

**Solid Oxide Fuel Cells – High
Efficiency Clean Power Generation
for the 21st Century**

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I hereby declare that, except where specifically indicated, the work submitted herein is my own original work. I also declare that the work I shall submit in the conference style paper is also my own.

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Summary

There is a growing environmental imperative and economic incentive for the development of 'clean' efficient power generation technologies.

The fuel cell principle represents the ideal means of extracting maximum work from suitable fuels. Numerous technologies have been developed to exploit the principle, of which solid oxide fuel cells are favoured for large scale power generation.

A computer simulation of a solid oxide fuel cell plant has been developed and validated. The simulation exhibits basic fuel cell properties, in particular high electrical efficiency of over 70%. Improved resistance modelling is required to give lower more realistic, but still impressive efficiency predictions.

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0.2 Introduction

As industrialisation spreads across the globe, and standards of living rise, the population's energy requirements are continually increasing. Despite a wide range of energy sources and ever more means of tapping them, most of the world's 115GW p.a. power consumption is still generated from the combustion of fossil fuels such as coal, oil and gas. The technologies employed, despite their advanced development, are inefficient (maximum efficiency is about 50%, with average efficiency in the USA about 35%) and dirty (generating significant proportion of our acid rain and greenhouse emissions). The technologies continue to be used for the simple reason that no alternative can match them on cost or scale terms.

Meeting our energy needs, without causing the collapse of the ecosystems upon which we depend, has become a major preoccupation of governments, industry and individuals alike. This preoccupation has brought about the development of a range of 'alternative' clean, renewable energy technologies such as solar photovoltaic and wind energy. However, these alone will not be enough due to their inherently variable output, the remoteness of prime locations, and the difficulty in efficiently and cost effectively storing & transporting energy. What is needed is a technology or combination of technologies which allow for the *clean cost effective supply of energy on demand on a large scale and in any location*.

There is one emerging technology which could allow this demand to be met. The technology is the fuel cell, a device which oxidises fuel, such as hydrogen, in a substantially isothermal electrochemical process; directly converting chemical energy into electrical energy with *optimal* efficiency. This paper introduces the fuel cell concept, explains why it is the optimal method of chemical energy extraction, describes the market which the technology is to revolutionise and describes the computer simulation and analysis of a particular fuel cell technology.

The initial objective of this Fourth Year Project was to develop a model of a Solid Oxide Fuel Cell (SOFC) which would predict theoretical performance and show the influence of system design (materials and geometry) on that performance. The code was to employ a finite element type approach, using a single cell model as an element, to determine the variation in temperature, chemical composition and electrical performance through a cell stack. This model was to be

incorporated into a combined cycle model, developed by fellow students working with a simple SOFC model and existing CUED combined cycle code, to produce an SOFC topped combined cycle model to investigate the practical performance characteristics of such a plant.

Alas, this wasn't to be. The basic single cell model proved very much more difficult to implement than expected, and as a result my project objective was reduced. My new objective was to produce a single cell model incorporating cell materials and geometry only in as much as they effect resistance. I have achieved this and am about to embark on a PhD during which I aim to fulfil my original objective!

Section One : The Fuel Cell Concept, Fuel Cell Technologies and Potential Fuel Cell Market

1.1 The Fuel Cell Concept and its History

The fuel cell concept arises directly from the operating principle of the galvanic cell; it is in effect a cell in which the electrodes are supplied with reactants, allowing continuous operation without depleting the electrodes.

As early as 1880 Wilhelm Ostwald wrote: "I do not know whether all of us realise fully what an imperfect thing is the most essential source of power which we are using in our highly developed engineering – the steam engine" - indicating a growing awareness that chemical processes, such as those in galvanic cells, could approach 100% efficiency whereas the efficiencies of heat engines were limited by the Second Law to the Carnot efficiency of around 60% (see next section).

The fuel cell was first demonstrated in 1839 by William Grove. Unfortunately development of viable technology for exploitation of the principle has been slow, primarily due to the incompatibility of the required material properties. The complexity and modernity of materials used is described in the technology overview (section 1.4). Inevitably the first uses were space and military applications, in which cost is of secondary importance to performance. With increasing understanding of fuel cell and relevant materials science, driven by these specialist applications, there have a number of false dawns when fuel cells have been proclaimed the solution to all of our energy needs, only to realise that there are inherent limitations on particular technologies applications. This roller coaster road to development has however generated a wide

range of fuel cell systems with one or more suitable for virtually every power application imaginable.

1.2 Fuel Cell Thermodynamics – The Ultimate

In order to fully appreciate the potential of fuel cells, one must consider the best possible method of releasing chemical energy from fuels, rather than simply comparing LCV efficiencies. Fuel cells are not to be considered a slightly better type of heat engine – they are fundamentally different.

Using Maximum Work (Exergy) Analysis, the maximum possible amount of work that can be extracted from fuel can be evaluated. Consider a system at constant temperature, T , with inlet reactant flow at temperature, $T_1 = T$, with enthalpy h_1 and entropy s_1 , and outlet product flow at temperature, $T_2 = T$, with enthalpy h_2 and entropy s_2 . The ambient temperature to which the system exhausts is T_o . Exergy analysis gives:

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

Where, $\Delta H(T)$ is the enthalpy of reaction; $\Delta S(T)$ is the entropy change of the reaction; and $\Delta G(T)$ is the change in Gibbs Potential of the reaction. This equation shows that during isothermal oxidation the available energy of the fuel is split into two components – the Gibbs Free Energy and the necessary heat rejection due to the entropy change of the reaction.

A fuel cell is a device which isothermally oxidises fuel. It can be proven that an ideal fuel cell converts the total Gibbs Free Energy directly into electrical work, with the remainder being rejected as heat. Direct conversion to electrical energy is not limited by Carnot efficiency and hence the entire Gibbs Free Energy is converted to work. The remaining heat energy can then be converted to work using a standard heat engine with the Carnot efficiency limit.

Comparing this with the process in a heat engine, in which all of the enthalpy of reaction is converted to heat and only the Carnot limited amount recovered as useful work, clearly demonstrates the superior potential of fuel cells. This is illustrated in Figure 1. It shows the variation of $\Delta G(T)$ with temperature for methane and hydrogen. Note that $\Delta G(T)$ for methane is very near equal to $\Delta H(T)$ at all temperatures, indicating that the entropy change during oxidation is very small – a fuel cell directly oxidising methane could reach electrical efficiencies of almost

100%. In the case of hydrogen, $\Delta S(T)$ is significant resulting in a decrease in $\Delta G(T)$ with temperature; despite this $\Delta G(T)$ is greater than Carnot efficiency up to 1100K.

The majority of this report is concerned with determining the feasibility of making a fuel cell, and the extent to which practical cells fall short of this ideal.

1.3 Fuel Cell Practicability and Practical Characteristics

Thermodynamic analysis of the fuel cell principle indicates that fuel cells are theoretically brilliant. But are they practically brilliant? And if so why are they not already in widespread use? The answer to the first question is a conditional yes. The condition being that very challenging materials and design problems can be overcome; wherein lies the answer to the second question. The development of fuel cell technology is limited primarily by the evolution of materials simultaneously having the required chemical, thermal, electrical and mechanical properties. The materials used in a range of fuel cell technologies are described in the next section, but before moving on to a survey of the characteristics of specific technologies, it is worth considering some more general characteristics.

- Scale vs. Efficiency– The high theoretical efficiency of fuel cells can be approached by plants of all sizes, making them ideal for the local generation of power, eliminating further significant grid distribution and battery storage losses.
- Part load Efficiency – There are very low part load efficiency penalties in fuel cells due to the low fixed losses (e.g. no moving parts), inherent modularity of plants and efficient throttling simply through fuel flow control.
- Load Following – The inherently fast chemical reactions of fuel cells allow plant to be designed with very rapid load following and short start up time, essential for transport applications.
- Reliability – Once initial teething problems (not trivial!) are solved the simplicity of fuel cell plant will make for very predictable and reliable performance.
- Quality & Controllability of Power – The inherent modularity and steady flow (in the literal sense) operation of fuel cells means that current and voltage specifications can be relatively freely specified and consistently fulfilled.

- Flexibility of Fuel – Hydrogen used in fuel cells can be derived from virtually any energy source. Fuel cells do not represent a new source of energy but a better and more flexible way of using existing sources, hence they are not tied to a single finite resource such as fossil fuels.

1.4 Fuel Cell technologies

Unfortunately a direct methane fuel cell has not yet been developed. Almost all fuel cell technologies use hydrogen, which can be derived from other fuels by reforming or even electrolysis of water. The fact that methane cannot be converted directly, causes the first reduction in practical efficiency below ideal.

Fuel cell technologies can be classified by a diverse range of categories such as use, temperature, fuel type, oxidiser type, or charge carrier; however the most common classification is by type of electrolyte, which is the method used here:

- Polymer Electrolyte (PEFC) : The electrolyte in this fuel cell is an ion exchange membrane that is an excellent proton conductor, such as fluorinated sulfonic acid polymer. Charge carriers are hydrated protons, which means that the membrane must remain hydrated, requiring tight water management. Temperatures are limited to below 120°C by the polymer properties; which, combined with the water management requirements means that only H₂ rich gas with minimal CO (a poison at low temperature) can be used as fuel. The low temperature also means that higher catalyst loading (platinum in most cases) than in other types of cell is required in both the anode and cathode.

PEFCs deliver high power density, which offers low weight, volume and cost (despite the platinum requirement). They also exhibit a relatively low sensitivity to orientation and contain no corrosive fluids which makes them ideal for transport applications.

Commercialisation is underway with numerous car and bus demonstration systems in use. Typical operating conditions are 80°C, 0.285MPa and H₂ supply with less than 100ppm CO. Efficiencies of up to 60% are predicted for on board H₂ supply or 40% with on board reforming. Smaller units have also been developed, suitable for powering lap tops and other low power devices.

- Alkaline (AFC) : The electrolyte in this fuel cell is concentrated (85 wt.) potassium hydroxide in high temperature cells (~250°C), or less concentrated (35-50 wt.) KOH for lower temperature (<120°C) operation. The electrolyte is retained in a matrix (usually asbestos), and a wide range of electrocatalysts can be used (e.g., Ni, Ag, metal oxides and noble metals). Charge is carried by hydrated protons which flow to the cathode (air electrode) as in PEFCs. Unfortunately the cells are very prone to poisoning, so require an H₂ supply containing no other reactive constituents. This also applies to the oxidiser flow.

AFCs were the first type of fuel cells to be developed (as early as 1930), being used in the early 1960s for the Apollo space vehicle, where their high power to weight ratio, capacity to operate on pure hydrogen (used in the main engines), and potable water by-product made them a perfect solution. However, they have had relatively little success in terrestrial applications due to the high cost of producing high purity fuel and oxidiser streams, plus corrosion problems. Typical efficiency is 60%.
- Phosphoric Acid (PAFC) : The electrolyte in this fuel cell is 100% concentrated phosphoric acid retained in a matrix which is usually silicon carbide. Operating temperatures are in the range 150 to 220°C, the lower limit due to loss of ionic conduction and CO poisoning of Pt catalysts, the higher limit due to loss of stability of the acid. Use of 100% concentrated acid makes water management simpler than in AFCs due to the lower water vapour pressure in the cell. Like PEFCs and AFCs charge carriers are cathode seeking hydrated protons. Poisoning is less of a problem in PAFCs, than in lower temperature cells, however CO, CO₂ and S concentrations must be below a few hundred PPM due to the Pt catalysts.

PAFCs were the first to reach commercialisation with over 60MW of demonstrators in operation. At present they offer the lowest cost per kW and are used mainly for plants of 50 to 200kW capacity, though some 1 to 11MW plants have been built.

Development interest is however dropping off, and PAFCs are expected to be superseded in the next few years.

Typical efficiency is low at just 40%.
- Molten Carbonate (MCFC) : The electrolyte in this fuel cell is usually a combination of alkali carbonates, such as Na and K, which is retained in a ceramic matrix of LiAlO₂. The fuel cell

operates at about 600 to 700°C where the alkali carbonates form a highly conductive molten salt, with anode (fuel electrode) seeking carbonate ions providing ionic conduction. Due to the high operating temperatures in MCFCs, Ni (anode) and nickel oxide (cathode) are adequate to promote reaction eliminating the need for expensive and impurity sensitive noble metal catalysts, reducing catalyst costs giving greater fuel flexibility.

MCFCs are considered to be second generation fuel cells because they will reach commercialisation after PAFCs. Their much higher operating temperature makes materials selection and mechanical design constraints very different, plus they have anode seeking charge carriers which result in water formation on the fuel side requiring different water management techniques, all of which have taken time to develop.

MCFCs offer higher electrical efficiencies than PAFCs at around 60% plus the possibility of cogeneration (water heating) which makes overall efficiencies of 80% feasible. At present there are numerous demonstration plants of up to 3MW capacity, though most are of multi-hundred kW capacity. Most existing plants do not take advantage of the combined cycle possibility (using hot fuel cell gases to drive a bottoming cycle), due to the low Carnot limit, and practical difficulty of designing specialist plant.

- Solid Oxide (SOFC) : The electrolyte in this fuel cell is a solid, nonporous metal oxide, usually Y_2O_3 -stabilised ZrO_2 . Cells operate at 650 to 1000°C where efficient conduction of anode seeking oxygen ions takes place. Typically, the anode is Co- ZrO_2 or Ni- ZrO_2 cermet, and the cathode is Sr-doped $LaMnO_3$. Like the MCFC operating temperatures are high enough to allow internal reforming and promote rapid kinetics with non precious materials. Even higher temperatures than the MCFC result in by-product heat of a temperature suitable for use directly in standard steam turbine bottoming cycles, but mean that materials and mechanical design requirements are even more stringent.

SOFCs slightly lower electrical efficiencies, around 45%, than MCFCs due to their higher operating temperature (see section 1.2), and less advanced development. However, cogeneration plants of 80% overall efficiency are already in operation, with combined cycle (fuel cell in place of combustion chamber in a gas turbine) plants of 60% electrical efficiency under development.

1.5 The Market for Fuel Cells

Before going further into the science and technology of fuel cells it is important to appreciate what the market for the technology is. Products must be designed to meet consumer demand, not just maximise exploitation of fuel potential!

1.5.1 Market Size and Growth

The Fuel Cell market has only just begun to emerge, with few commercial systems in operation. However, there is a multitude of technologies, with capacities of Ws to MWs, undergoing demonstration. By 2010 it is expected that systems capable of full filling most sectors of the projected 160GW, US\$150,000 billion p.a. (1/3 of gross world product), global energy market will be in production.

Drivers for Market Growth:

- Favourable Characteristics - Their high efficiency regardless scale, combined with good part load characteristics, rapid load following, flexibility of fuel supply and flexibility of load factor gives fuel cells a strong position in a wide range of applications.
- Government market stimulation programs - ranging from tax breaks in the form of green taxes, subsidies in the form of preferential rates for clean energy and government build programs (currently mainly transport applications) have had a dramatic effect on the Japanese, German and American markets. The desire to develop comparative advantage in an emerging industry combined with international CO₂ quotas will ensure continuing governmental support.
- Sustainability Culture – Environmentalism has been an important part of world cultures for several decades (particularly in developed countries where people are at leisure to worry about such things). But it has not played a large part in global economics (with the exception of environmental disasters) until very recently. Increasing awareness of the economic cost of environmental degradation has led the world's financial institutions to take an interest, making vast amounts of capital available for development and marketing.

Barriers to Market Growth:

- Cost – Competition in the power generation market is fierce, with cost per kW and risk (real and perceived) being the key factors in technology selection. Fuel cells simply cannot

compete at present with established turbomachinery plant. Costs must be driven down through technology and economies of scale.

- Over Hyped – Fuel cells have been heralded as the answer to all our energy needs several times in recent history, each time before they were ready even to fill their role in an integrated energy strategy, let alone save the world. The benefits of the technology must be forcefully but realistically presented to overcome doubt inherent in something presented as being ‘too good to be true’.
- Institutional Inertia – There is a very highly developed carbon based economy, with much vested interest which means that (conspiracy theories aside) transition to a hydrogen (or more realistically, a partially hydrogen) economy will not happen fast until the technology is developed sufficiently to force change.
- Chicken and Egg – In order for use of hydrogen technologies to spread a hydrogen infrastructure must be developed, but a hydrogen infrastructure will not develop until there is a sufficiently large adoption of hydrogen technologies. This is a barrier integrated fossil fuel reforming can help climb.

1.5.2 Market Sectors

The energy market is diverse with very different characteristics demanded by different sectors.

The basic market segments are:

- Standalone Power Generation – large (kW & MW) scale plants for industrial and residential supply.
- Integrated Power Generation – variable scale plants using solar and wind technology combined with water electrolysis plant and fuel cells to provide totally clean, renewable energy on demand.
- Transport – intermediate (100s of W & kW) scale plant which is robust and able to cope with rapid load changes for use in personal and commercial transport.
- Mobile – small scale (W & 10s of W) plant for portable electrical and electronic equipment.
- Space & Military – very high specification variable scale plant for transport, mobile power generation, and small scale uses.

1.6 Summary of Section One

In principle fuel cells are the ultimate means of generating energy from suitable fuels, boasting theoretical efficiencies well in excess of those possible from heat engines.

There are fuel cell technologies in production today with the capacity to fulfil the needs of most sectors of the energy market - low temperature PEFCs for portable and transport applications; PAFCs for small scale power generation; and MCFCs and SOFCs for large scale combined cycle (possibly plus water heating) applications.

In the power generation sector, Solid Oxide Fuel Cells have the greatest potential, despite their less advanced status, due to their higher operating temperature which allows for their integration with proven, 'off the shelf', bottoming plant. The solid state of the electrolyte also allows for greater flexibility of design which will enable greater optimisation. It is this technology which has been the subject of this project and is detailed in the rest of this report.

Section Two: Solid Oxide Fuel Cell Power Generation

In this section of the report an analysis of a Solid Oxide Fuel Cell Plant is presented. The analysis is split into several sections, beginning with the layout of a typical plant and moving on to describe the chemical processes which take place within the stack. There is then a section on the calculation processes required to analyse the plant, before an overview is given of the Fortran 77 code written to analyse plant performance. The data from this computer model is presented in a format, which illuminates plant characteristics as well as validating the model against the results of other studies and underlying thermodynamic and chemical properties.

2.1 The Plant

A schematic of a solid oxide fuel cell plant is shown in Figure 1. Typically plants are supplied with natural gas, the main constituent of which is methane (CH_4). A plant has three components:

- The Preheater – which raises the temperature of the fuel and air inlet gases to near cell operating temperature. As well as heating, the preheater substantially reforms the fuel to yield a hydrogen rich gas stream, by means of steam reforming. This process occurs naturally at cell

operating temperatures, but is catalysed to increase the rate. It is important to have stack entry gases of a suitable temperature and composition in order to maximise the utilisation of the expensive cell area.

- The Cell Stack – which electrochemically oxidises the hydrogen stream, drawing oxygen ions through an electrolyte layer from the air stream. This is the most complex part of the plant; with anode, cathode and electrolyte layers little more than tens of microns thick and centimetres across, connected in series by the hundreds and in parallel by the thousands. Flow rates are relatively slow, of the order of metres per second, but channels are small, of the order of millimetres, making flow and heat management critical.
- The Bottoming Cycle – which utilises exhaust exergy. Initially as gas turbine, but could be a full gas turbine/steam turbine combined cycle. Optimal operating conditions will probably be quite different from standalone or even traditional combined cycles due to stack exhaust temperature restrictions and preheating requirements. This section of the plant is outside of this project's remit. A bottoming cycle of efficiency 65% of Carnot efficiency has been assumed to be representative of power output, after allowance for preheating. The bottoming cycle has no effect on the stack analysis. The current model was chosen as it gives acceptable correlation with the results of other investigations.

The division of chemical and thermodynamic processes into these plant components is not entirely consistent. One of the key benefits of solid oxide fuel cells is the capacity to internally reform fuel, i.e. incorporate the reformer into the cell stack. Furthermore, reforming continues through the electrochemically active section of the module as a result of the changing gas composition (depletion of H_2 formation of H_2O). For calculation purposes this is not a problem as the gas composition calculation takes into account the variation of all species due to both reforming and oxidation reactions. The next section explains the chemical processes involved in these reactions and the modelling systems which have been used in calculations.

2.2 The Chemistry

As described above there are two types of reaction involved in the fuel cell stack; the chemical reforming reactions and the electrochemical oxidation reaction.

2.2.1 The Reforming Reactions

The reforming process consists of two reactions – the endothermic Methane Reformation reaction, in which steam and methane at sufficient temperature react to give hydrogen and carbon monoxide; and the exothermic (at this temperature) Water Gas Shift reaction, in which carbon monoxide (in this case from the Methane Reforming reaction) reacts to give carbon dioxide and hydrogen. Hence, the overall reforming reaction is the production of hydrogen and carbon dioxide from methane and water.



It has been assumed that reaction kinetics are fast, i.e. the time scale for reaction is very much smaller than the time scale for flow over the cell. This is not strictly true, particularly for the reforming reaction, and should be the first assumption eliminated from the code in the next stage of development. However, as this code does not take into account flow rates (i.e. time), it does not affect the validity of the solutions produced.

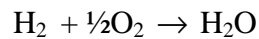
With the fast kinetics assumption, the rate of reaction can be replaced by an equilibrium constant, K_p , which describes the relative concentrations of reactants and products. For ideal gasses, K_p is a function only of temperature. Hence by the further assumption of ideal gas behaviour, which is a valid assumption for the gasses, temperatures, pressures and length scales in question, empirical $K_p(T)$ curves can be used to determine gas component partial pressures as a function of temperature.

Before moving on, it is important to note that there are several other reactions possible given the reactants supplied (including oxidiser side gases) – dissociation reactions and a second methane reforming reaction. Luckily (in the interest of ease of calculation), consideration of the kinetics and equilibrium constants reveals that the kinetics of these reactions are relatively fast but that the concentrations of the resulting species are negligible, with the exception of three dissociation reactions which result in carbon formation. However, as carbon formation is

unacceptable (clogging the cell), an operating point must be chosen to inhibit these reactions. The concession necessary to eliminate carbon formation is simply that excess water must be supplied in order to make the ratio of steam to methane greater than two to one.

2.2.2 The Electrochemical Reaction

In this model only one electrochemical reaction is considered, that of hydrogen, shown in Figure 1. In this reaction oxygen ions from the oxidiser stream, liberated at the cathode, pass through the electrolyte to the fuel side where they combine with hydrogen ions, liberated at the anode, to form water.



The by-products of the reaction are a small amount of heat, and a significant amount of electrical work in the form of an electron flow in the external circuit. The kinetics of the reaction are complex and do not need to be analysed in a model of this detail. For a simple, chemical and thermodynamic model, the electrochemical reaction can be reduced to a single parameter – Fuel Utilisation (FU): the fraction of the hydrogen supplied to the cell which is oxidised i.e.

$$FU = \frac{\textit{Amount of Hydrogen Oxidised by Cell}}{\textit{Amount of Hydrogen Supplied to Cell}}$$

This parameter is analogous to the Heat Exchanger Effectiveness parameter, in that it has a maximum of one, but realistically must be set lower because of the finite hydrogen concentration required to drive the cell reaction. To some extent it can be considered to give a qualitative measure of stack size – higher utilisation requiring larger stacks, but does not actually include any physical parameters. Definitions of Fuel Utilisation are generally vague, making it difficult to determine what definition has been used in specific papers. This definition has been chosen as it describes the function of the fuel cell stack alone, independent of the type of fuel supplied to the plant and the associated reforming reactions.

In the second stage of code development, in which materials and geometry (in the form of cell resistance) were introduced, another parameter, current density, was introduced. It gives a quantitative relationship between the amount of hydrogen oxidised and cell stack size. Current density, measured in Amperes per unit area, is limited by materials because it is a measure of the

number of active oxidation sites per unit area multiplied by the rate of reaction of individual sites. The relationship between current density and operating conditions such as pressure, temperature and gas composition is complex and is not generally investigated in basic models. From empirical studies a sensible range of values can be determined, but these values do not taken in to account current density limit variation with other parameters such as temperature, pressure and gas composition. Such information will be critical for the next stage of code in which the variation of operating points across a stack will be considered.

Finally, it is important to note that other reactions are possible, including the elusive direct oxidation of methane and a carbon monoxide oxidation reaction. However once again their effects are negligible in a cell designed for hydrogen oxidation, in this case due to the hydrogen specific materials used. Note that if other reactions were to be included, the definition of Fuel Utilisation would have to be extended to include the fraction of other species oxidised.

2.3 The Calculation Processes

There are two components to the calculation process:

- Chemical calculation to determine stack gas flows
- Energy calculation to determine plant component temperatures

Clearly, the two are not independent – gas flows depending strongly on temperature. In fact both the chemistry and the energy calculations are iterative, with the chemistry calculation being iterated within the temperature iteration.

2.3.1 Chemistry Calculation

Turning the chemistry of the methane reforming, water gas shift and electrochemical reactions into equations yielding gas composition is no trivial matter. The derivation is included here as it is the most fundamental calculation of the code, the remaining calculations following from their definitions.

The temperature based equilibrium constant values are given by the empirical quartic curve fit:

$$K_p(T) = AT^4 + BT^3 + CT^2 + DT + E$$

Where the coefficients, with pressure in bar, are:

	Reforming	Shifting
A	$-2.631212 \times 10^{-11}$	5.47301×10^{-12}
B	$1.2406499249 \times 10^{-7}$	$-2.574790444 \times 10^{-8}$
C	$-2.2523227562279 \times 10^{-4}$	$4.637424146458 \times 10^{-5}$
D	$1.95027891237256 \times 10^{-1}$	$-3.91500691429325 \times 10^{-2}$
E	-66.1394885948301	13.2097235346611

The composition based equilibrium constant values are by definition:

$$Kp_{\text{reforming}} \equiv \frac{P_{H_2}^3 \times P_{CO}}{P_{CH_4} \times P_{H_2O}} \qquad Kp_{\text{shifting}} \equiv \frac{P_{CO_2} \times P_{H_2}}{P_{CO} \times P_{H_2O}}$$

Which by use of Dalton's Law of partial pressures:

$$\frac{p_j}{P_{\text{tot}}} = \frac{n_j}{n_{\text{tot}}}$$

Can be rewritten in terms of mole number:

$$K_{\text{reforming}} = \frac{n_{H_2}^3 \times n_{CO} \times P_{\text{tot}}^2}{n_{CH_4} \times n_{H_2O} \times n_{\text{tot}}^2} \qquad K_{\text{shifting}} = \frac{n_{CO_2} \times n_{H_2}}{n_{CO} \times n_{H_2O}}$$

Expressions for the species mole number are derived by applying species balances from inlet to exit of the reaction zone on the fuel side:

$$\begin{aligned} CH_4^e &= CH_4^i - x \\ CO^e &= CO^i - y + x \\ CO_2^e &= CO_2^i + y \\ H_2^e &= H_2^i + 3x + y - z \\ H_2O &= H_2O^i - x - y + z \end{aligned}$$

Where, x is the number of kmols of methane consumed by the methane reforming reaction, y is the number of kmols of carbon monoxide consumed by the water gas shift reaction, and z is the number of kmols of hydrogen consumed by the electrochemical reaction. Direct substitution of these expressions into the molar equilibrium expressions gives two equations (for reforming and

shift reactions) in three unknowns (amount of reactants consumed by reforming, shifting and electrochemical reactions).

The equations can be solved introducing the Fuel Utilisation efficiency, which gives z in terms of x and y :

$$z = FU \times (x + y)$$

Hence, the fuel side flow composition can be calculated using an iterative method, in two variables x and y (methane and carbon monoxide consumption), to determine the gas composition at which K_p has the same value for both the temperature and composition based expressions. The method chosen was the Newton-Raphson method, which gives very rapid convergence.

Finally, by consideration of the electrochemical reaction, the amount of oxygen required per kmol of methane supplied can be determined. Then, with the excess air ratio specified (more oxygen is supplied than is required in order to enhance cathode kinetics), and air composition known (79:21 $N_2:O_2$) the air side inlet stream composition can be determined completing the chemical calculation.

2.3.2 Energy Calculation

The energy calculation is a First Law energy balance across the cell stack. The only work output is the electrical work (W_{elec}), the stack is assumed to be effectively insulated and the only flows are the air and fuel side gas flows (of enthalpy H_{out} and H_{in}) giving:

$$- W_{elec} = H_{out} - H_{in}$$

The electrical work output of the stack is the product of its current and mean voltage. The current is determined directly from the definition of current, as Coulombs per second, and the knowledge that two electrons flow in the external circuit per molecule of hydrogen oxidised :

$$I = 2zF$$

Where z is the number of kmols of hydrogen oxidised per kmol of methane supplied, and F is Faradays Constant (the product of Avogadro's number (kmol) and the charge on an electron). Calculating the mean cell voltage is more involved. There are three stages:

- Determining the Gibbs Potential of the electrochemical reaction, a *thermodynamic property* and strong function of temperature
- Determining the Nernst Potential of the electrochemical reaction *in the reaction conditions*. The Nernst Potential is equal to the Gibbs Potential minus a correction for the partial pressures of reactants in the electrochemical reaction
- Determining the cell voltage with the specified cell *materials*. This is the effective cell voltage, after cell internal resistance losses have been accounted for.

The Gibbs Potential follows directly from the fact that isothermal oxidation in an ideal fuel cell yields electrical energy equal to ΔG , that $2F$ is the electron flow for hydrogen oxidation and that electrical energy is the product of potential and charge moved.

$$E_{Gibbs} = \frac{\Delta G}{2F}$$

The Nernst Potential is non-trivial to derive, it is given by:

$$E_{Nernst} = E_{Gibbs} + \frac{RT}{2F} \ln \frac{P_{H_2} P_{O_2}^{1/2}}{P_{H_2O}}$$

Where, p_j is the species partial pressure, R the molar Gas Constant, and F Faraday's Constant. The partial pressures used are the average of those between stack inlet and exit.

The cell voltage is given by application of Ohms Law ($R = V/I$)

$$V_{cell} = E_{Nernst} - i_{density} \times ASR_{cell}$$

Where $i_{density}$ is the current density of the electrochemical reaction, and ASR_{cell} is the Area Specific Resistance of the cell i.e. the resistance seen by the current density.

The energy balance calculation has to be carried out iteratively because an initial guess of preheat temperature is required to calculate the Nernst Potential and hence the electrical work, and the flow into the stack and hence the change in enthalpy across the stack. The method used is again Newton-Raphson, chosen for fast convergence.

2.4 The Model

Before moving on to consider coding it is important to clarify the features of the chosen model. The model implemented in the code is very basic, considering only the three points – preheater entry, preheater exit and stack exit (illustrated in Figure 1). Significant approximations have been made, some described elsewhere, they are listed below:

- Adiabatic operation – reasonable. Stack can be effectively insulated.
- Equilibrium reforming and shift reactions – catalysed, but not a good approximation. But has no effect on the calculations as no reference to time is made.
- Cathode and Anode inlet and exit streams of equal temperature – not a physically valid assumption, but has no effect on overall calculations.
- Total Air side molar flow unchanged for K_p calculation – valid as most reforming happens before entering the cell.
- Ideal Gas – good assumption.
- K_p independent of pressure – true if Ideal Gas approximation holds.
- Only three chemical reactions relevant – good provided certain restrictions are observed
- Pressure losses negligible – unclear, to be investigated in the future.
- Temperature across cell stack constant – not true, considerable temperature change across the stack results in varying performance across the stack. This is an averaged solution.
- Resistance a function only of Temperature – not true, results in loss of important pressure variation in operating characteristics.

2.5 The Code

The heart of the code consists of two Newton-Raphson iterative loops, one called both independently and from inside the other. The inner loop – the ‘consumption’ iteration - calculates the consumption of CH_4 and CO , due to the methane reformation reaction and the water gas shift reactions respectively, required to give correlation between the equilibrium constant, K_p , calculated from the gas composition and from an empirical temperature curve. This iteration in two variables has proven to be the source of most difficulties due to its sensitivity to the values of initial guesses. The outer loop – ‘the energy balance iteration’ – is considerably simpler depending on only one variable; it determines the temperature to which the inflow gases must be

heated to give a First Law energy balance between electrical work output and enthalpy change across the cell stack.

Auxiliary calculations determine iteration convergence, full flow data throughout the system, cell resistance, and system efficiencies. These are analytical calculations requiring little coding time or complexity.

The code can be run at a single operating point or can be set to run over a range of cell temperature, pressure, fuel utilisation coefficient, current density, number of series connected cells and fuel inlet operating points. Matlab routines have been written to allow graphical interpretation of the effect of variation in operating point.

Output files are created throughout the code to monitor internal variable variation. To further facilitate understanding and to aid in validation of the code additional output routines have been incorporated to show the variation in basic thermodynamic properties with temperature.

2.5.1 Objective – To model the performance of a solid oxide fuel cell supplied with air and a fuel mixture consisting of CH_4 , CO_2 , CO and H_2O within a sensible operating region.

2.5.2. Overview – There are four calculation steps involved in the code:

1. Iterative consumption calculation for whole stack determines equilibrium outlet gas composition and hence current.
2. Resistance calculation gives cell resistance for specified stack configuration and temperature.
3. Iterative energy balance calculation calling consumption calculation across the preheater to determine preheater exit temperature and flow, hence giving preheater exit temperature and electrical work output.
4. Auxiliary calculations determine system work and efficiency parameters

The majority of the calculations in the code are simple analytical, the notable exceptions being the consumption and energy balance calculations.

2.5.3 Structure – The structure has been chosen to make the code as clear as possible, with almost all of the calculations carried out within subroutines. Wherever possible the structure of the code has been made to emphasise chemical, thermodynamic and calculation processes. The important routines and subroutines are described below:

'Consumption' – This is the most critical routine in the code, all other calculations being based on the flows derived from the output of this routine. It is a Newton-Raphson iteration in two variables, methane and carbon monoxide consumption. The routine is very sensitive to the initial guesses chosen, and was very problematic. In order to better understand and more readily determine feasible initial guesses, the calculation was broken down into very small sections each of which was investigated and validated independently.

Subroutines within *'Consumption'* are:

'KpT' – this is the simplest routine in the program simply determining the values of $K_{p_{\text{reforming}}}$ and $K_{p_{\text{shifting}}}$ from an empirical quartic equation. It is important to note that the equations return the natural log of K_p . The variation of $K_{p_{\text{reforming}}}$ and $K_{p_{\text{shifting}}}$ is plotted on Figure 4. Note that both curves are monotonic.

Input: Temperature

Output: $K_{p_{\text{reforming}}}(T)$, $K_{p_{\text{shifting}}}(T)$

'KpC' – calculates $K_{p_{\text{reforming}}}$ and $K_{p_{\text{shifting}}}$ as functions of gas composition. It is derived from the definition of K_p in terms of partial pressures, utilising Dalton's Law to re-write it in terms of molar composition and total pressure. To give correlation with *'KpT'* it also returns the natural log. The variation of $K_{p_{\text{reforming}}}$ and $K_{p_{\text{shifting}}}$ with CH_4 and CO consumption is plotted in Figure 3. Both curves are also monotonic and lie in the same K_p range as those calculated from the temperature curves. Note that there is a limited range over which the functions are valid and that the range of validity also varies with pressure (not shown).

Input: CH_4 , CO & H_2 consumption, fuel side inlet gas composition, cell pressure

Output: $K_{pC_{\text{reforming}}}$, $K_{pC_{\text{shifting}}}$

'dKpC' – calculates the variation of *'KpC'*s with methane and carbon dioxide consumption. Values are determined analytically by differentiation of the relevant *'KpC'* expression by the relevant species consumption. It is in fact the variation in the log of K_{pC} s. The variation of individual single dK_{pC} terms with species consumption are the cause of many consumption iteration problems. There are sharp variations in many places and even asymptotes across the range of validity. Any initial guess that coincides with

these features will result in convergence failure. Worse still, if an initial guess is selected such that the iteration has to converge across this asymptote an oscillatory convergence results. This causes ‘glitches’ in characteristic curves at some operating points.

Input: CH₄, CO & H₂ consumption, fuel side inlet gas composition

$$\text{Output: } \frac{dKpC_{refor\ min\ g}}{dCH_{4\ consumption}}, \frac{dKpC_{refor\ min\ g}}{dCO_{consumption}}, \frac{dKpC_{shifting}}{dCH_{4\ consumption}}, \frac{dKpC_{shifting}}{dCH_{4\ consumption}}$$

‘Solve’ – solves two simultaneous equations. In this case the variation in CH₄ and CO consumption to give an improved guess of equilibrium values.

$$\text{Input: } \frac{dKpC_{refor\ min\ g}}{dCH_{4\ consumption}}, \frac{dKpC_{refor\ min\ g}}{dCO_{consumption}}, \frac{dKpC_{shifting}}{dCH_{4\ consumption}}, \frac{dKpC_{shifting}}{dCH_{4\ consumption}},$$

difference between temperature and composition based Kps.

$$\text{Output : } dCH_{4\ consumption}, dCO_{consumption}$$

‘Flow’ –Determines the air and fuel side gas flow given an inlet composition to and consumption of CH₄, CO and H₂ within a reaction zone. It is called to give the flow compositions at preheater exit and at cell stack exit.

Input: Inlet flow composition, CH₄, CO & H₂ consumption

Output: Outlet flow composition

‘Thermo’ – calculates the thermodynamic properties of Hydrogen for use in electrical work output calculation (voltage) and Carnot work calculation. The first time the routine is called at each temperature it also calculates ΔH and TΔS (plus methane properties) for illustration of fuel cell principles. Thermodynamic properties of gases with a specified pressure, temperature and composition are obtained by use of subroutines written by Prof. Young (Ref.1)

Input: Temperature

Output: Gibbs Potential, ΔH, TΔS, ΔG...

Resistance – Determines the cell Area Specific Resistance, based on geometry and materials properties contained within the routine. By determining the resistance in the form of an ASR - the resistance seen by the current per unit area of active cell – geometry and materials characteristics

can be reduced to a single parameter, allowing easy comparison of cell designs and performance. The expressions used for determining resistance are those used in the IEA Bench Mark. These equations do not take into account variation of over potentials with pressure, instead using the crude correlation that over potential are of similar magnitude and have a temperature dependence similar to the electrolyte material.

Input: Temperature

Output: ASR of cell, effective ASR of over potentials

In the body of the code an additional calculation is implemented to determine the effect of adding cells in series to give increased stack output voltage. This calculation creates a new cell resistance which is the effective resistance seen by a single cell when connected in series, allowing the remainder of the plant calculations to be implemented as before.

$$V_{cell} = N_{series} \times E_{Nernst} - (N_{series} \times ASR_{cellcomponents} + ASPR_{anode} + ASPR_{cathode})$$

E_balance – this routine applies the First Law of Thermodynamics to the cell stack to determine the preheat temperature necessary to make the magnitude of the enthalpy change across the stack equal to that of the electrical work output. It is a Newton-Raphson iteration in one variable – the preheat temperature. Fixing the stack temperature and iterating on the preheat temperature places far less strain on the consumption iteration as the preheater has only one possible fuel utilisation value (zero) and one inlet flow composition. Note that the cell current is fixed by the stack temperature; the variation in electrical work is due to the effect of mean stack composition on the mean Nernst potential of the stack.

Subroutines within '*E_balance*' are:

'Consumption' – called to calculate the consumption of CH₄ and CO across the whole system and within the preheater in order to determine the change in composition within the stack. The routine is described fully above. The resulting consumption values are passed to 'Flow' in order to determine fuel and air side gas compositions.

'SystemDelH' - Calculates the change in enthalpy across a the inlet and outlet flows. Used to determine the net enthalpy input to the cell stack.

Input: Stack inlet and outlet flows, temperatures and pressure

Output: Change in Enthalpy across stack

'Welec' – calculates the electrical work output from the cell stack taking into account stack temperature (in calculation of stack current), mean gas composition across the stack (in calculation of Nernst potential) and cell resistance (in calculation of cell voltage)

Input: Gibbs potential, stack inlet and outlet flows and temperature, stack temperature and pressure, cell resistance.

Output: Nernst potential, current, electrical work

Efficiency – There are three efficiencies which are of interest in considering cell performance:

$$\text{Electrical: } \quad NU_{\text{electrical}} = \frac{W_{\text{electrical}}}{m_f LCV}$$

$$\text{Combined: } \quad NU_{\text{combined}} = \frac{W_{\text{electrical}} + W_{\text{carnot}}}{m_f LCV}$$

$$\text{Net: } \quad NU_{\text{combined}} = \frac{W_{\text{electrical}} + 0.65W_{\text{carnot}}}{m_f LCV}$$

Where:

$W_{\text{electrical}}$ is the electrical work output from the cell

W_{carnot} is the maximum heat engine work available from the exhaust gas

m_f is the mass of fuel (CH_4) supplied per second

LCV is the lower calorific value of methane

2.6 Results & Validation

The presentation of results which follows has been devised to show the effect of successively more 'real characteristics' on ideal cell performance. By doing so it illuminates the underlying thermodynamic, chemical and electrical characteristics responsible for the overall performance of a fuel cell plant. Many of the results presented have already been produced by other people, hence they are not so much providing new information on cell operation as they are validating my code.

It is worth stating explicitly that the general objective of power plant design is to derive the maximum work per unit of fuel supplied, in this case the maximum electrical work. As electrical

work is the product of current and voltage, the objective is to increase cell voltage without decreasing current per unit fuel and vice versa. Account will not be taken of the other key parameter in power plant design – specific work. This is a subject for further study.

Note that where parameters are not being investigated they have been given default values based on empirical studies, primarily those used by Gardner (ref.4). The default (Gardner) settings are:

Stack Temperature	= 1173K
Stack Pressure	= 101325Pa (1atmosphere)
Water(kmol)/Methane(kmol)	= 2
Current Density	= 4000A/m ²
Fuel Utilisation	= 0.85

All calculations are carried out with a methane inflow of 1kmol per second.

- Fundamental Thermodynamics

Figure 2 shows the variation in work components in the isothermal oxidation of hydrogen and methane. This plot agrees with thermodynamic theory and with the plot presented by Gardner in ‘Thermodynamic Processes in Fuel Cells’. It illustrates that ΔH - and hence total energy output - is substantially independent of temperature for both fuels, but that electrical work output falls with temperature as the $(T-T_i) \cdot \Delta S$ term increases. Comparison of the characteristics of the two species shows why direct oxidation of methane is so desirable - ΔS for methane is almost negligible meaning that almost the entire ΔH of the fuel could be electrochemically released. It is this factor which means that reforming methane to hydrogen results in loss of efficiency regardless of how efficiently the reforming process is carried out. Inclusion of the Carnot Efficiency curve illustrates that electrical work output alone is greater than the maximum heat engine work output at temperatures lower than 1100K.

- Theoretical Cell Potential variation with temperature

Figure 3 shows the variation of Gibbs and Nernst Potential (and cell voltage, see below) with temperature. The Gibbs Potential is of the order 0.95 and the Nernst Potential of the order 0.9. As expected the Gibbs potential drops off with temperature in the same way that ΔG does (being proportional to ΔG). The curve agrees with the one presented in Gardner’s ‘Thermodynamic Processes in Fuel Cells’. The Nernst Potential curves show the expected

reduction as a result of partial pressure terms. Note that the loss is smaller at higher pressures due the compensation of the positive cell pressure term for the negative H_2O partial pressure in the Nernst Potential expression (see section 2.3.2). These curves suggest that electrical work will be higher at low temperature and low pressure – but do not take into account current variation.

- Equilibrium constant variation with temperature and Gas composition

Figure 4 shows the variation of the temperature based equilibrium constant expression $K_p(T)$ with temperature. The value of $K_p(T)$ is independent of pressure and the curves agree with those presented in ‘The Fuel Cell Handbook’.

Figure 5 is a plot of the composition based equilibrium constants, $K_{\text{reforming}}$ and K_{shifting} , against CH_4 and CO consumption. The plot shows that they are single valued indicating that to get agreement with equilibrium constants based on temperature there is only one set of CH_4 and CO consumption values – i.e. there are no alternate physical solutions. Using a range of different initial guesses for a range of operating points it can be shown that if the iteration converges, it converges to the same consumption values for each operating point – i.e. there are no false numerical solutions. Hence it can be assumed that if the consumption iteration converges it does so on the correct values.

Similar analysis of the energy balance calculation shows that it also has only one solution.

- Fuel side Gas composition variation with temperature

Figure 6 shows the variation of fuel side flow composition with temperature with no electrochemical reaction term. The curves agree with those presented in Gardner’s ‘Thermodynamic Processes in Fuel Cells’. The key feature of this plot is the maximum in hydrogen mole number at 1050K. This, combined with the decreasing Nernst potential with temperature suggests that electrical work output will peak in this temperature region.

Figure 7 shows the effect of the electrochemical reaction on gas equilibrium. The fuel utilisation efficiency for this plot is the default value of 0.85, which by definition means that 15% of hydrogen produced in the reforming reactions is exhausted from the cell ‘unused’.

Introduction of the electrochemical reaction results in the formation of H_2O from H_2 with the simple result that H_2 partial pressure falls and H_2O partial pressure rises. What is of interest is

that the H₂O mole count increases considerably within the cell (to around 3.4 kmol), hence recirculation of stack gasses offers the potential of reducing the amount of energy required by the preheater by reducing the amount of H₂O which must be added per unit fuel.

Figure 8 shows the variation of gas equilibrium composition through a plant with preheat temperature 850K and stack temperature 1173K (i.e. the default plant). The second part of the plot is not of particular relevance, it is the point at which the electrochemical reaction is introduced which is of interest. At this point the equilibrium composition changes dramatically, which for a real plant would mean extreme non-equilibrium and non uniform performance. Modelling the characteristics of this section of the cell is beyond the scope of the code, but it is something which must be taken into account when considering preheating.

- Hydrogen consumption variation with pressure and temperature

Though the equilibrium constant K_p is independent of pressure, the gas composition is not due to the pressure term introduced by use of Dalton's law. Figure 9 shows the variation of hydrogen consumption with temperature for three cell pressures (1atm, 3atm, 5atm) . Above 800K cell pressure has negligible effect on consumption, but below 800K increasing pressure results in increased hydrogen consumption and hence higher stack current

- Preheat temperature variation with cell temperature

Figure 10 shows the variation of preheat temperature for a cell operating at atmospheric pressure for a range of fuel utilisation values. The preheat temperature is inversely proportional to the enthalpy change across the stack and hence for high electrical work output one would expect a low preheat temperature in order for the enthalpy change to balance the electrical work. This is clearly the case, with preheat temperature equal to stack temperature at low stack temperatures, when electrical work is small, and falling off rapidly around 800K, when the electrical work increases. Further confirmation of this is given by the variation in preheat temperature with fuel utilisation – lower fuel utilisation values give higher preheat temperatures as a result of the reduced electrical work output from the cell. Preheat temperatures in the region of 800K, for standard operating points, obtained from the code agree with those found by other investigations.

- Electrical work variation with temperature and pressure

Figure 11 shows the variation of electrical work with pressure and temperature. As would be expected from voltage and current characteristics, the work output peaks around 800K and is slightly higher at higher pressures for temperatures greater than 800K. Below 800K however, the low pressure curve shows a higher work output. This is due to the effect of cell pressure on species partial pressures, which causes an increase in the current (as seen in Figure 9).

- Resistance – The introduction of resistance significantly changes cell performance. The explanation to this lies in the variation of resistance with temperature shown in Figure 12. At typical operating temperatures the Area Specific Resistance of a cell is $0.3\text{m}\Omega/\text{m}^2$. At temperatures below 800K the resistance of the electrolyte increases significantly, with total breakdown of cell performance below 600K. The effect of resistance from an energy point of view is to reduce the electrical work from the cell which, among other things, results in a higher preheat temperature as illustrated on Figure 15.

Before moving on to consider the further effects of resistance on plant performance, consideration is given to the effect of electrochemical materials and cell configuration selection.

- Cell effective resistance variation with number of cells connected in series.

Figure 13 shows the variation of effective cell resistance with number of cells connected in series. It shows that for less than 7 cells there is a sharp increase in voltage due to the diluting of the overpotential voltage losses (see equation in section 2.5.3). However the total change in voltage is only 0.16%, so is not of great consequence in a model of this accuracy. Typical stacks have around 120 cells in series giving an overall voltage of about 115V.

- Cell voltage variation with current density

Figure 14 shows the variation of cell voltage with current density. Over the feasible range ($1000 - 6000\text{A}/\text{m}^2$) there is a loss of cell voltage of 0.6% due to the increased internal resistance loss (see equation in section 2.5.3). This is of little significance, however current density plays an important part in determining overpotentials, which is not included here, so should not be disregarded.

- System Efficiency variation with temperature and fuel utilisation.

Figure 16 shows the variation in electrical, combined and net efficiency with temperature and fuel utilisation efficiency. As expected efficiency is low at low temperatures where reforming and shifting reactions are limited and is similarly low at low fuel utilisation efficiencies (both factors reducing the amount of hydrogen undergoing reaction and hence the cell current). A balancing factor in efficiency increase with temperature is the fall in Gibbs potential with temperature (as a result of the fall in ΔG), which causes the cell voltage to fall. Hence, for each fuel utilisation we see a peak in efficiency at a specific temperature.

For a fuel utilisation of 0.85 peak electrical efficiency is approximately 72% at 800K, compared with approximately 98% for full direct oxidation of methane. For the same stack combined efficiency is approximately 83% at a slightly higher temperature of 850K.

However, this does not take into account preheating requirements which bring the efficiency down to around 79%. This is in fact a very high efficiency, considerably higher than the 60% efficiency plants currently under development, suggesting that the allowance for preheating was too small and that insufficient losses have been included in the model.

- System efficiency variation with temperature and pressure.

Figure 17 shows the variation in efficiencies with temperature and pressure. The plot shows that efficiency rises continuously with pressure with a 3-4% gain between 1 and 5atmosphere. The advantage of increasing pressure arises from the increase in Nernst Potential resulting in higher cell voltage. Note, that there is an additional more important cause of efficiency variation with pressure which is not included here which is overpotential decrease with increasing pressure which results in even greater benefits for high pressure operation. Pressure is unfortunately limited by materials properties – high pressured placing excessive stress on cell. Most cells run at near atmospheric pressure, hence the choice of 1 atmosphere for default pressure.

- System efficiency variation with temperature and water inlet fraction

Figure 18 shows the variation in efficiencies with temperature and water input. It is clear that increasing water fraction above the stoichiometric requirement causes a drop in efficiency.

The drop is significant around 4% for increasing the water fraction from 2 to 5. The drop is due to the energy input required to heat the water and also to its detrimental effect on Nernst Potential (see equation in section 2.3.2). Minimising the water ratio would seem attractive, but there is a constraint - the water to methane inlet molar ratio must be greater than 2 to prevent carbon formation by methane cracking and CO reduction. By default the ratio is set to 2 throughout this report.

2.7 Conclusions

Section One: Fuel Cells

- There is great need and financial imperative to develop a means of providing a *clean cost effective supply of energy on demand on a large scale and in any location.*
- Fuel cell thermodynamic analysis suggests that, in theory, fuel cells derive the maximum amount of work possible from suitable fuels.
- Fuel cell technologies have been developed which exploit the benefits of the fuel cell principle and meet market demand.
- Fuel cell technology is still in its infancy, and its growth is limited primarily by the development of materials with the required thermal, chemical, mechanical and electrical properties.
- Existing fuel cell technologies do not exploit the direct electrochemical oxidation of methane, instead relying on the supply of hydrogen from a sufficiently pure source, generally steam reforming of methane. All technologies based on hydrogen production from methane suffer an inherent loss due to the chemical properties and oxidation reactions available.
- For large scale power generation high temperature molten carbonate and solid oxide fuel cells are the preferred technologies. Molten carbonate fuel cell development is ahead of solid oxide, but solid oxide may prove more successful, despite reduced theoretical efficiency, due to the higher temperature exhaust which is suitable for direct use in existing heat engine cycles.

Section Two: Solid Oxide Fuel Cell Modelling

- Solid oxide fuel cells operate at between 650 and 1000°C, which is sufficiently high to allow internal steam reforming of methane without the need for expensive, easily poisoned, catalysts.

- A solid oxide fuel cell plant can be modelled in three stages: a preheater (and reformer) to generate hydrogen, a stack which electrochemically oxidises hydrogen and a bottoming cycle which recovers exergy from the exhaust gas.
- Solid oxide fuel cell performance cannot be determined analytically, it requires two coupled iterative calculations to be solved. These are to determine flow composition as a function of temperature and preheat temperature as a function of stack temperature.
- Voltage reduction has two sources in a solid oxide fuel cell – partial pressures, from which the Nernst Potential is calculated, and resistance from which the cell voltage is calculated ($\approx 1V$).
- Current generation in a solid oxide fuel cell is limited by two factors – the generation of hydrogen by the reforming reactions, and the oxidation of that hydrogen by the cell stack.
- Electrical work output from a fuel cell stack is given by the product of stack current and effective cell voltage. The condition for maximum work is generally a compromise between factors which increase one to the detriment of the other.
- The model developed exhibits an operating range with associated characteristics similar to those of modelling and empirical studies carried out by other researchers. Electrical efficiency of 70% at a standard operating point is similar to that of other simple models, it is however considerably higher than that expected in practice.
- The model developed exhibits a temperature dependence of the expected form, but with a maximum efficiency temperature slightly lower than expected, at around 850K. This is primarily due to poor resistance modelling.
- The model developed exhibits part of the pressure dependence of solid oxide fuel cells, giving the correct (empirically confirmed) characteristic of increasing efficiency with pressure. The variation of just 3-4% for an increase of pressure from atmospheric by 400% is lower than empirical because of the omission of pressure dependence on polarisation effective resistances.
- The model developed represents a good starting point from which to develop a more realistic model with improved resistance modelling. It is these material properties which are the key to developing fuel cells with performance comparable with theoretical performance, hence it is on this that effort should be concentrated before any kind of finite element analysis is attempted.
- There is a long, prosperous and exciting future in fuel cell development – watch this space!!!

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Appendix – Plant and Cell Diagrams & Results and Validation

The following nine pages contain, primarily, fuel cell characteristics produced using code developed by the author. The code, (FuelCell.f) written in Fortran 77, utilises code (Gasprops.f) written by Prof. J B Young (ref. 11) to determine thermodynamic properties of gas mixtures.

A list of figures is given at the beginning of the paper.