacks typically consume up to 90% of the fuel supplied to them. This allows the heat of the exhaust to be boosted via the injection of oxygen (or air) in to the exhaust stream if required.

If the exhaust stream of the fuel cell is used to provide heat for a fuel processor then the performance (in terms of life time and cell level electrical efficiency) can be increased because the fuel utilisation of the fuel cell stack can be reduced. This increases the life and performance of the fuel cell stack as high concentrations of exhaust products (CO_2 and H_2O) combined with low concentration of fuel gases (CO and H_2) can lead to lower performance and higher degradation. Clearly running the SOFC at lower fuel utilisation will result in a reduction in the efficiency of the fuel cell stack, however, if the heat from combusting the remaining fuel gas in the exhaust stream can be efficiently recycled via the integration of the fuel cell with a gasifier the total overall system efficiency (coal to power) can be increased.

2.2.3 A direct gasification system

A direct gasification system is a fully integrated system where the fuel and fuel cells are typically contained within one chamber. The fuel in this design is separated from the air via the fuel cell membrane. This type of system was the basis of the contained energy concept that looked to integrate

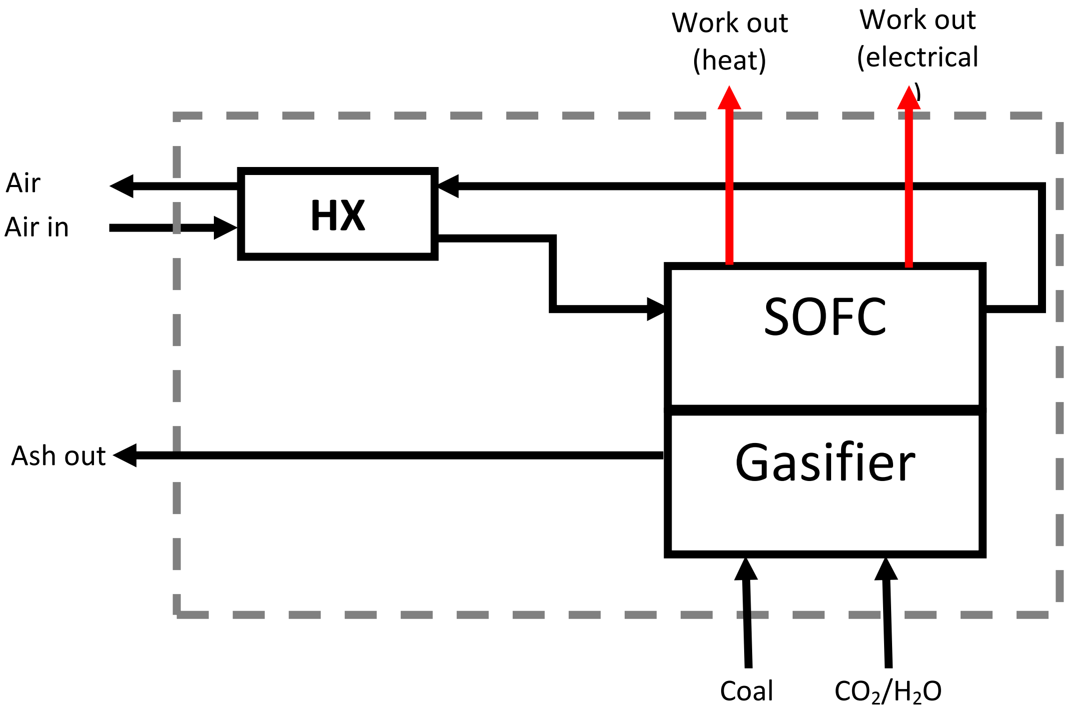


Figure 2-5 **System configuration direct gasifier fuel cell system. Figure adapted from [6].**

a fluidised bed reactor with a fuel cell [**1**]. The figure above shows the system with a barrier between the fuel cell and the gasifier in reality this barrier is often not present with the fuel cell coming into direct contact with the fuel. In both systems the reactions and heat flow are essentially the same with the waste heat and products of the fuel cell being consumed in the gasification process which then produces more fuel for the fuel cell. Additional CO_2 or H_2O may be added to the system although this is typically not needed as both these species are produced via the anode reactions. The gasification reactions occur in close proximity to the anode providing good thermal transfer between the fuel and the fuel cells but are not electrochemical in nature (i.e. do not produce power).

2.2.4 Direct reaction system

Direct reaction systems share many of the system components with direct gasification systems and in terms of physical appearance may be very similar. The coal is fed directly to the fuel cell surface where the chemical and electrochemical reactions occur directly on the anode surface. Molten salt DCFC's operate in this manner and more recently a solid state system has been pioneered at CSIRO and involving a mixed ionic electronic conducting anode materials [**7**]. These systems typically operate a mixed reaction mechanism with some of the gasification reactions involving the electrode and thus being electrochemical (power generating) in nature [**7-8**]. This is different to the direct gasification systems where the fuel cell consumes CO and H_2 with these chemical species being produced within the anode chamber via chemical (non-power generating) reactions. In terms of number of system components and degree of system complexity this is the simplest. The main challenges of directly feeding coal to the fuel cell are the delivery mechanism and the second is the close proximity of the chemical impurities within the fuel to the fuel cell anode. It is not envisioned that this system would be able to operate on an unprocessed raw coal without some degree of pre-processing.

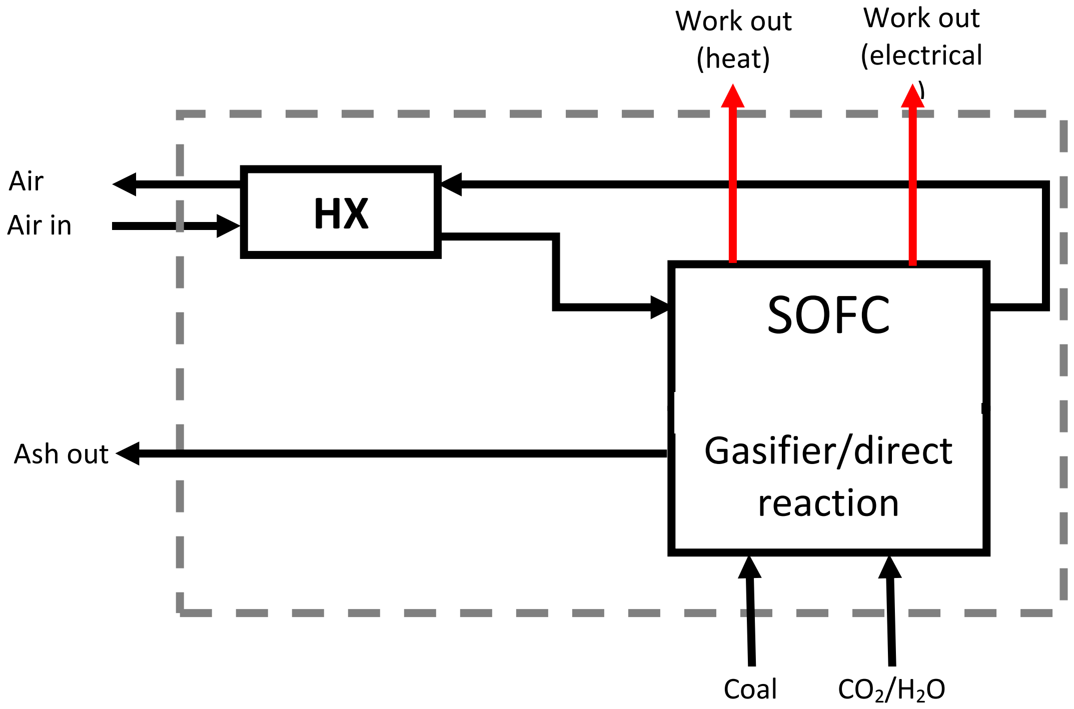


Figure 2-6 **System configuration for direct reaction fuel cell**

2.3 Comparison of system concepts and their suitability for use with Victorian brown Coal.

When assessing the viability of a fuel cell system concept there are four key factors that need to be taken into account: efficiency, lifetime, power density and scalability. These factors ultimately affect the price per kWh of power produced. **Figure 2-7** graphically depicts how these factors interact and the key issue that they relate to. Each factor is discussed in more detail individually for the system concepts described above.

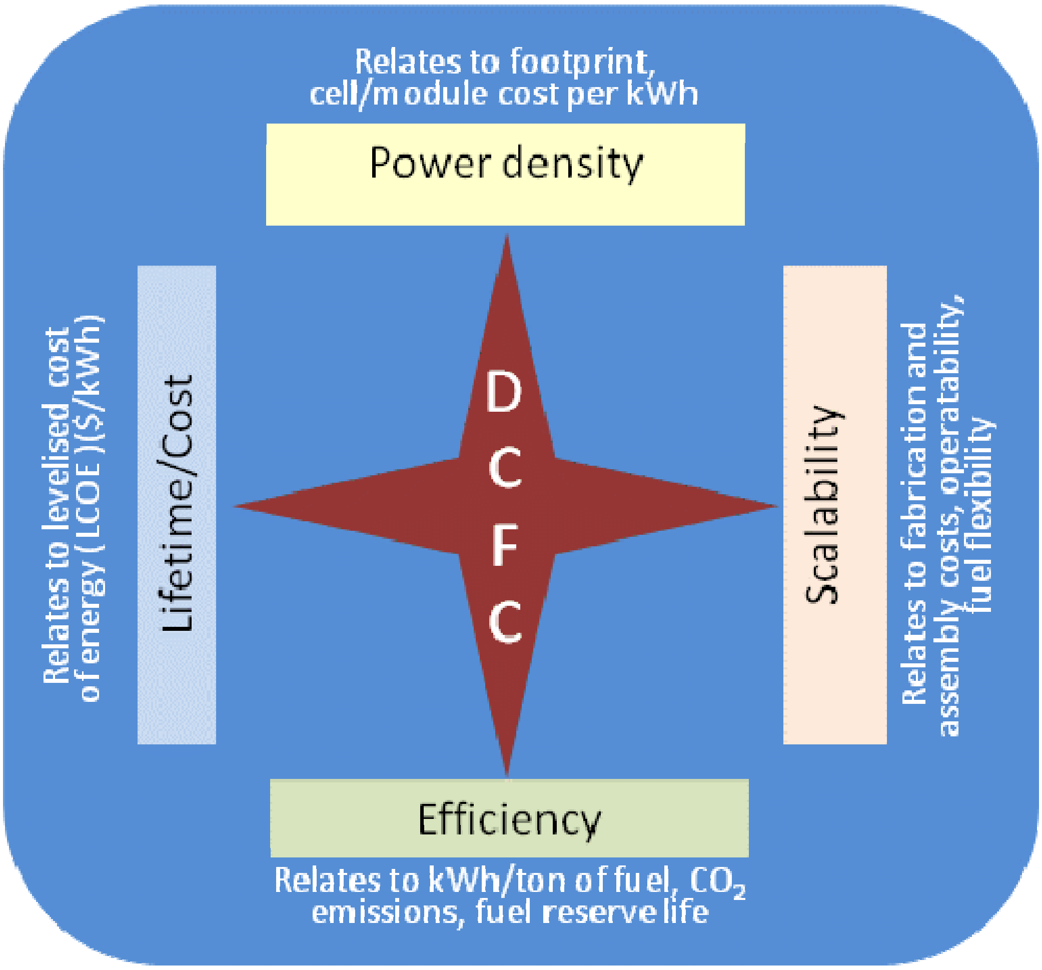


Figure 2-7 **Graphic depiction of the important factors to consider when considering a fuel cell system design.**

2.3.1 Efficiency

In general, the total system efficiency of a fuel cell is largely governed by the electrical efficiency of the fuel cell, fuel utilisation and the efficiency of any thermal recycle/fuel processing internally within the system. There are other losses as discussed in the introduction but it is largely these three factors that determine the absolute efficiency of a system.

The fuel cell stack efficiency of the majority of high temperature SOFC type fuel cell stacks is high, with a value of around 50% being typical [**1-2**]. In the first three concepts described previously the stack efficiency will remain reasonably constant as the fuel cell stack in all three concepts is operating on a mixture of CO and H_2 produced via gasification so is largely the same in terms of operation. Slight improvements may be possible in the system in **Figure 2-4** (the thermally integrated gasification system) as the fuel utilisation in this type of system could be lowered slightly provided the heat could be efficiently recovered in the gasifier. The final concept where a proportion of the solid fuel is directly reacted at the surface of the electrode surface has the potential to have a much higher stack efficiency. When operated in this mode fuel cells operated in laboratory conditions have been reported to offer efficiencies in the range 60–80% [**1**].

In terms of confidence in achieving these efficiencies in commercial fuel cell stacks there is a clear divide between the direct reaction systems and the separate systems. There are a number of commercial fuel cell systems operating on CO and H_2 from methane reforming that offer 50% stack efficiency so it is reasonable to expect efficiencies in this range for a system operated on syngas produced via gasification (i.e. **Figure 2-3 and 2-4**). There is yet to be a full scale demonstration of a fuel cell stack operating in direct reaction or direct contact with a solid fuel so the ultimate efficiency of a commercial system of this type is still unknown although it would be reasonable to expect that for a mature system that the stack efficiency would be higher for a direct reaction type system.

The fuel utilisation within any given system would be 100% with the fuel cell stack only consuming in the range 75–95% of the fuel and the remainder oxidised chemically within the off gas burner to generate heat for the fuel processor, maintain the systems operating temperature or used to preheat the fuel as it enters the fuel cell stack. If, as in the first concept (**Figure 2-3**), the heat from the off gas burner is not recovered within a gasifier then the fuel cell stack would be operated with the maximum fuel utilisation possible (i.e. around 95% fuel utilisation). This can reduce stack life, reduce the stack efficiency and reduce fuel cells power density. In all other system concepts there is a high degree of thermal recycle. This is the key differentiator between fuel cell systems in terms of efficiency.

Table 2 compares the electrical efficiency of a number of commercial systems and a number of modelled DCFC concepts from various literature sources. The PEM fuel cell operated on natural gas has the lowest efficiency of all the commercial systems with the molten carbonate fuel cell (MCFC) and the SOFC having 10–20% greater efficiency. This relates to the quality of the waste heat produced from the fuel cell stack. PEM systems are low temperature operating at around 80°C with the high temperature systems (MCFC and SOFC) operating well above 600°C. The high temperature systems also typically upgrade the waste heat that they produce to a higher temperature via an off gas burner. In a high temperature natural gas system, this waste heat is consumed within a steam reformer to create a mixture of H_2 and CO. This allows these fuel cell systems to effectively recycle some of the heat into the incoming fuel by converting the natural gas into a hydrogen rich syngas stream which has a thermal value of 25% more than the incoming raw fuel. This leads to an increase in system efficiency of the high temperature systems. The low temperature operation of the PEM system does not allow for thermal recycle and thus, despite low temperature PEM systems having almost 100% fuel utilisations and a more than 10% higher maximum theoretical efficiency, the PEM system is still less efficient when operated on hydrocarbon fuels.

Number	Fuel cell type	Fuel	System type	Efficiency	reference
1	*PEM*	*natural gas*	*autothermal reformer*	*35-40%*	*[**9**]*
2	*SOFC*	*natural gas*	*thermally integrated reformer*	*45-60%*	*[**2**]*
3	*MCFC*	*natural gas*	*thermally integrated reformer*	*45-55%*	*[**10**]*
4	SOFC	pure carbon	autothermal reformer	35%	[**6**]
5	SOFC	Black coal (various)	autothermal reformer	33-35%	[**6**]
6	SOFC	Black coal (various)	autothermal reformer + bottoming cycle	49-50%	[**6**]
7	SOFC	pure carbon	thermally integrated gasifier	58%	[**6**]
8	SOFC	Black coal (various)	thermally integrated gasifier	39-54%	[**6**]
9	SOFC	Black coal (various)	thermally integrated gasifier + bottoming cycle	54-65%	[**6**]
10	SOFC	pure carbon	Direct gasifier	58%	[**6**]
11	SOFC	Black coal (various)	Direct gasifier	40-55%	[**6**]
12	SOFC	Black coal (various)	Direct gasifier + bottoming cycle	54-63%	[**6**]
13	SOFC	Vic. brown coal	thermally integrated gasifier + bottoming cycle	46%	[**5**]
14	SOFC	Coal (unspecified)	thermally integrated gasifier + bottoming cycle	62%	[**11**]
15	SOFC	Coal (unspecified)	thermally integrated gasifier + bottoming cycle	49%	[**11**]
16	SOFC	Coal (unspecified)	thermally integrated gasifier + bottoming cycle	52%	[**11**]
17	SOFC	Coal (unspecified)	thermally integrated gasifier + bottoming cycle	45-51%	[**12**]
18	SOFC	Coal (unspecified)	thermally integrated gasifier + bottoming cycle	55%	[**13**]

Table 2 **Summary of system efficiencies of different fuel cell concepts (entries in Italics are for commercial systems)**

The simplest system concept described in this report is the non-integrated autothermal reformer (system layout presented in **Figure 2-3,** systems 4 and 5 in **Table** 2). This system operates in similar manner to a PEM fuel cell with none of the waste heat from the fuel cell used anywhere else within the system. This system consists of an autothermal coal gasifier with no thermal recycle. This leads to comparably low system efficiencies. Lee et al. carried out detailed modelling looking at a range of carbon and black coal fuels and found the efficiency in all cases to be around 35% [**6**]. The inclusion of a simple steam turbine bottoming cycle greatly increases the efficiency to around 50% (system 6 in **Table 2**) highlighting the importance of utilising the waste thermal energy within a high temperature fuel cell [**6**].

The thermal integration of the fuel cell stack (as in **Figure** 2-4, systems 7 and 8 in **Table 2**) and the gasifier has three main benefits with respect to system efficiency:

1. It utilises the waste heat from the fuel cell stack operation
2. It eliminates the requirement for an air separation unit or steam generator as the exhaust of the fuel cell can be used within the gasifier.
3. The system efficiency becomes less sensitive to the fuel utilisation within the fuel cell stack.

In a like-for-like comparison Lee et al. found the efficiencies of this type of system when compared to a simple autothermal system to be between 5–25% higher (39–54% electrical efficiency) [**6**]. If a bottoming cycle is included this efficiency can be increased to over 60% (**Table 2**) [**6**]. One of the major challenges, however, is that as the system becomes more integrated the efficiency becomes more fuel dependant with the range of efficiencies in **Table 2** increasing on greater thermal integration. This modelled variation is purely related to the fuel with Lee et al. keeping the system largely constant. In terms of the efficiencies to expect from Victorian brown coal there is only limited information available. Kuchonthara et al. have carried out a modelling study looking at utilisation of Loy Yang coal within an integrated fuel cell–gas turbine–gasifier system [**5**]. This study suggested that system efficiencies around 46% are attainable with brown coal. Although earlier studies by the same group on an idealised fuel suggest that, with appropriate levels of steam recycling, efficiencies in excess of 60% could be attained [**14**].

One method to further increase efficiency is to reduce the thermal losses between the gasifier and the SOFC stack. This is best achieved via the reduction in the distance between the gasifier and the fuel cells with the ultimate high efficiency solution being to carry out the gasification reactions within the fuel cell anode chamber. Lee et al. modelled this assuming no electrochemical reaction between the fuel cell anode and the fuel [**6**]. The results of this are shown in **Table 2** (systems 7 and 8 thermally integrated but separate gasifier, systems 10 and 11 direct gasification). There is only a modest increase in this instance over a thermally integrated but physically separate gasifier (i.e. the difference between **Figure 2-4**, thermally integrated but separate and **Figure 2-5** direct internal gasification). The improvement in efficiency varied slightly dependant on the fuel characteristics but overall the the increase in efficiency was approximately 1%. This is largely due to the fact that any increase in thermal efficiency is largely offset by reductions in fuel utilisation and due to the fact that the thermal losses in the separate thermally integrated gasifier system proposed by Lee et al. are not significant enough to dramatically reduce the total system efficiency.

Lee et al.'s work and work by others looking at total system efficiency of thermally integrated fuel cell systems suggests that simply improving the thermal efficiency of an integrated system is unlikely to result in a significant increase in that of the fuel cell system [**1, 5-6, 11-14**]. If a step change in efficiency is required then it is necessary to increase the efficiency of the fuel cell stack. This can only realistically be achieved if some or all of the gasification of the fuel occurs at the anode electrode of the fuel cell and if these reactions are electrochemical (i.e. electrical power generating in nature). These reactions will occur in multiple steps, however, and it is highly unlikely that all of these steps will be constrained to the electrode surface. It has been shown experimentally that it is possible to achieve cell efficiencies of up to 80% in molten salt systems with near 100% fuel utilisation [**1**]. If this could be translated into a real system this would likely result in a total system efficiency of around 70%. Although this is attractive, oxidation of carbon in a molten salt is unlikely to be practical due to the highly reactive nature of the molten salt towards other fuel cell components such as electrodes and bi-polar plates which separate each cell.

CSIRO has pioneered a cell design that is entirely solid state using ceramic oxides that can conduct both ions and electrons (mixed ionic electronic conductors—MIEC) [**7-8**]. This system has the advantage of allowing at least partial reaction of solid fuels on the electrode surface. This cell design can also consume gaseous fuel in a conventional manner to a commercial fuel cell which improves its practicality as in any mature system design the fuel will at least partially gasify before reaching the cell. This hybrid fuel cell design offers the potential to increase the efficiency but further work will need to be carried out before the final benefits of the design can be understood. However, fundamentally this fuel cell design is not limited to total system efficiencies below 70% as is the case with hydrogen fuel cells (DCFC have a theoretical maximum efficiency of around 100% at 800 ^{o}C).

In terms of potentially increasing the efficiency significantly past 50% for a realistic Victorian brown coal system the current options are:

1. Use of an advanced thermally integrated gasifier and fuel cell system with a steam turbine for recovery of waste heat (**Figure 2-4** with bottoming cycle)
2. Processing of the fuel to bring it to a more optimal form for use in an integrated direct gasification fuel cell system without a steam turbine (**Figure 2-5**)
3. Use of an advanced fuel cell concept with a higher efficiency (such as the CSIRO's solid state DCFC) without gasifier or steam turbine (**Figure 2-6**)

These three options would most likely lead to a final mature system with efficiency of around 55–65%.

2.3.2 Lifetime

There are now a number of commercial fuel cell systems on the market that can provide some good indications of expected lifetime of systems with little or no integration of system components (**Figures 2-3 and 2-4**). The 2 companies currently producing large scale fuel cell systems that would be suitable for utility scale power generation are Bloom Energy (who manufacture SOFCs) and Fuelcell Energy (who manufacture MCFC). POSCO power in South Korea also manufacture MCFC power plants via a licensing agreement with Fuelcell Energy. The largest single plant currently in operation is 60 MW MCFC based in South Korea.

Both SOFC and MCFCs have a system life time of around 20 years although the fuel cell stack will typically need to be replaced after 3 (MCFC) or 5 (SOFC) years of operation. Both of the high temperature systems mentioned here operate on natural gas or bio-gas and have integrated internal reformers. This would make these systems inherently thermally unstable if operated directly on syngas although this is what the fuel cell stack consumes. Fundamentally there is no reason why a high temperature fuel cells cannot operate on the (cleaned) syngas from a gasifier (mainly CO and H_2) with the simplest system being based on the concept shown in **Figure 2-3** with the fuel cell being modified to allow it to maintain its thermal stability (i.e. the reformers in a fuel cell play an important role in the thermal management of the system, supply of syngas directly to a commercial fuel cell system would likely make it thermally unstable).

The main technical challenge to this approach is fuel cell lifetime with the impurities within a conventional gasifier stream leading to rapid degradation of the fuel cell. The major impurities that can result in fuel cell degradation are the acidic gases (mainly sulfur) which can lead to rapid degradation of the SOFCs with levels of 100 to 500 ppm range and at less than 100 ppm for MCFCs. Clearly it is possible to purify the gas produced from a gasifier to a level that is required for a conventional fuel cell stack but this can make thermal integration challenging. As discussed above, without adequate thermal integration the efficiency is not sufficient to warrant the additional cost of a fuel cell system over a conventional gas turbine. There are a range of emerging technologies particularly membrane separation based on materials other than Pd-Ag alloys that could alter the technological landscape by providing a low cost purification method that can be used at elevated temperatures.

It is possible to increase the lifetime of the fuel cell stack by the use of ceramic anodes but these are yet to be fully developed to the point where they can perform to the same level as current generation of Ni-YSZ anodes. CSIRO's DCFC concepts all typically use ceramic anodes that would be more tolerant of fuel base impurities. Although it is possible to purify the syngas to a level required for a high temperature fuel cell today most fuel cell organisations have focused exclusively on developing a natural gas fuelled products where only desulfurisation is required.

One clear advantage of having a separate gasifier and fuel cell is that the gasification process can remove many solid and molten ash impurities. This process may not be 100% efficient with some solid impurities potentially entering the fuel cell system, however, the level of impurities would be significantly reduced. This is because these impurities will not be transferred to the fuel cell stack in the gas stream; however, if the fuel is within the same chamber as the fuel cell then these impurities can be transferred to the surface of the fuel cell. This can be particularly damaging if Si in combination with Na or K are transferred to the electrodes. It is likely that the key challenge for any direct carbon or coal fuel system will be the interaction of fuel cell impurities with the fuel cell stack.

2.3.3 Power density

In general power density is the second main cost driver to lifetime as it determines the size of the system and all of the peripheral components. In terms of differences between the systems described here, essentially all of the systems operate on syngas with the exception of the direct reaction concept which also relies on some direct reaction of fuel at the electrode. In terms of power density the first two systems concepts operate very much in a similar manner to a conventional fuel cell and should offer the highest performance. The direct gasification system has some design constraints put on it by the fact that the fuel is in the anode chamber which reduces the flow rate of reactants and will lower the performance of the fuel cell. Direct reaction systems offer the lowest performance as the fuel must be in contact with the electrode which partly impedes the flow of reactants to the surface of the electrodes. The contact of the fuel with the electrode also limits the use of materials that can be used for the fuel cell anode which can further reduce power density. Contact of the fuel with the electrode is not all negative with the fuel acting as an electrical current collector which can reduce the ohmic losses of a fuel cell and increase power density.

In terms of a like-for-like comparison of fuel cell performance of the concept systems described above there is very little information available in the literature. There is a number of reports where people have operated fuel cells in excess of 300 mW/cm^2 in systems that directly react solid fuels with the electrode or via systems that a gasify the fuel before consuming it within the fuel cell [**1,2**]. These power densities are in line with fuel cells operated on reformed natural gas and suggest that there is no significant difference with respect to power density when operating fuel cells within a gasification based system. As part of this project a number of targeted experimental studies have been conducted to provide a quantitative assessment of what the different modes of operation relate in terms of a percentage performance difference in power density.

2.3.4 Scalability

The final factor to consider with any potential system relates to the practical operation of the fuel cell system at scale. If any fuel cell system is to be considered as a potentially viable source of power then it must be possible to manufacture, install and fuel these devices at an industrial scale. This means that the fabrication, assembly, installation, fuel cost and maintenance cost must all be competitive with existing technologies.

Currently there are no fuel cell systems operating on solid fuels at a commercial scale. It is therefore difficult to provide a definitive assessment of which technical path is superior. However, there have been a number of studies looking into the feasibility of operating various fuel cell systems on gasified coal and a limited number of technical small scale pilot trials. These studies are, in general, focused on the potential to develop a system with high efficiency and low cost per kWh of power generation when combined with carbon capture.

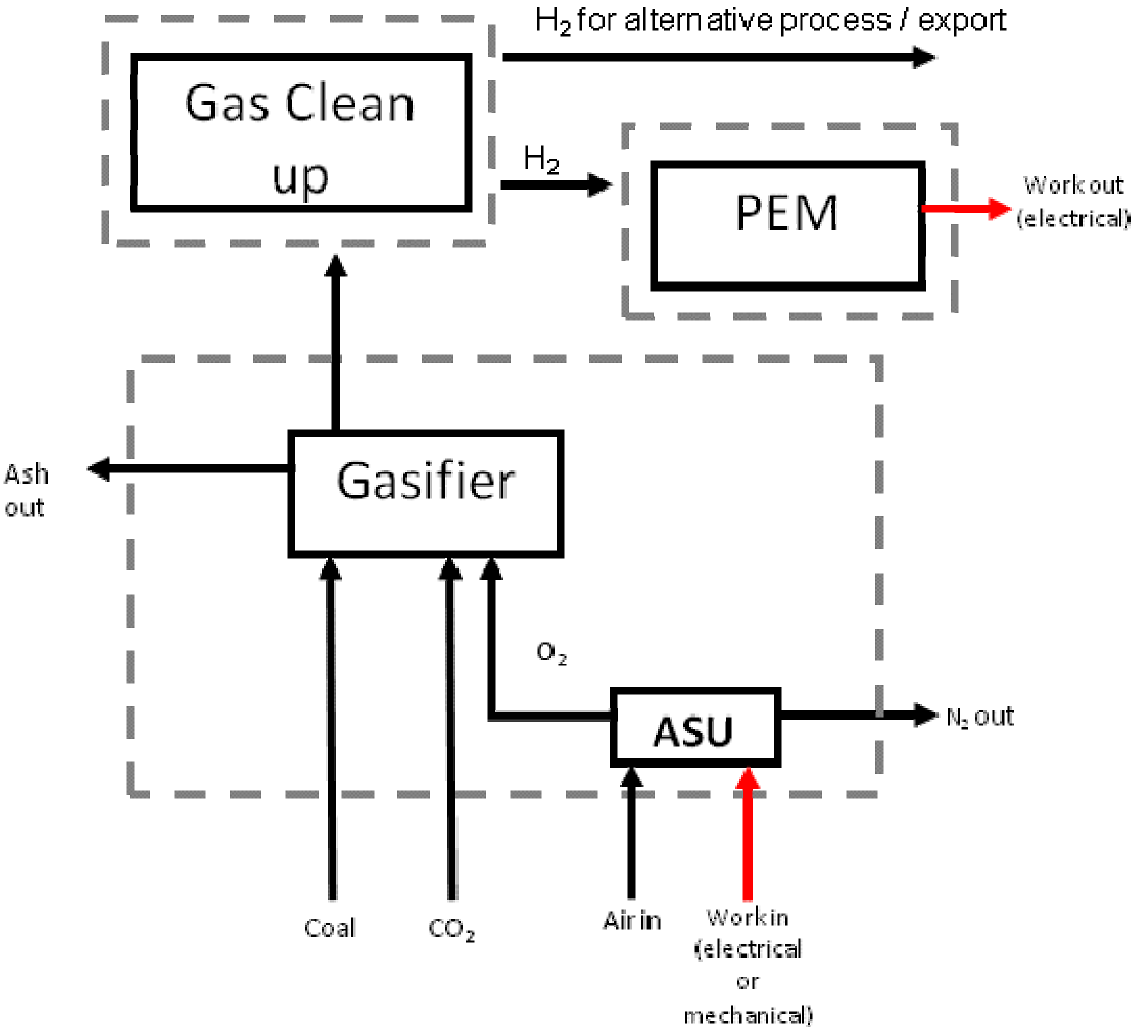
In terms of pilot demonstrations the most advanced concepts are based on autothermal gasification based systems similar to that shown in **Figure 2-3** providing syngas to a modified commercial fuel cell stack. Trials of systems of this type have been conducted on coal at small scale (20 kW) with a large scale project (2 MW) abandoned in 2006 due to issues relating to the gasifier [**15**]. Although a complete demonstration was not possible, the fuel cell system in this project was operated on syngas (derived externally from natural gas) and at an efficiency of 37% was achieved [**15**]. In terms of scalability and shortest path to market this technology approach appears most attractive, however, the comparatively low efficiency of this system would in general only make it attractive for a combined heat and power applications or other novel applications where there may be other advantages to operating the fuel cell instead of a conventional heat engine (such as combined power and carbon capture [**16**]).

In terms of integrated gasification systems (similar in design to those shown in **Figure 2-4**) there are currently no full scale system trials underway. There are two organisations that are involved with the development of systems such as these (Fuelcell Energy and LG Fuel Cell Systems). These organisations are part of the Solid State Energy Conversion Alliance (SECA) program in the United States which has invested over $100 million USD in these organisations to develop two system concepts: a fully pressurised system and an atmospheric pressure system. Full scale trials of these systems are scheduled for between 2020 and 2025 [**17**].

Modelling carried out by NETL (the US National Energy Technology Laboratory) has suggested that the pressurised system under development will have the highest efficiency and lowest normalised cost of power of any gasification system with carbon capture above 90% [**11**]. (There were no direct gasification or direct reaction systems considered in this study.) This feasibility study concluded that an overall system efficiency of 56% was attainable [**11**]. The high cost of these programs is in large part related to the system complexity and size with a single plant output being around 600 MW.

In terms of the direct gasification and direct reaction systems proposed here (**Figures 2-5** and **2-6**) these systems have a scale advantage over the more complex systems above with only a single unit used to gasify and produce power. This would allow these units to be constructed at much smaller unit size (10–100 kW). Initial trials and development could be carried out at this small scale. Once developed, larger systems could be constructed consisting of multiple smaller units to give a higher total power output. The higher potential efficiencies of these systems also have the advantage of reducing the requirement to utilise any waste heat from the system removing the need for integration with other devices or processes. The major disadvantage of these systems is the requirement for a complex fuel feed mechanism and the fact that any impurities within the coal would come into contact with the fuel cell increasing degradation issues. This increases the demands on fuel purity making it more desirable to use fuels with a low ash and sulfur content.

2.4 Use of Victorian brown coal for the production of hydrogen with electrical power as a secondary output



This scenario is significantly different in comparison to other fuel cell concepts considered above. This is because this concept would utilise existing commercial fuel cell systems which require little or no further development before they can be deployed in multi-MW fuel cell power stations. The main output of a scenario such as this is pure hydrogen and not electrical power and is only included in this report for completeness as this report focuses mainly on power generation. In terms of cost, typical cost of low temperature fuel cell systems are around $3–8 million (USD) per MW of installed capacity and are available from a number of different commercial suppliers including Fuji Electric, Doosan Fuel Cell Systems, Ballard, Altergy and many more. Currently most of these systems are deployed as combined heat and power units operating of natural gas with the largest systems typically operating at small industrial sites and large commercial or residential buildings. These applications typically have a 5–10 MW thermal load as so the fuel cells are scaled accordingly (i.e. a typical fuel cell system will provide a 1:1 thermal to electrical power ratio so a low temperature fuel cell system are typically in the order of 5–10 MW). There is fundamentally no reason why these systems could not be deployed in larger configurations if a local low cost hydrogen source was available.

2.5 Summary

Four broad system concepts have been discussed in terms of their potential end efficiency, lifetime, power density and scalability. These systems range from the relatively mature but comparably inefficient autothermal gasification type systems to more novel concepts that involve direct gasification or direct reaction of fuel within the fuel cells themselves. CSIRO's current strategy focus is on the development of a novel direct reaction system. In addition to the other benefits of DCFCs, this system concept has the advantage of being completely self contained and can be trialled at small scale before being deployed at a larger scale. This leads to the capital investment for the development of this technology being smaller than for the other technology paths considered. The system also has the highest potential efficiency of any of the systems proposed here. The main technical unknowns with this system design is the effect of coal impurities on the lifetime of the fuel cell and the ultimate power density achievable with these fuel cells.

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3 Suitability of brown coal for use in a DCFC

3.1 Background: Coal use in Fuel Cells

Direct carbon fuel cells are at an early stage of development with a number of different concept designs being trialled [**1, 2**]. These designs vary significantly in performance, efficiency and technical maturity. However, in terms of materials reactivity only the manner the fuel is presented to the fuel cell is critical. In these terms there are three separate families:

1. Direct contact: where the fuel is fed directly to the surface of the fuel cell
2. Fuel within the anode chamber: where the fuel is fed to the anode chamber and gasified
3. Gasification driven fuel cells: where the fuel cell is connected to a gasifier

These families have different degrees of materials reactivity issues. The impact of impurities in the fuel is lessened as the fuel is moved further from the active (oxidising) sites on the fuel cell surface as most degradation processes are diffusion controlled. Hence by increasing the distance between the active sites within a fuel cell and the impurity any degradation cause by materials reactivity can be dramatically slowed.

The most challenging systems are where fuel cell directly reacts electrochemically with the fuel to produce power. This is because the fuel impurities are co-located, and in some cases concentrated, at the sites where electrochemical reactions occur. If the fuel is fed to the anode chamber where it is gasified and then the resulting CO and H_2 are oxidised within the fuel cell, the effect of the impurities can be significantly reduced even if the fuel remains in contact with the fuel cell as any impurities must diffuse to the active sites to cause degradation in performance. Clearly if the impurity can be gasified then it can diffuse freely within the anode via gas diffusion.

In the case of these impurities the only way to stop them from causing significant degradation is to eliminate them from the fuel, design materials that do not react with the impurity or to produce the fuel via gasification and then to remove it prior to introduction to the fuel cell. If the fuel is gasified in a separate reactor and then fed to the fuel cell surface then there is a potential to remove many of the harmful impurities within the gasified fuel stream. This can add cost and complexity to the fuel cell system but largely eliminates fuel reactivity and materials reactivity issues. This approach has been favoured by many in the high temperature fuel cell community as it would effectively allow the use of a conventional SOFC. There has been significant work carried out by a number of groups globally looking at the effect of impurities and combinations of impurities on the performance and life of SOFC [**3-8**]. These studies show that it is feasible to operate SOFC on gasified solid fuels from a full spectrum of sources including coal and bio-mass. The challenge with this approach is how to design the system so as to maintain the high efficiency of the fuel cell system whilst keeping the cost of the overall plant low enough to make the process economically viable.

CSIRO's DCFC design is has a hybrid cell design that can be used to react both directly with solid fuels or with a gasified fuel stream containing mainly CO and H_2. In addition, the fuel cell also has a mixed ionic electronic conducting (MIEC) anode, this anode type can utilise the entire anode surface for electrochemical reactions so is significantly more tolerant to fuel impurities than a conventional anode. These factors lead to the CSRIO design being more resilient than conventional fuel cells, however, if fuel is to be place directly in the anode chamber a greater understanding of the materials reactivity of the fuel cell anode must be obtained. This study looked at a wide range of fuel impurities found in Victorian Brown coal and their reactivity to fuel cell materials with particular emphasis on the reactivity of yttria stabilized zirconia (YSZ) and gadolinium doped cerium oxide (CGO). These 2 materials (or variations on these compositions) are the most comonly used materials within high temperature fuel cells and will likely make up a significant part of any fuel cell electrode or electrolyte in a mature system.

3.2 Common Impurities in Victorian Brown Coal and their Potential Effect on Fuel Cell Performance

Rady et al. performed a detailed review of fuels for direct carbon fuel cells [**9**]. This work complied information from a number of different sources and found that there are ten common impurity elements found within Victorian brown coal from a wide range of sources: Si, Al, Fe, Ca, Mg, Na, K, Ti, S and Cl. This review also gave an overview of the other more utilisation-technology-dependent constituents including tars, higher hydrocarbons and water content. Each of these impurities will be discussed in detail with reference to the literature and experiments where appropriate. In addition to the inorganic materials found in Victorian brown coal, these coals also contain high amounts of water, oxygen and hydrocarbons.

3.2.1 Silica

Silica is a very detrimental impurity and can severely limit the ionic conductivity in any commonly used high temperature fuel cell materials; it is well known to diffuse and accumulate on grain boundaries. It is particularly detrimental in combination with alkaline metals such as Na and K as these will reduce the melting point of any phase formed and accelerate the degradation of materials. Additions of Al_2O_3, MgO and CaO can result in the formation of more refractory phases that do not react with fuel cell materials [**10**]. Silica will not react with YSZ even if heated to high temperature but will accumulate at grain boundaries blocking ionic diffusion. If the silica is presented to the YSZ in a molten form this reaction can take as little as a few hours to completely block ionic diffusion. The effect on CGO is somewhat different with it forming detrimental phases such as $Ce_2Si_2O_7$. The mechanism is different but the form of the silica is equally as critical.

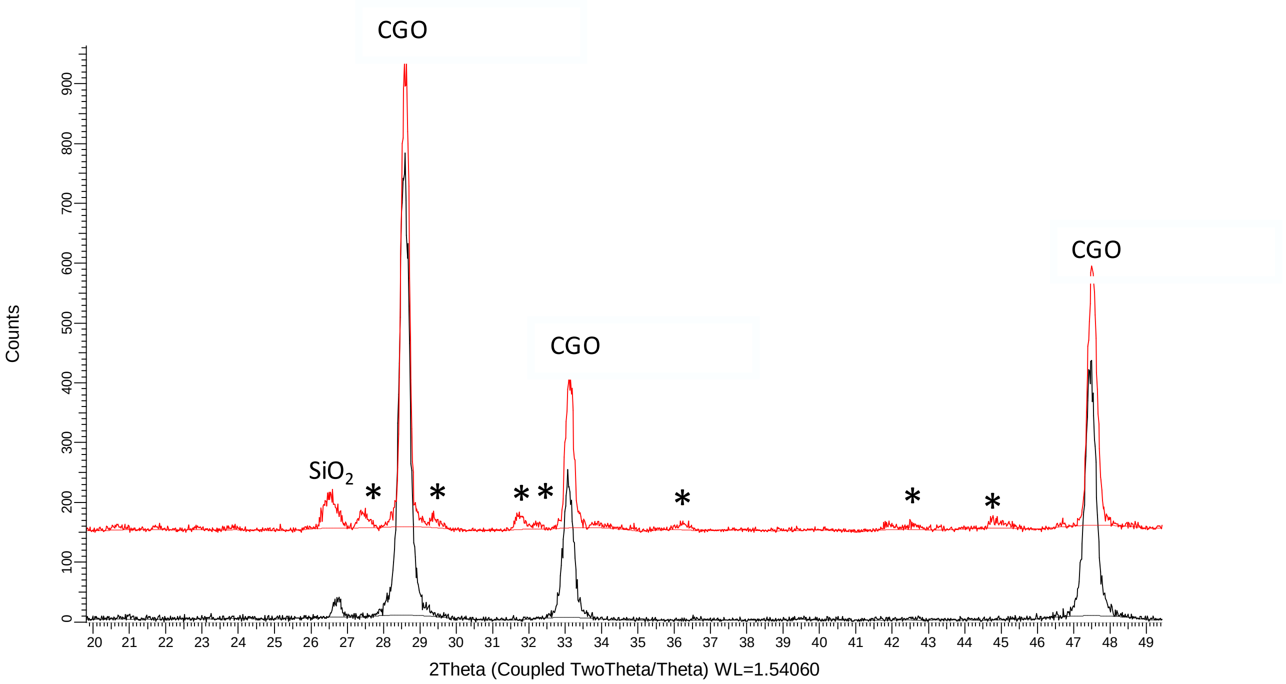

Figure 3-1 reaction products of CGO with Quartz heated to 1450 °C (red) and 800°C (black). * mark unknown reaction product

At 800°C there is little-to-no reactivity between quartz and CGO but at higher temperatures, impurity phases do form (**Figure 3-1**). If the silica is in an unreactive form (such as quartz or a high melting point aluminosilicate) then it is unlikely to cause rapid degradation of either YSZ or CGO systems.

3.2.2 Alumina

Alumina normally exists within oxide phases (typically silicates) in coal and overall is a beneficial element within the mixture of elements found within Victorian brown coal. This is because it is well known to form stable silicate phases (such as mullite) that do not melt at DCFC operating temperatures. These phases will absorb free silica within the fuel that can be removed with the ash. Using Al_2O_3 (or fuels with a high Al_2O_3 content) is particularly attractive for DCFC as it will also react with Na and K silicate phases even at the relatively low DCFC operating temperatures to form higher melting point ash phases which will likely result in less degradation [**11**].

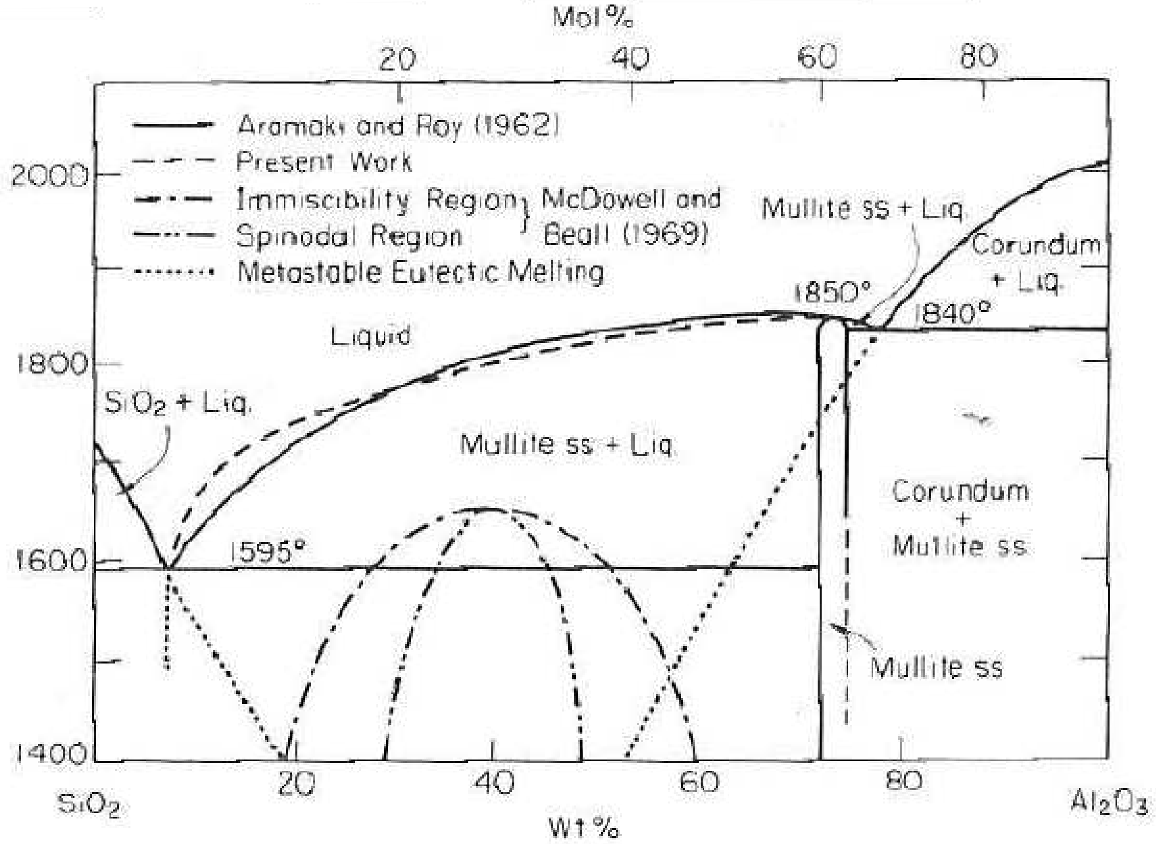

Figure 3-2 Phase diagram for Al_2O_3 and SiO_2 from ref [12]

Al_2O_3 is routinely added to YSZ materials to allow the use of lower purity (high silica) materials in oxygen sensors [**10**]. This approach is not used with CGO, as at high temperature Al_2O_3 is known to react with cerium oxide to form a number of phases with low ionic conductivity [**13**]. At typical operating temperatures of DCFC this reaction is unlikely to occur between CGO and Al_2O_3. At high temperature (1450°C) some reaction was noted (colour change) between CGO and Al_2O_3 but the reaction kinetics were slow and an identifiable phase had not formed after 10hrs of heat treatment. No reaction between powdered of CGO and Al_2O_3 was noted at 800°C under typical DCFC operating conditions. There was no reaction between powdered YSZ samples and Al_2O_3 at either the high (1450°C) or low (800°C) temperatures used in this study.

As with all inert phases excessive amounts of Al_2O_3 will block active sites and result in low performance. The low ash content of Victorian brown coal makes this unlikely to be an issue with this fuel source.

3.2.3 Iron Oxide

Iron oxide has been used as an addition in a number of fuel cells to increase the performance of the fuel cell stack [**2, 9, 14**]. Iron oxide has low solubility in YSZ at the temperatures found in DCFC environments and will partially reduce to form electrically conducting phases in DCFC environments. Iron oxide will also increase the production of CO resulting in improved performance but potentially lower efficiency. Iron oxide is partially soluble in Ceria containing materials and can lead to electrical conductivity developing in the electrolyte which would be detrimental to the performance of the fuel cell. However, the temperatures required for this reaction to occur would be far higher than would be expected during operation in a DCFC. Any reaction would also occur in the anode where an increase in electrical conductivity would improve performance.

Iron oxide is also a useful addition as it is likely to react with sulfur present in the coal. If the iron can then be removed from the fuel chamber this will effectively reduce the amount of sulfur to which the fuel cell is exposed and improve the overall performance of the fuel cell. No reaction was noted between either CGO or YSZ in this study at DCFC operating temperatures (800°C) or at high temperature (1450°C).

3.2.4 Calcium Oxide

Calcium is soluble in both YSZ and CGO lattices. It is well known to stabilise the cubic ion conducting phase in both materials. In general, calcium is not used as a stabilising agent in these materials as it results in a lower ionic conductivity than the more commonly used Y (in Zirconia) or Gd (in Ceria). The rate of diffusion of calcium oxide at fuel cell operating temperatures is unlikely to be fast enough to result in a sufficient quantity of Ca entering the lattice to reduce the conductivity of either material by a significant amount.

Calcium can react with SiO to form a number of glasses and glass ceramics especially when in combination with Mg and Al [**15**]. The majority of these phases have melting points well in excess of 1000°C making it in general a good addition to the fuel mix. Ca also has good catalytic activity assisting the formation of CO and is one of the main sources of the increase performance observed when operating a fuel cell directly on Victorian brown coal in previous studies on button cells with limited gas circulation [**16**]. No performance enhancement was noted in this study between Morwell char (high in Ca) when compare to synthetic pure carbon fuels such as XC-72 as discussed in greater detail in section 4. No reaction was noted in this study between CaO with either CGO or YSZ at 800°C in DCFC environments. Ca did diffuse into both YSZ and CGO at 1450°C resulting in a small variation in the peak shape and lattice parameter. The kinetics of this diffusion were slow and the reaction did not reach completion.

3.2.5 Magnesium Oxide

Magnesium oxide has a very similar effect to alumina in fuel cells being both fairly inert and reacting readily with silica. It will react with many of the silica impurities forming much higher melting point refractory compounds such as forsterite [**15**]. This will be beneficial as it will reduce the reactivity of silica contain phases with the fuel cell. Magnesium is soluble in both YSZ and CGO but would be unlikely to react with any of these materials at typical DCFC operating temperatures due to the slow reaction kinetics.

Mg will result in a significant drop in the ionic conductivity of both YSZ and CGO if it enters the lattice of these materials. The effect on performance would also be less dramatic as for impurities such as sulfur or silica that can block active sites. The composition of materials within the fuel cell would have to be altered by 1–5% before there would be any noticeable effect on performance. As such MgO in isolation would be a fairly neutral addition to the fuel. If high levels of silica, in particular with sodium or potassium where present than MgO would be highly beneficial as it would increase the melting point of any silica phases formed.

3.2.6 Sodium and Potassium (including Chlorides and Oxides)

Sodium and potassium are soluble in YSZ and CGO but do not dramatically affect the ionic conductivity at low levels. They are, in isolation, generally a much larger concern for other parts of the fuel cell system especially any metallic components which may have a protective coating applied to them. On exposure to Na and K salts these metals can often undergo rapid corrosion.

The chlorides of potassium and sodium are very damaging as they are molten at DCFC operating temperatures and will rapidly increase the kinetics of any degradation reactions. In particular the combination of alkali impurities with silica results in very high levels of degradation. In this instance they produce low melting point silica phase. Many of these phases melt well below the temperature found in DCFCs. If this occurs then rapid and irreversible damage will occur at the surface of the anode and the interface between the anode and electrolyte as the highly mobile silica species with diffuse rapidly along grain boundaries. This is one of the most damaging mechanisms of degradation and can result in compete failure of the fuel cell even if only low (sub 1%) levels of impurity are present.

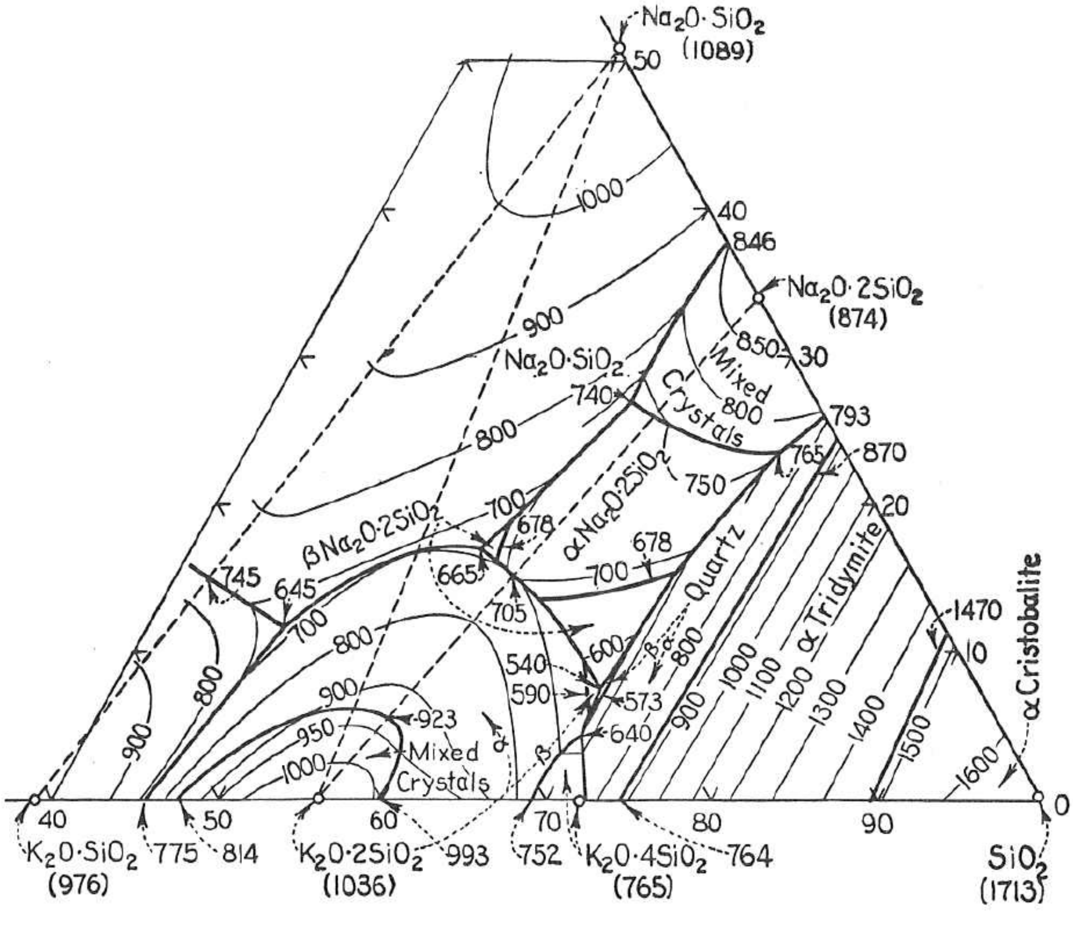

Figure 3-3 Phase diagram for SiO-K$_2$O-Na$_2$O showing low melting point phases

In addition to chemical reaction, molten phases within the anode chamber increase the degradation rate of a fuel cell by increasing the sintering of the electrodes. This will quickly reduce the surface area of the electrode and the performance will drop accordingly. Alkali impurities also have a fairly low vapour pressure at DCFC operating temperatures which will allow them to penetrate deep within the electrodes rather than just damaging the surface of the anode.

YSZ is particularly susceptible to attack from sodium or potassium silicates as the silica will coat the grain boundaries in this material reducing the ionic conductivity rapidly and then the Na or K ions then diffusing into the lattice resulting in a rapid loss of strength in the material and resulting in mechanical failure. On exposure to molten salts YSZ typically fails after 100-1000 hrs operation. Ceria is very resistant to molten salt attack by suffers similar rapid loss in performance when exposed to molten silicate phases.

3.2.7 Titanium Oxide

Titanium oxide is only present within Victorian brown coals in low levels. Overall this material has low reactivity with YSZ and CGO. If it does react with these materials it can reduce ionic conductivity and increase electrical conductivity (especially in reducing atmospheres) which would drop the performance of the fuel cell in terms of both power output and efficiency. It is unlikely that at the temperatures DCFC operate at and levels that TiO_2 is found in brown coal that it will have any significant effect on the fuel cell performance. TiO_2 was found not to react with YSZ or CGO at DCFC operating temperatures but some reaction was noted at 1450°C.

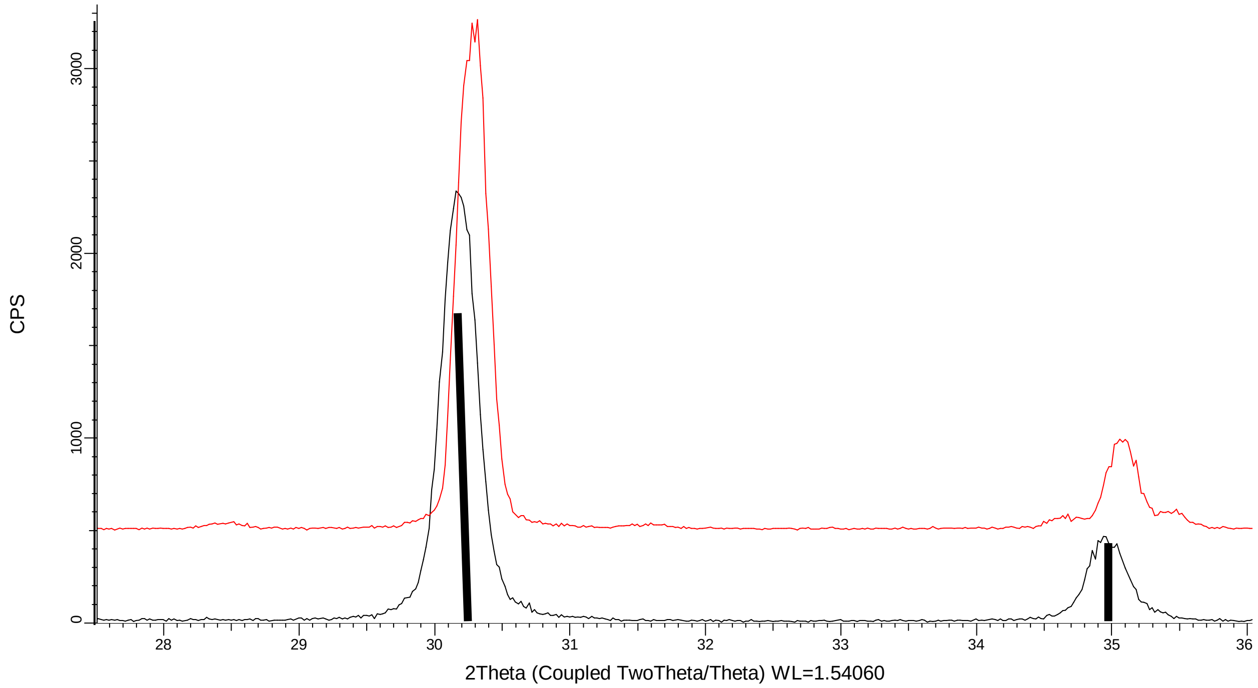

Figure 3-4 Reaction of TiO_2 with YSZ (top – heated to 1450oC for 10hrs) and sample heated to 800oC showing no shift (no reaction). Black lines indicate position of YSZ peaks from untreated sample.

3.2.8 Sulfur

Sulfur in isolation is a very damaging impurity for conventional fuel cells this is due to its reaction with the Ni within the anode. This deactivates the anode and rapidly reduces performance of the fuel cell. When present as hydrogen sulfide it is particularly damaging as it can attack the triple phase boundaries leading to very low impurity levels being required to have a large effect on the performance of the fuel cell. The MIEC anodes used in CSIRO’s fuel cell design will likely be far more tolerant to sulfur as they do not contain Ni. Sulfur can react with Fe-containing phases to form a solid material in the ash but this requires a large excess of Fe to be an effective mitigation strategy.

3.2.9 Water and oxygen

Water and oxygen will have an effect on the efficiency of the fuel cell system although this will not be as dramatic as for combustion-based systems. This is because in a combustion system heat is required to produce power, any cooling results in a drop in performance. In a fuel cell heat is rejected from the system and not required for the generation of power. If the fuel cell is to remain thermally self sustaining then the water content must not exceed a certain value for a given system as this would result in cooling of the fuel cell stack. In low efficiency systems there is a higher degree of heat available therefore higher water contents can be tolerated.

In terms of the performance of the fuel cell and degradation, overall both water and oxygen in the coal will have a positive effect on the performance of the system as both of these compounds will result in gasification of the fuel. Both H_2 and CO are highly reactive and can be consumed as a fuel by the fuel cell. The larger the proportion of these species the higher the performance of the fuel cell.

In extreme cases high levels of steam can cause increased degradation of the fuel cell anodes as it increases sintering of materials will result in higher degradation. This effect is present in all high temperature oxide ion conducting fuel cells and occurs at high fuel utilization in hydrogen rich fuels. It is well understood and strategies are in place that mitigate the effect of high steam content either via controlling the microstructure of the anode or via the altering of the system to reduce the steam content. This effect will be less of an issue when operating on brown coal verses hydrogen or natural gas as the higher carbon content will reduce the concentration of water at high fuel utilisation. In some instances it may be beneficial to dry the fuel at lower temperature (say 200-300 ^{o}C) before introducing it to the system. This could potentially be achieved by passing the exhaust of the fuel cell over the fuel. A fuel cell exhaust contains no oxygen which would assist in suppressing any combustion in the fuel caused by drying.

Water and CO_2 have a mild catalytic effect on the fuel cell reactions that occur at the anode. In practice this effect is very seldom reported as there is almost no situation where water or CO_2 can be excluded from the anode chamber of an operating fuel cell.

3.2.10 Tars and Higher Hydrocarbons

Tars and higher hydrocarbon fuels can cause significant issues within a fuel cell system by blocking channels and pipe work but in terms of the fuel cell will cause few issues. Build up of tars on the surface of the fuel cell can result in a drop in performance but these tars can be removed by periodically reducing the operating voltage. This leads to the surface of a DCFC anode becoming highly oxidising and thus any fuel physically deposited on the surface will likely be consumed by the fuel cell. If the accumulation of tar continues for long periods then physical damage to the electrode may occur that will be irreversible. The oxygen is provided from below the surface of the anode and hence if the surface of the anode becomes blocked it will still be possible to oxidise the material on the surface. Careful design of the fuel cell anode is necessary as one of the decomposition products of any hydrocarbon fuel is carbon. If this forms in the pores of the anode then this will result in mechanical failure and delaminating of the anode.

3.3 Summary

In comparison to other coals and bio-fuels with higher ash contents Victorian brown coal is overall a very attractive fuel for use with DCFCs either in direct contact, internal gasification or if fed to an external gasifier. This is largely due to the low ash and sulfur content. In terms of materials commonly found within Victorian brown coal that are potentially detrimental the combination of sodium and silica are a particular concern. If the fuel is to be consumed within the anode chamber then it would be necessary to reduce the content of these impurities or ensure that the levels of alumina, calcium and magnesium are sufficiently high to react with these materials to form a more refractory ash that can be removed from the fuel cell. Sulfur content within the fuel is low and if combined with high iron content then it may be possible that Victorian brown coal could be used with reasonably conventional Ni containing fuel cell anodes however this would be highly dependent on the system design.

There are a number of attractive impurities that are found within Victorian brown coal including Fe and Ca which improve fuel cell power output and those that reduce the impact of more detrimental impurities such as Al and Mg. In terms of which of the Victorian brown coals would be most appropriate for use within a DCFC from the understanding we currently have and using data from Brown [**18**], coals from Morwell and Yallourn appear most attractive due to their low Si content and high iron content [**9, 16**]. If conventional Ni containing anodes are to be used then the high Fe content and low S content of Yallourn coal would make it particularly attractive. In both cases the high Na content would have to be reduced or a non YSZ containing electrolyte used such as doped Ceria. If conventional fuel cell materials were to be used fuel cleaning may lead to a significant increase in the cost of the fuel and as such it may be appropriate to source a fuel for DCFC's from an upstream process that is utilising Victorian Brown coal for another application. Victorian Brown coal chars have been used both in this study and previously with little degradation of either the materials or fuel cell performance noted [**9, 16, 18**]. Additional work would be required to understand the partial decomposition of perovskite based anodes if these were to be used in a mature system.

3.4 References

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4 DCFC testing

As part of this project three series of tube cell tests were performed to ascertain the performance of CSIRO's fuel cell design in both direct and non-contact modes. Initial experiments where used to modify the fuel cell test station to allow for the testing of fuel cells in both gasification and direct contact modes. The second series of experiments where on a fuel cell with modified electrodes to improve performance (referred to as the 2^{nd} generation fuel cell). The development of these electrodes where carried out in a parallel program of work funded by CSIRO. A final tube cell test was conducted on a fuel derived from a Morwell coal examining the performance of the fuel on the 2^{nd} generation fuel cell.

4.1 Experimental

In all cases an electrolyte supported tubular cell was fabricated with 8 mol% yttria-stabilised zirconia (Tosoh Corporation, Japan) as the electrolyte, lanthanum strontium cobalt ferrite (Fuel Cell Materials Inc, OH, USA) as the cathode and LSCF-Ag composite as the anode. The details of the cell fabrication are already reported [1]. In brief, the cell materials used were as follows. Electrolyte: 8 mol% Y_2O_3 – ZrO_2 powder (8YSZ); cathode: LSCF-HP of composition $La_{0.6}Sr_{0.4}Co_{0.2}Fe_{0.8}O_{3-d}$ powder obtained from Fuel Cell Materials Inc., OH, USA; anode: LSCF-HP of composition $La_{0.6}Sr_{0.4}Co_{0.2}Fe_{0.8}O_{3-d}$ powder and Ag powder (Alfa Aesar).

The electrolyte tube with one end closed was fabricated by isostatic pressing of the electrolyte powder and sintering at 1500°C for 2 hours, resulting in final dimensions of the tube as 8.7 mm ID, 9.9 mm OD and 170 mm length. The anode ink for the first generation fuel cells was prepared by milling LSCF and silver powders with ink vehicle in 30:20:50 wt% ratio. For the 2^{nd} generation cells the ratio of silver to LSCFC was increased with the ratio being 35:15:50 wt% (Ag:LSCF:ink vehicle). The electrodes were prepared by coating 40 mm length of the electrolyte tube near closed end with anode and cathode inks outside and inside the tube respectively followed by heat treatment at 800°C in air for 2 hours. The current collection from anode was achieved by winding a 0.5mm diameter silver wire (5 mm spacing) around anode, and from cathode, it was achieved by inserting a spiral made from a 1 mm diameter silver wire (1 cm spacing) inside the tube contacting the active area of the cathode. The active area of the cell obtained this way was 10.9 cm^2.

The cell was assembled and operated either above a bed of carbon (gasification non-contact mode) or immersed in a packed bed of carbon (direct contact mode). In all experiments the fuel cell and fuel were contained in a SS crucible of 35 mm ID and 130 mm depth. This fixture has been used previously to test fuel cells fully immersed in a carbon bed [**1**]. In the full immersion configuration the fuel directly reacts at the surface of the fuel cell anode with gas being supplied only to maintain an inert atmosphere around the fuel. In order to increase the residence time of the gas within the fuel cell bed the anode gas inlet tube was extended and a stainless steel sparger was used to disperse the gas through the carbon as shown in **Figure 4-1**. The first generation fuel cell tests were performed under flowing N_2, CO_2/N_2 (40:60 ratio) mix and pure CO (BOC, Australia). The tests of the 2^{nd} generation fuel cells were performed in N_2, pure CO_2 and CO. Pure CO_2 (instead of CO_2/N_2 mixtures) was used in the 2^{nd} generation fuel cell test as it was found to give more reproducible results. The temperature of the cell near the middle of the active area was measured by inserting a thermocouple made from a twin bore ceramic tube (3 mm diameter) inside the cell (cathode) that also was used to supply air to the cathode. The whole cell assembly with the SS reactor was then inserted into a heated vertical chamber of a furnace up to the SS reactor flange. In the first 2 series of fuel cell tests XC-72 (Carbot corp.) was used as the fuel. In the final test a char was produced via heating Morwell Victorian brown coal to 600^{o}C under flowing nitrogen for 2 hrs and in previous studies [**2**]. All fuel cell tests unless otherwise stated in the text were carried out at 800 ^{o}C.

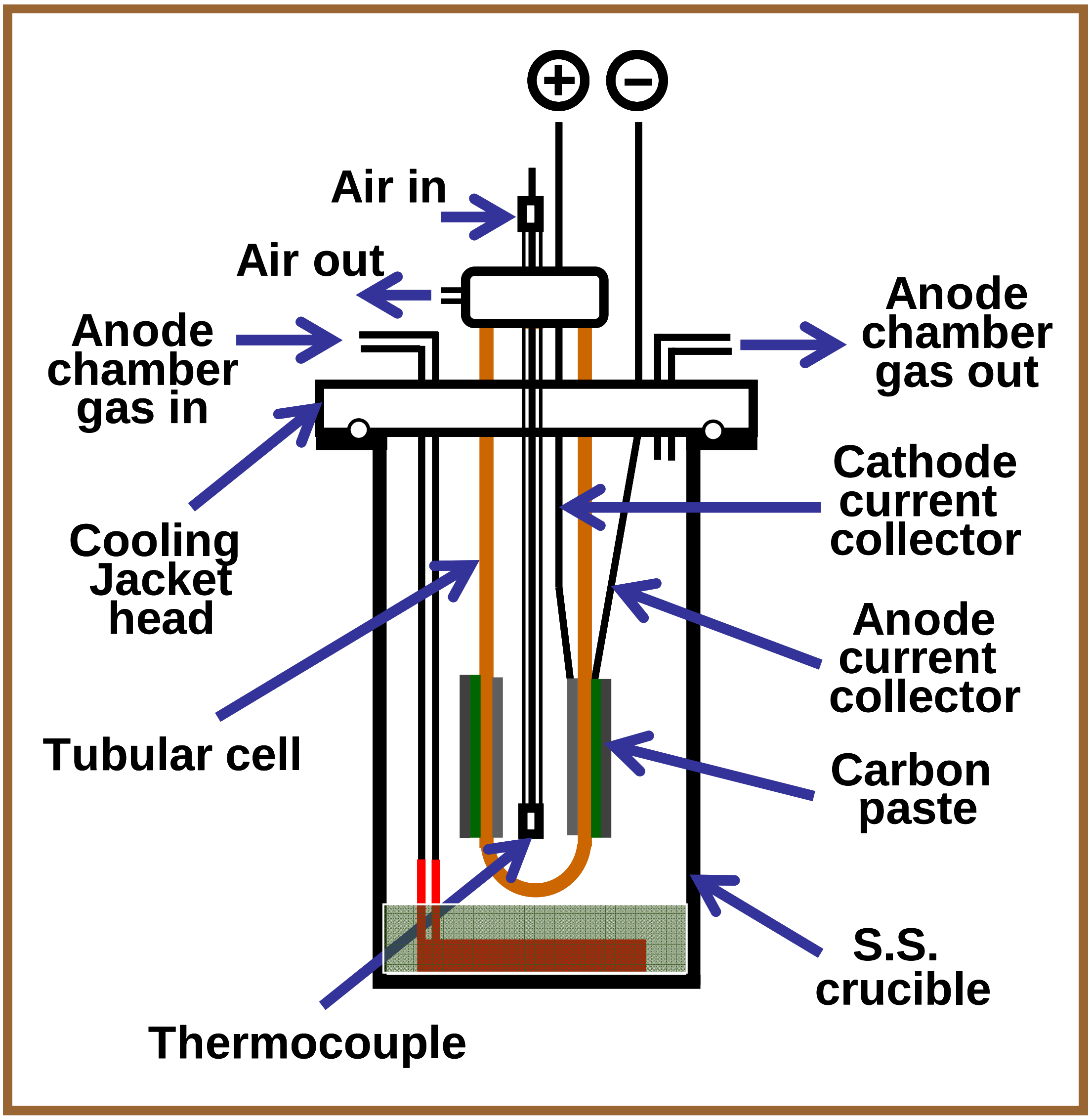

Figure 4-1 **Schematic of the reactor design used in this study with the modified sparger (shown in red) and powder bed (shown in dark green). This figure was modified from ref [1].**

4.2 Results and discussion

4.2.1 Initial testing of first generation fuel cells

In order to establish how the performance of the CSIRO fuel cell design varies with the method and state of fuel supply, the reactor has been modified to allow for gasification of fuels. This has involved the modification of the conventional test fixture to include a gas sparger at the base of the test reactor to uniformly distribute and increase the contact area of the purge gas with the carbon bed (**Figure 3-1**). The performance of the reactor has been assessed with N_2, CO_2/N_2 mixed gas and with pure CO. The N_2 test was used as a baseline to determine the performance of the cell under very low fuel supply, the CO_2/N_2 mix was used to simulate an air blown gasification stream at 800 ^{o}C. Pure CO was used to determine the performance of the fuel cell at high fuel concentration levels and to understand the effectiveness of the gas sparger for gasification of the fuel. The carbon source used for these experiments was a carbon black with a high surface area (XC72). This is widely used within the DCFC community as a 'standard' fuel and allows for comparison to pervious work as well as cell designs proposed by other groups globally. There have been a number of studies that have shown that this carbon source will gasify even under a high purity N_2 blanket [**2**]. **Figure 4-2** shows a thermo-gravimetric (TG) curve of this carbon source heated in a high purity N_2 atmosphere.

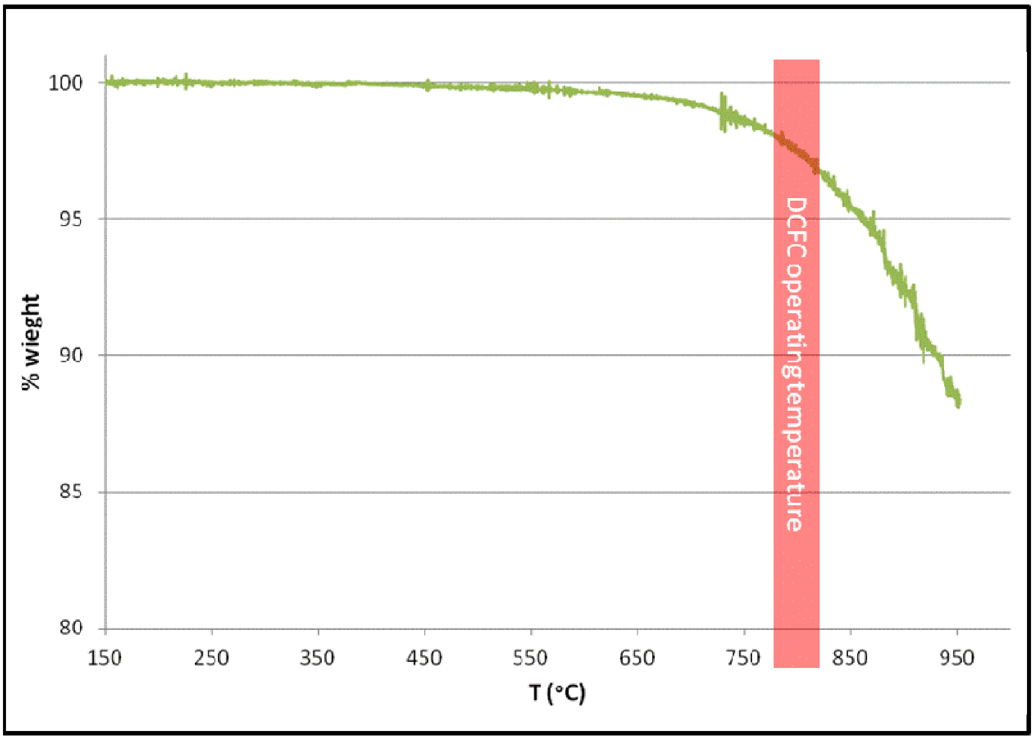

Figure 4-2 **Thermogravimetric analysis of XC72 within a high purity N_2 environment area highlighted indicates typical operating temperature of DCFCs.**

It can be seen that there is significant weight loss in this atmosphere within the typical operating window of a DCFC. This results in a small amount of CO being generated and is the origin of the electrical potential at zero load (open circuit voltage, OCV) and allows a small amount of electrical current to be drawn from the fuel cell.

The low concentration of CO produced leads to a significant drop off in the V-I curve shown in the red area in **Figure 4-3**. This is common in fuel cells that are starved of fuel and is the result of the concentration of the fuel at the electrode dropping to near zero which then limits the cell performance. In order to confirm that the fuel cell performance was indeed related to the low concentration of combustible material in the fuel stream when operated under N_2, impedance analysis was carried out at open circuit voltage (i.e. no current drawn from the fuel cell) and at 0.5 V (i.e. with the cell in operation). This was also carried out within a CO_2/N_2 environment (**Figure 4-4**).

Impedance spectroscopy can be used to isolate various phenomena (electrochemical reaction steps) occurring in the fuel cell via their time constants (i.e. the speed that the reaction takes place). This is performed by supplying a voltage signal of varying frequency and monitoring the cell's response as current signal. At high frequency only high speed reactions can be observed (such as electrical conductivity or motions of ions in the electrolyte). As the frequency is progressively reduced it is possible to isolate slow processes occurring within the electrode, most critically in the case of this experiment, gas diffusion in the electrode.

The results from impedance analysis are typically depicted in a Nyquist plot (**Figure 4-4**). These plots consist of a series of overlapping semi-circles with each semi-circle relating to a different rate limiting process. The larger the semicircle the higher the resistance of the process associated with that semicircle. High frequency (fast) processes are to the left of the figure and low frequency (slower) processes are to the right of the figure. At open circuit voltage when no current is drawn the gas concentration at the electrode is similar to that in the main part of the reactor. At 0.5 V a current is drawn and the combustible components within the gas stream at the fuel electrode are consumed. This leads to the combustible gas concentration at the electrode being determined by how fast the reactants diffuse in to the electrode and how fast the products diffuse out of the electrode. This in turn is related to the relative differences in concentration between the gases within the electrode and the gases outside of electrode.

Figure 4-4 shows that the high frequency response of the fuel cell is not affected by the gas composition with only the low frequency region changing. This confirms that the variation in performance of the fuel cell is largely dependent on variation in the gas phase of the fuel with the low frequency resistance of the fuel cell being more than 4 times greater in N_2 than the N_2/CO_2 mixture at open circuit. Through altering the operation voltage from open circuit to 0.5 V the gradient of the low frequency arc in the N_2 atmosphere tends to 45^o. This is referred to as the Warburg effect and occurs once almost all of the combustible products have been consumed at the electrode. This is the result of the concentration gradient between the fuel electrode and the gas in the reactor not being sufficiently high to drive diffusion of reactants consumed at the electrode. In comparison in the N_2/CO_2 atmosphere the arc reduces in size. This is common for fuel cell electrodes that are not diffusion limited, as under load the electrode performance increases. This is due to a number of reaction products increasing reaction kinetics. This reduction in the low frequency arc size suggests that in the CO_2 containing atmospheres there is sufficient supply of reactants (most likely CO) for the fuel cell performance not to be limited by the fuel but rather other resistances in the cell.

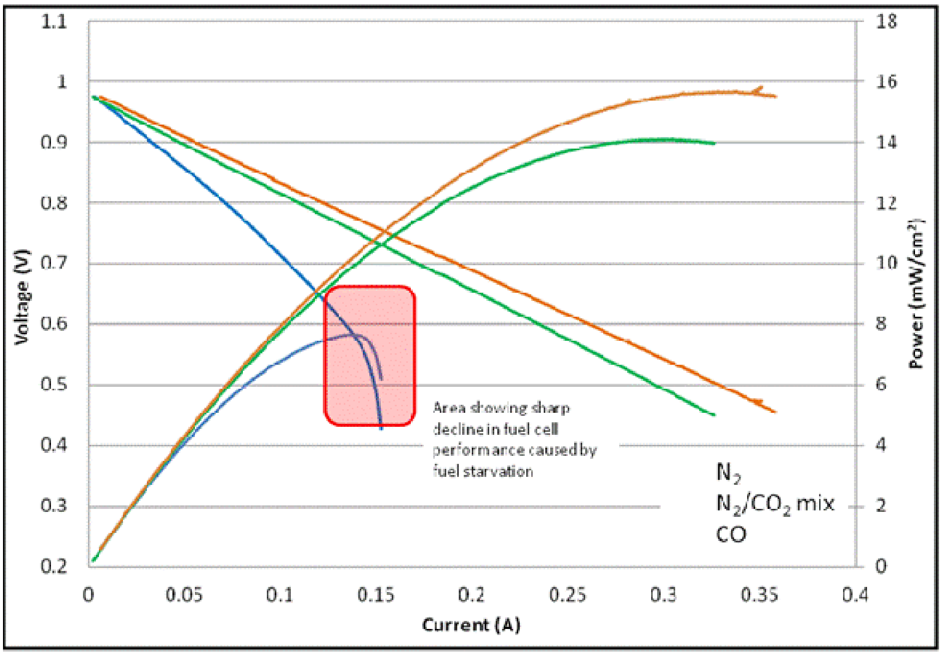

Figure 4-3 Performance of a fuel cell operated above a packed bed of carbon with a N_2, N_2/CO_2 and CO purge gas stream (gasification mode, 800°C).

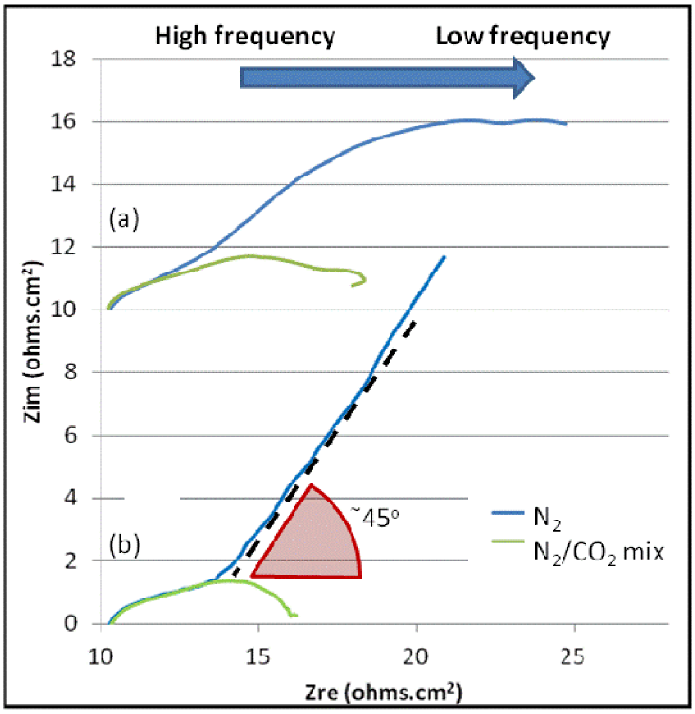

Figure 4-4 Impedance response of fuel cell in N_2 and N_2/CO_2 environment.

Figure 4-3 also compares the performance of the fuel cell when operated with the packed bed gasifier (**Figure 4-1**) being fed with a CO_2/N_2 mixed gas stream and on pure CO. Pure CO is the best case scenario for the electrode as this represents the highest concentration (100%) of fuel possible and should give the highest performance possible. Under 100% CO the fuel cell produces 164 mW (15.6 mW/cm^2) of power where as under the simulated gasification flow it gives 148 mW (14.1 mW/cm^2) or approximately 90% of the best case scenario.

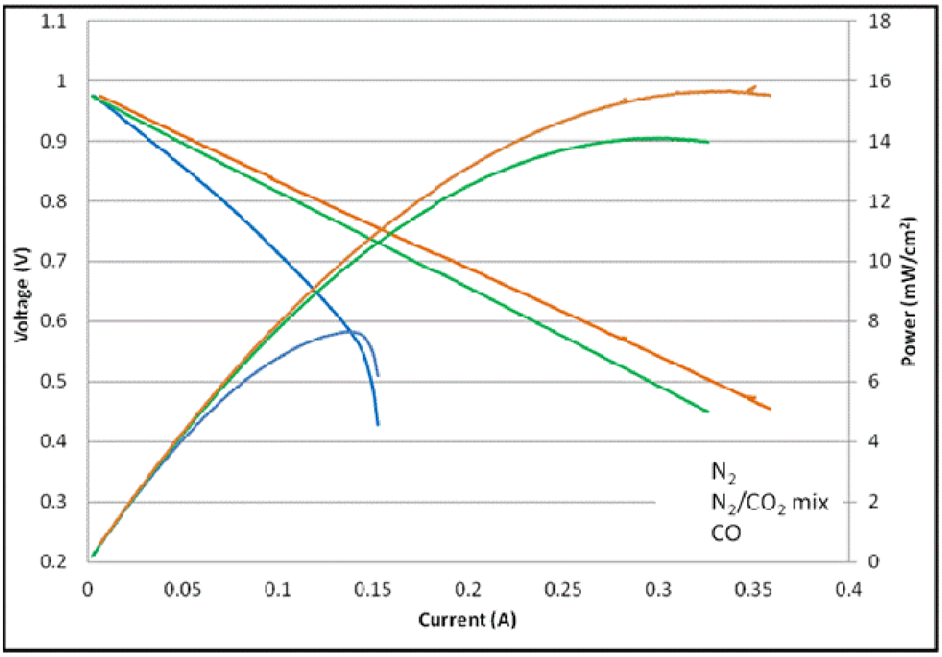

Figure 4-5 **Power output and voltage characteristics of fuel cell operate in a packed bed of carbon with a N_2, N_2/CO_2 and CO purge gas stream (direct contact mode, 800°C).**

Figure 4-5 compares the performance of the fuel cell when operated in direct contact mode. In this mode of operation the reactor was filled with Vulcan XC 72 carbon powder to cover the whole area of the anode. The key observations are that in direct contact there is no loss relating to drop in concentration at the fuel electrode under pure N_2 and that the power densities are higher in all cases. There are number of factors that have probably attributed to the higher performance of the cell in this mode. These are longer residence time for purge gases to produce more CO, carbon being in direct contact with fuel electrode produces CO close to the reaction sites, and carbon in contact acting as a current collector which reduces the overall current losses of the fuel cell. The difference between the simulated gasifier mixture and pure CO is 210 mW (20 mW/cm^2) vs 292 mW (27.8 mW/cm^2) or 70%. The larger difference in performance in contact mode vs pure gasification and the reasons of this as indicated above will be further investigated as part of ongoing work.

4.2.2 Testing of 2nd generation fuel cell on synthetic fuel (XC-72)

Testing of the first generation fuel cells showed that the main losses resulted from the poor electrical conductivity of the anode. These losses were increased significantly when the fuel cell was operated in non-contact mode as the fuel (being electrically conducting) acted as a current collector. In order for the fuel cell to operate effectively in non-contact mode it was necessary to increase the electrical conductivity of the fuel cell electrode. This was achieved by increasing the silver content of the electrode. This improvement resulted in an overall increase in performance and a reduction in the difference between direct contact and non-contact fuel cell operating modes. The performance in direct contact mode improved from approximately 26 mW/cm^2, for the first generation, to 59 mW/cm^2 for the 2nd generation. In gasification mode the performance increased from approximately 14 mW/cm^2 to 48 mW/cm^2. The improved electrodes were also found to be far more effective at operating in low fuel concentrations with less variation between CO, CO_2 and N_2 environments (**Figure 4-6**). Although they were found to be more sensitive to low air flow conditions. This sensitivity to low air flow relates is largely a result of the higher current densities in these fuel cells.

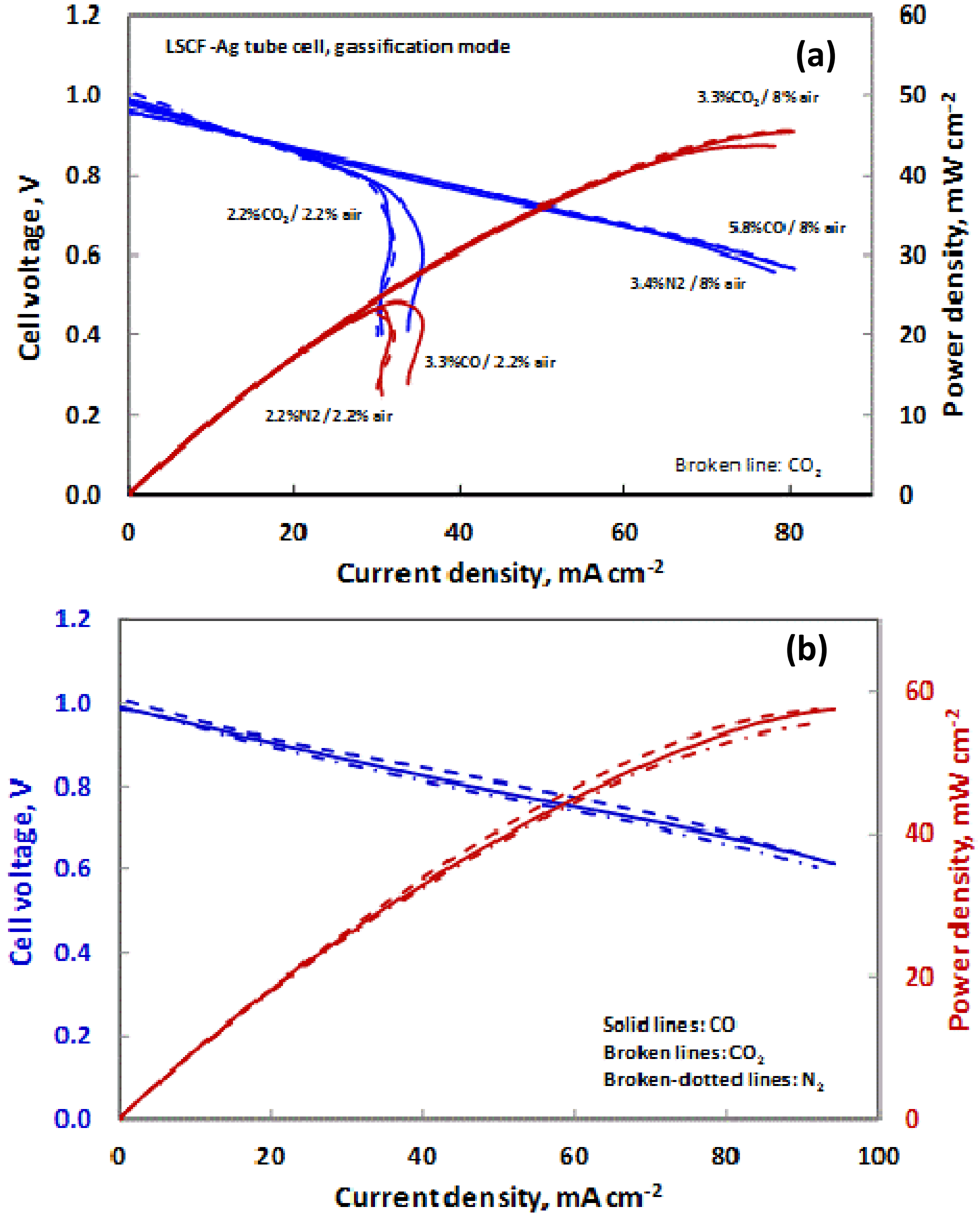

Figure 4-6 Power output and voltage characteristics of fuel cell operate in non-contact gasification mode (a) and a packed bed of carbon (b) with a N_2, CO_2 and CO purge gas stream. Low performance of cells with low air flow shown in figure 3-6(a). Both experiments were conducted at 800 °C.

4.2.3 Testing of 2nd generation fuel cell on char produced from Morwell coal

In order to verify the performance and stability of the fuel cells operated on Victorian brown coal derived fuels, a Morwell char was produced and used for operation of the fuel cell. The fuel cell was operated for 40 hours with the current periodically interrupted to perform diagnostic tests to determine the performance of the fuel cell. **Figure 4-7** shows the performance of the fuel cell over the 40 hour test period.

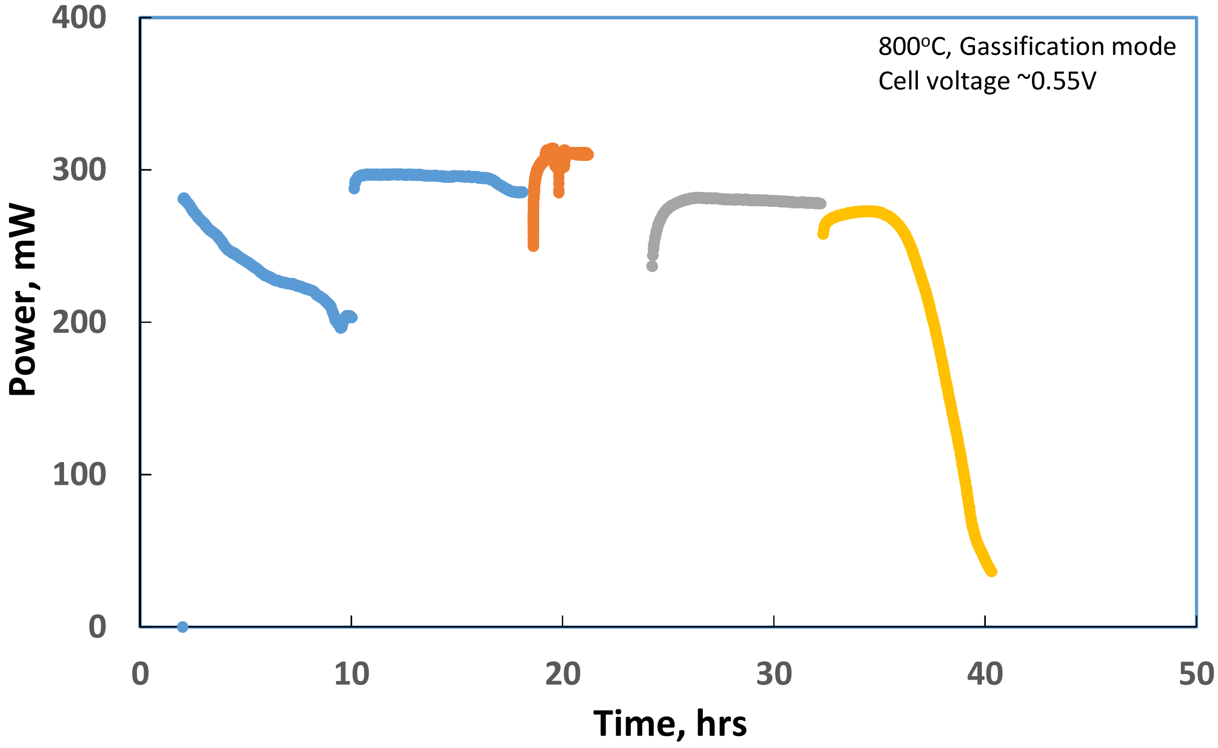

Figure 4-7 **Power output of fuel cell operated for 40 hours on Morwell Char. Discontinuities are due to interruptions for diagnostic testing.**

Initial operation of the fuel cell showed a significant drop in performance. The performance is unusual for this cell design which has been used for a number of different studies subsequent to the completion of this project. One suggested mechanism was that this drop in performance could be due to a build up of volatile impurities (tar) on the surface of the fuel cell or the deposition of carbon on the surface of the fuel cell. This layer would block the surface of the fuel cell restricting the access of gas to the surface of the anode and the removal of reaction products. The blocking of the surface would result in a drop in performance of the fuel cell as is evident up to 10 hours of operation. Diagnostic testing (at 10 hours) involved the operation of the fuel cell at lower voltages. This results in the anode becoming highly oxidising which would remove any carbon based impurity layer from the electrode and result in the improved performance as observed after 10hrs of testing. Further work is required to confirm deposition of a carbon based layer on the surface of the cell as an initial limiting factor on the performance of the fuel cell but this is currently considered the most likely cause of the initial drop in performance.

After the initial performance was recovered, the fuel cell remained stable operating at 300 mW (approximately 30 mW/cm^2) for around 30 hours before a steep decline. This decline in power was the result of the fuel being fully consumed in the anode chamber. **Figure 4-8** shows the performance of the fuel cell at 3 time intervals 2hrs, 10hrs and 40hrs.

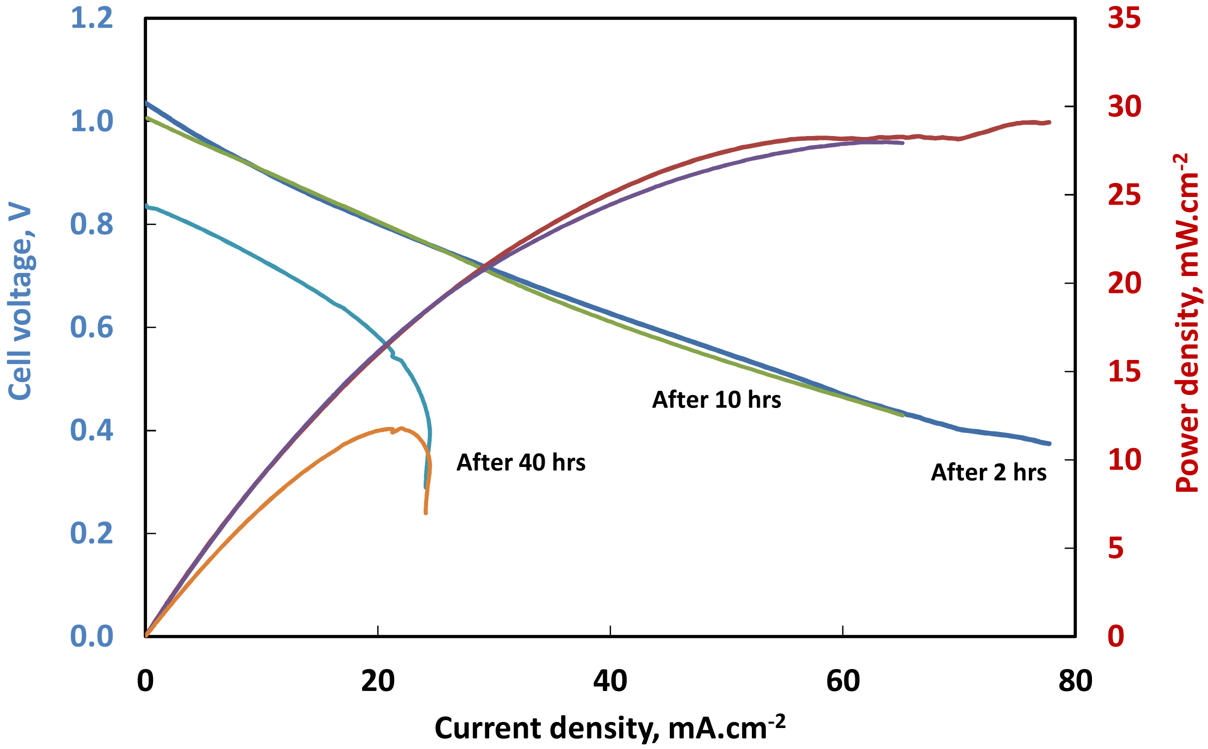

Figure 4-8 **Comparison of power output of tube cell operated on Morwell char after 2hrs (power - red, voltage - dark blue), 10hrs (power - purple, voltage - green) and 40 hrs (power - orange, voltage – light blue).**

After 40 hrs it is clear that the fuel cell performance was impeded via the restriction of fuel (as in **Figure 4-3**). The rate of fuel utilisation was far in excess of what would be required to operate the fuel cell with calculations based on the current utilisation showing only 30% of the fuel being used to produce electrical power. Despite the low fuel utilisation overall the fuel cell performance was very stable once the surface species deposited early in the experiment were consumed. Overall the power density was around 20% lower than that of the fuel cell operated in the same mode on XC-72 (**Figure 4-6** vs **Figure 4-8**). The reduction in performance of the fuel cell was related to higher polarisation and ohmic losses (**Figure 4-9**). These losses are most likely due to the incomplete clearing of the fuel cell electrode of the species deposited in the first hours of in operation which resulted in an increase of the ohmic resistance of the cell. Once these species where consumed the ohmic resistance drops but the availability of fuel decreases resulting in higher polarisation losses. Further investigation into the reasons for these losses is required to provide a definitive answer to why the fuel cell performance was low.

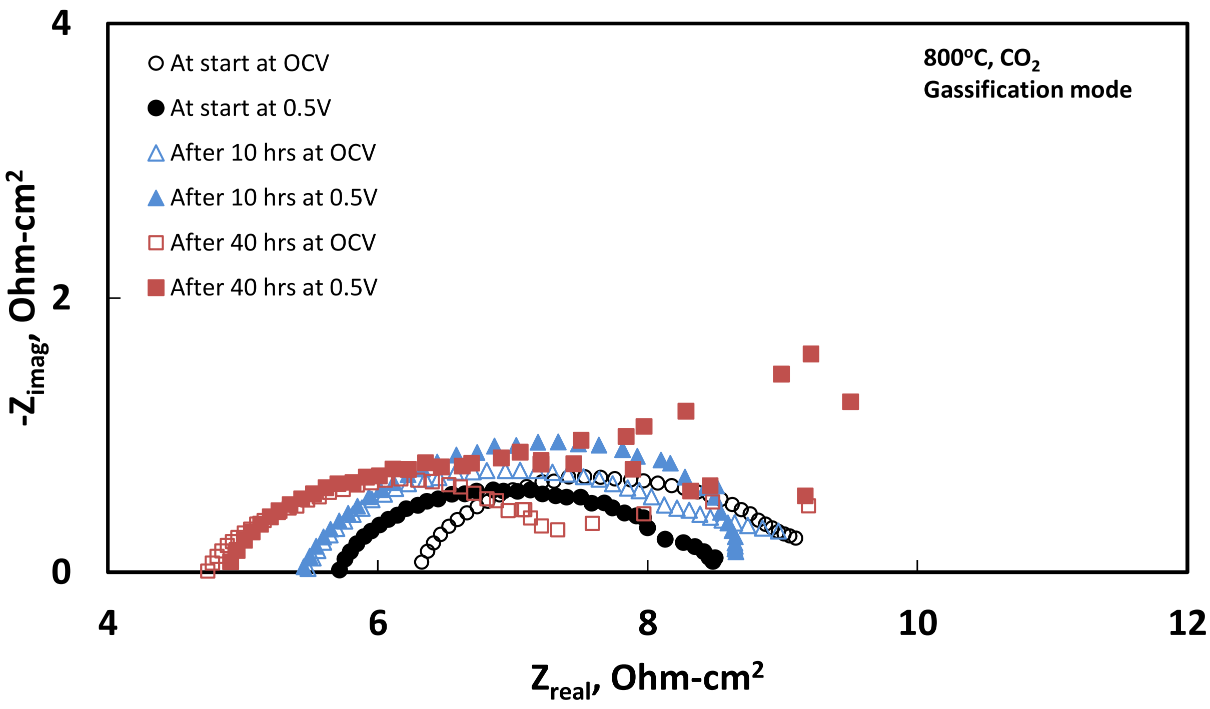

Figure 4-9 **EIS of fuel cell taken at various points during testing.**

There have been 3 previous studies carried out looking at the performance of CSIRO's solid state DCFC specifically on Brown coal chars [**2-4**]. All previous tests were carried out over a short time frame, less than 8 hours, and on small button cells (0.5 cm^2) as opposed to larger tube cells (10.5 cm^2). In these previous studies only a limited number of cells were tested on demineralised brown coal all of which were carried out in direct contact mode with no non-contact gasification studies carried out [**2-3**]. In this cell configuration the coal char behaves as a current collector, the current collection paths are shorter, the fuel is held via a spring loading mechanism to the surface of the cell and the electrolyte is supported – allowing it to be both thinner and made from lower strength materials such as cerium based electrolytes. The net result of these changes is a significant reduction in the ohmic resistance of the fuel cell. Rady et al. reported an ohmic resistance of 1 ohm-cm^2 on a button cell with identical electrodes as used in the initial tests in this study. The equivalent tube cells had a resistance of over 10 ohm-cm^2 (**Figure 4-4**)[**2**]. This lead to the power output of the fuel cell being 4 times greater than reported in the intial tests in this study for similar fuel (15.6 mW/cm^2 vs 65 mW/cm^2)[**2**]. Subsequent development of the fuel cell electrodes and current collection of the CSIRO tube cell design, as part of a parallel CSIRO funded development program not supported via the BCIA, resulted in the development of the electrodes that were tested in both gasification and direct contact mode (**Figure 4-6**). The optimised electrode and current collector combination had a far lower ohmic resistance than previously tested tube cells but the overall resistance of the fuel cell was still higher as it is necessary to use a thicker electrolyte (approximately double that of the button cell) and a higher strength but higher resistance material (YSZ). The net result of these changes is an increase of over 4 times in the ohmic resistance of the fuel cell. Further development of the fuel cell is out of the scope of this study, however, there is no fundamental reason why this resistance could not be further reduced.

In the button cell configuration there is limited gas flow to the fuel cell electrode. This leads to the fuel cells in previous studies on lower reactivity fuels, such as XC-72 or demineralised brown coal, having their performance limited via fuel starvation at higher current densities [**2**]. This effect is not noted with more reactive Morwell chars in button cells. These cells have far higher power densities on Morwell chars than other fuels. In this study the fuel was not compressed into the fuel cell electrode with a gas being fed through a bed of either carbon black (XC-72) or Morwell char. In this configuration the fuel cell operates largely on the gasified products. This is mainly CO in the case of the XC-72 and a mixture of CO, H_2 and potentially a range of other hydrocarbons in the case of Morwell char. In the tube cell configuration, with improved electrodes, the power output of the fuel cell was not restricted by the availability of fuel at the electrode surface. In addition, the insensitivity of the fuel cell output to input gas (**Figure 4.6 (b)**), lack of steep power decline at higher currents and the high OCV suggest that there was a significant excess of fuel gases being produced within the current reactor design. The current reactor appears to be better suited to XC-72 than to Morwell chars and there appears to be a negative interaction between the Morwell char and fuel cell when operated at relatively high voltages. Further investigation is required to completely understand the behaviour of this system and to further develop the reactor design and fuel cell for use with fuels derived from Victorian brown coals. Funding is currently being sought to progress this work via an ARC linkage grant.

4.3 Summary

A DCFC test fixture has been developed which is capable of operating with the anode functioning in either direct contact with solid fuels or indirectly under simulated gasification conditions. Operating under these two conditions has shown that there is a clear difference between direct contact and pure gasification modes, however, optimisation of the electrodes the difference in performance can be minimised with the CSIRO fuel cell design being able to operate in both a gasification or direct contact mode. Testing with a char derived from Morwell brown coal has shown stable performance although there is a reduction in the overall power output of the cell. The reduction in performance appears to be the result of a deposited layer on the surface of the electrode that can be removed by operating the cell at lower voltages. Further work is required to understand the interaction of the fuel with the fuel cell electrode and to optimise CSIRO's fuel cell design for use with Victorian brown coal. The stable performance in this study still suggests that Victorian brown coal is an attractive fuel source for DCFC's.

4.4 References

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[2] Direct carbon fuel cell operation on Brown coal, AC Rady, S Giddey, A Kulkarni, SPS Badwal, S Bhattacharya, et al. Applied Energy 120, 56-64 (**BCIA supported article**)

[3] Direct carbon fuel cell operation on brown coal with a Ni-GDC-YSZ anode, AC Rady, S Giddey, A Kulkarni, SPS Badwal, S Bhattacharya, Electrochimica Acta 178, 721-731, 2015 (**BCIA supported article**)

[4] Degradation mechanism in a direct carbon fuel cell operated with demineralised brown coal, AC Rady, S Giddey, A Kulkarni, SPS Badwal, S Bhattacharya, Electrochimica Acta 143, 278-290, 2014 (**BCIA supported article**)

5 Conclusions and future direction of DCFC research

This work has shown that at a fundamental level, the DCFC concept is, in general, sound, notwithstanding the variety of technology concepts within the DCFC family, and the immature stage of their development. It is clear that ongoing R&D will resolve many of the issues that have been raised in this report; however, as with many technologies, the research direction that will be taken is dependent on both technical and economic considerations.

In terms of use of Victorian brown coals as a fuel for direct carbon fuel cells, this fuel remains one of the most attractive options due to its low cost, high reactivity and low ash content. The performance of fuel cells is less affected by the absolute thermal value of the fuel than thermal technologies, making the traditional barrier to efficient Victorian brown coal utilisation (high moisture) less of an impediment. Furthermore, waste heat from fuel cells is readily accessible and can be used to dry, gasify or process incoming fuel making integrated high temperature systems possible at reasonably modest scales and high efficiencies.

CSIRO will continue to work in a number of relevant areas relating to the production of electrical power from Victorian brown coal relating to fuel cells. At this stage of development, the technical path CSIRO will follow with the current DCFC program is not finalised; however, it is clear from this work that other programs relating to Victorian brown coal gasification and new technologies for hydrogen production need to be considered as part of the DCFC technology development and scale-up strategy.

This study will form an important part of CSIRO's ongoing internal review of technology directions, and may be used to guide CSIRO with its engagement and further development activities. There is a clear case for investment in a number of the pathways suggested here most prominently the development of highly integrated systems with efficiencies of over 50% relying on thermal integration of a gasifier or direct reaction of carbon fuels on the fuel cell surface. Both of these paths will require significant investment if a commercial plant of this type is to be realised. Wider development work looking at the production of hydrogen from Victorian brown coal (amongst other feedstocks) will continue. If this progresses to a stage where high purity hydrogen can be produced then it could conceivably be used in a currently commercial fuel cell system to produce electrical power for use in Victoria.

Clearly, however, for DCFC technology to make a significant leap forward in terms of commercial readiness, then scale-up work and 'pilot' scale demonstration systems are required. This will serve two needs: to address industry perspectives of risk and readiness, and to provide important data and insights to support the development of robust techno-economic calculations, making the case for DCFC to form part of a viable energy mix. This system could only be produced after more fundamental studies to understand the underlying operation of a DCFC and to develop a high performance system.

6 Appendix 1 - Global research into Direct Carbon Fuel Cells

EU

- University of St Andrews (UK)
- Imperial college London (UK)
- Oxford university (UK)
- University of Cambridge (UK)
- AGH University of Science & Technology (Poland)
- Institute of power and energy (Poland)
- Polish academy of science
- Czestochowa Technical University (Poland)
- University of Limerick (Ireland)
- Queens University Belfast (Ireland)
- University of Southampton (UK)
- Royal Institute of Technology (Sweden)
- Technical University of Denmark
- Consejo Superior de Investigaciones Cientificas (CSIC) (Spain)

South Korea

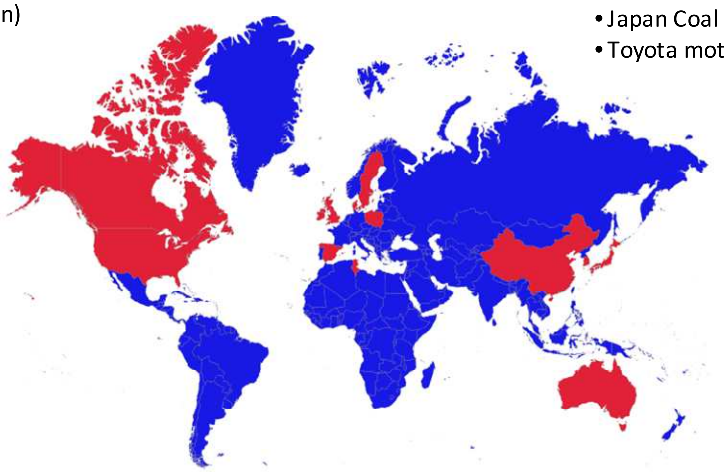
- Korean institute of Energy research (KIER)
- Gwangju Institute of Science and Technology (GIST)
- Korean institute of science and technology (KIST)
- Pusan national university
- Sejong university
- Hanbat national university
- Samsung heavy industries (patent only)

USA

- University of Pennsylvania
- Stanford University
- Point source power
- Contained energy
- Massachusetts Institute of Technology (MIT)
- Illinois Institute of Technology
- SRI International
- University of Akron (in partnership with First Energy)
- EGT enterprises INC (patent only)

Japan

- Central Research Institute of Electric Power Industry (CREPI)
- Kobe Steel Ltd
- Tokyo Institute of Technology
- Kansai University
- Japan Coal Energy Centre (Jcoal)
- Toyota motor company (patent only)



China

- Tianjin University
- Tsing Hua University
- Nanjing Normal University
- Southeast University
- Nanjing University of Technology
- Shanxi University
- Chinese Academy of Sciences
- Xi'an University of Science & Technology
- Dalian University of Technology
- Harbin Engineering University
- Ningbo University
- Hong Kong University of Science & Technology
- China University of Mining & Technology
- Huazhong University of Science & Technology
- Sanming University
- Shenhua Ningxia Coal Ind Grp Co Ltd
- Tsing Hua University
- Xiamen University
- South China University of Technology
- China University of Mining & Technology
- Southeast University – China
- Dalian University of Technology
- CNPC Fertilizer Factory
- China Hina Huaneng group clean energy technology (patent only)
- Yangzhou Power Electric Co., Ltd (patent only)
- Dongying Jieda chemical technology co ltd. (patent only)

Other

- University of Sfax (Tunisia)
- University of Carthage (Tunisia)
- ET-Energy crop. (Canada – patent only)

Australia

- CSIRO
- Monash university
- Newcastle university
- University of Queensland

Figure 6-1 **List of every institution to have published a Journal article or patent in the DCFC area in the last 5 years**

Globally there is increasing interest in the development of fuel cells, with a particular emphasis on novel systems that utilise fuels other than natural gas or pure hydrogen. **Figure 6-1** shows every institution globally to have published a journal article or patent in the last 5 years specifically relating to direct carbon fuel cells. In general, there are a wide variety of DCFC programs across the globe. These programs are at an early stage with no organisation at a stage where they could make electrical power at a commercial scale. There is a single commercial product capable of producing power from solid high carbon fuels which has been developed for low power applications such as battery charging and LED lighting (Point Source Power, **Figure 6-2**).

Figure 6-2 **"Voto", a low power battery charger that operates on a solid fuel cartridge [1].**

These early programs give some confidence that the technology is fundamentally capable of being developed to a level where it can effectively generate power. Similarly there are now a wide number of groups that have demonstrated power densities at lab scale operating on high carbon fuels that can be considered near to the level required for commercial application (100 mW/cm^2 +). There have also been lab scale demonstrations that have shown that fuel cells operated on high carbon fuels can produce power at high efficiencies. The highest reported single cell electrical efficiency is 80%, and after system losses this would likely translate to around 65–70% electrical efficiency at device level [**2,3**]. To date there have been no large scale trials of DCFCs considering system level issues or lifetime issues. A significant amount of work being carried out is a very small scale looking at fundamental reaction mechanisms and materials properties. This is often carried out on a wide range of different cell geometries and fuel cell designs, however, there are now a few key designs emerging that are attracting more attention. **Figure 6-3** provides an overview of these designs and their relationship to each other.

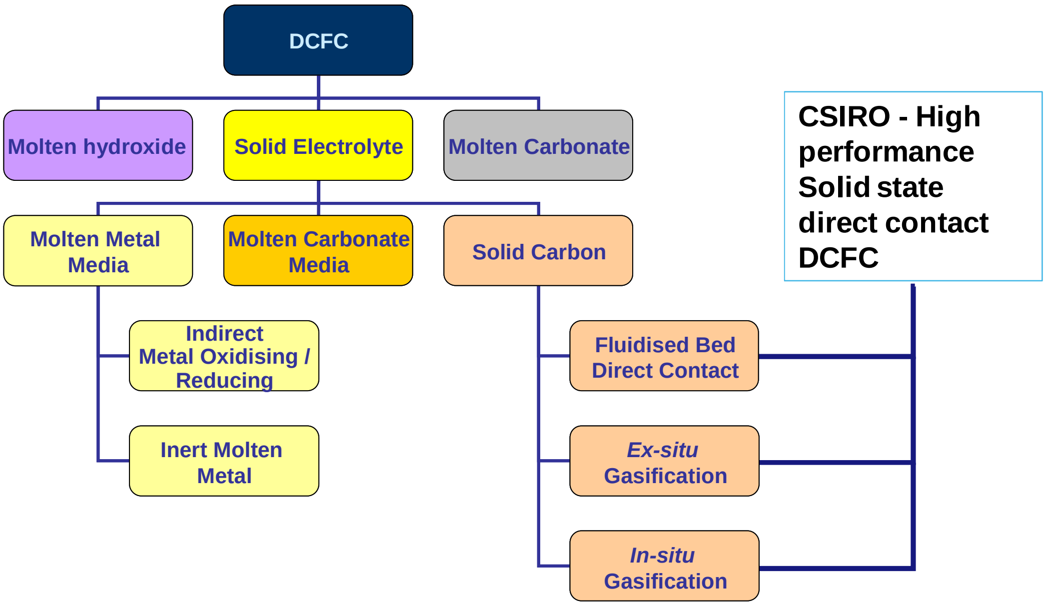


Figure 6-3 Different design approaches and their relationship to each other. The CSIRO design is flexible in terms of operation and can be operated in any of the 3 modes common within solid electrolyte systems. Figure modified from ref [2]

The CSIRO solid state direct contact cell design has been shown to be one of the most flexible designs currently under consideration and can be operated in direct contact mode, internal gasification (fuel in anode chamber) and ex-situ gasification mode (fuel gasified externally and then fed to the fuel cell). This flexibility relates to the mixed ionic electronic conducting materials used in the anode that can directly oxidise solid or gaseous fuels. Other fuel cell designs that remain popular are gasification driven systems and fuel cells containing a molten carbonate components. Gasification based cells are actively under investigation at Stanford University (USA) and KIER (South Korea) with molten carbonate cells being developed mainly in the University of St. Andrews (Scotland) and DTU (Denmark). There has been a significant shift in geographic location of research programs from the USA in the 90’s and early 2000’s to China and South Korea from 2010 onwards. Although the Chinese programs are typically less developed, China now accounts for over 20% of all direct carbon fuel cell publications (including patent applications).

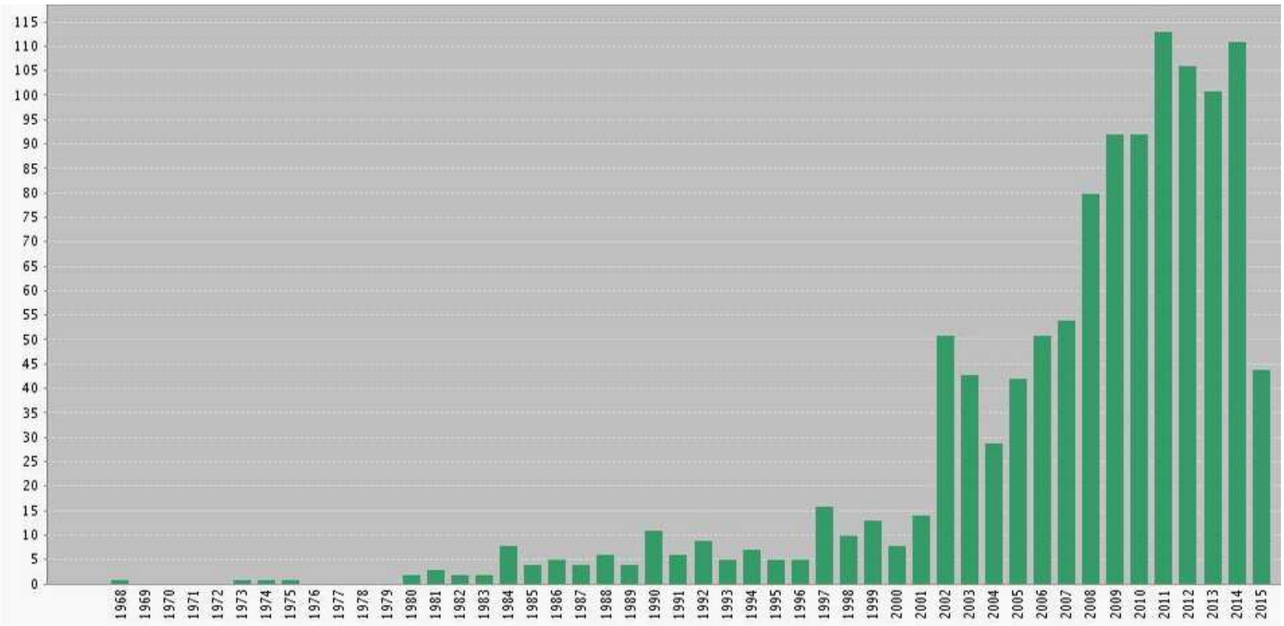


Figure 6-4 Number of articles published per year under "direct carbon fuel cells" or "coal" AND "fuel cells". Web of Science citation report Apr-2015. (http://apps.webofknowledge.com/UA_GeneralSearch_input.do?product=UA&search_mode=GeneralSearch&SID=Q2UA6TzZTsPKWW

In terms of overall growth in the field the number of research groups has expanded dramatically in the past 5 years with over 75% of publications in this field occurring in that time (**Figure 6-4**). Growth in Australia has been significant with 80% of publications in DCFC being after 2010. 50% of all DCFC publications in Australia have been by or part funded by CSIRO.

Over the last 5 years there has been a marked increase in the number of groups and scale that these groups are operating at to develop fuel cells that operate on coal as the primary fuel. These systems are particularly attractive due to their high efficiency and the ability for them to be used with carbon capture. The technologies under investigation range from systems that gasify the fuel to systems that directly consume the coal within the fuel cell. There are a number of groups globally that are also looking at hybrid systems that produce hydrogen as opposed to power. These systems, depending on the cell design, often contain a modified direct carbon fuel cell as the core to the system with steam being provided to the cell as opposed to air.

6.1 References

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