

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

by Ben Todd

Abstract

The fuel cell principle represents the ideal means of extracting maximum work from suitable fuels. 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%, increasing efficiency with increasing cell pressure and reduced efficiency with excess steam addition. Improved resistance modelling is required to give lower, more realistic, but still impressive efficiency predictions.

Introduction

Fuel cells have characteristics which make them ideal for the development of clean high efficiency power plant. Numerous technologies have been developed to exploit the fuel cell principle, of which solid oxide fuel cells are favoured for large scale power generation because of the high temperature of exhaust gas, which is suitable for direct use in existing gas and steam turbine plant. In this paper ideal fuel cell thermodynamics are considered; followed by a description of, and results from a Fortran 77 simulation.

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. Considering a system at constant temperature, T which exhausts to a reservoir at T_0 . Exergy analysis gives: $W_{\max} = -\Delta G(T) - (T - T_0) \Delta S(T)$ Where $\Delta S(T)$ is the entropy change of the reaction and $\Delta G(T)$ is the change in Gibbs Free Energy 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 which shows the variation of $\Delta G(T)$ and Carnot work with temperature for methane and hydrogen. Note that $\Delta G(T)$ for methane is very near equal to W_{\max} at all temperatures, indicating that the entropy change during oxidation is very small. 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 work up to 1100K.

Solid Oxide Fuel Cell Plant

Typically plants are supplied with natural gas, the main constituent of which is methane (CH₄). 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.
- The Cell Stack – which electrochemically oxidises the hydrogen stream, drawing oxygen ions through an electrolyte layer from the air stream
- The Bottoming Cycle – which utilises exhaust exergy. This section of the plant is outside of this project's remit. A Carnot plant is used to give theoretical work values.

Note that the division of chemical and thermodynamic processes into these plant components is not entirely consistent as reforming continues through the electrochemically active section of the stack as a result of the changing temperature and gas composition.

Solid Oxide Fuel Cell Plant Modelling

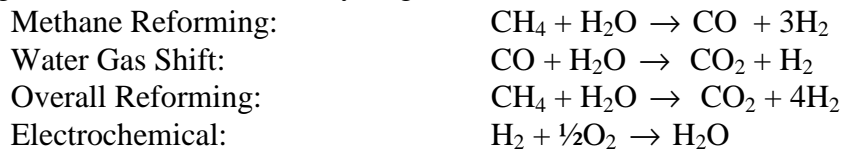
There are two key components to the modelling process:

- 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.

The Chemistry

As described above, there are two distinct reaction processes in the cell stack, reforming of methane to form hydrogen and oxidation of that hydrogen:



It has been assumed that the kinetics of both reforming reactions are fast. This is not strictly true, but 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 partial pressures of reactants and products.

$$Kp_{\text{reforming}} \equiv \frac{P_{\text{H}_2}^3 \times P_{\text{CO}}}{P_{\text{CH}_4} \times P_{\text{H}_2\text{O}}} \qquad Kp_{\text{shifting}} \equiv \frac{P_{\text{CO}_2} \times P_{\text{H}_2}}{P_{\text{CO}} \times P_{\text{H}_2\text{O}}}$$

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

Where the coefficients, with pressure in bar, are:

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

By applying Dalton's Law of partial pressures the equilibrium constant equations can be rewritten in terms of mole numbers. The species mole numbers n_j are calculated by means of species balances from reaction zone entry to exit:

$$\begin{aligned} \text{CH}_4^e &= \text{CH}_4^i - x & \text{CO}^e &= \text{CO}^i - y + x & \text{H}_2^e &= \text{H}_2^i + 3x + y - z \\ \text{CO}_2^e &= \text{CO}_2^i + y & \text{H}_2\text{O} &= \text{H}_2\text{O}^i - x - y + z \end{aligned}$$

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. Finally, the electrochemical reaction can be introduced through the fuel utilisation efficiency - the fraction of hydrogen generated by the reforming reactions which is oxidised. This gives an expression for z in terms of x and y : $z = FU \times (x + y)$. Hence, the fuel side gas composition calculation can be reduced to two equations in two variables. These equations are solved by a two variable Newton-Raphson method.

In order to take account of materials and geometry two additional parameters must be introduced, cell Area Specific Resistance and current density. 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. Cell Area Specific Resistance is the resistance seen by a current density. Values for the resistance calculation are taken from Bench Mark Data [ref.1] which gives a crude temperature dependence but does not include the effect of pressure on polarisation resistance.

Finally, it is important to note that other chemical and electrochemical reactions are possible. All of which can be neglected as their effects are negligible in a cell designed for hydrogen oxidation 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.

The Energy Balance

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: $-W_{\text{elec}} = H_{\text{out}} - H_{\text{in}}$.

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, giving: $I = 2zF$

Calculating the mean cell voltage is more involved, there are three stages: determination of the Gibbs Potential of the electrochemical reaction, determination of the Nernst Potential of the electrochemical reaction *in the reaction conditions* (which is equal to the Gibbs Potential minus a correction for the partial pressures of reactants in the electrochemical reaction); determination of the cell voltage with the specified cell *materials*.

$$E_{\text{Gibbs}} = \frac{\Delta G}{2F}; \quad E_{\text{Nernst}} = E_{\text{Gibbs}} + \frac{RT}{2F} \ln \frac{p_{\text{H}_2} p_{\text{O}_2}^{1/2}}{p_{\text{H}_2\text{O}}}; \quad V_{\text{cell}} = E_{\text{Nernst}} - i_{\text{density}} \times \text{ASR}_{\text{cell}}$$

Where, z is the number of kmols of hydrogen oxidised per kmol of methane supplied, F is Faradays Constant, p_j are the species partial pressures (the average of those between stack inlet and exit), R the molar Gas Constant, i_{density} the current density of the electrochemical reaction, and ASR_{cell} is the Area Specific Resistance of the cell.

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.

2.6 Results & Validation

Many of the results presented here have already been produced by other people, hence they are not so much providing new information on cell operation as they are validating the new code. 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; Water kmol/Methane kmol=2; Current Density=4000A/m²; Fuel Utilisation=0.85; Methane Inflow=1kmol/second.

Fundamental Thermodynamics

Figure 1 shows the variation in work components in the isothermal oxidation of hydrogen and methane. 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 $(T-T_i) * \Delta S$ 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. 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.

Cell Voltage variation with temperature

Figure 2 shows the variation of Gibbs Potential, Nernst Potential and cell voltage 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 (being proportional to ΔG), with Nernst Potential slightly lower 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 in the Nernst Potential expression. The lower curve shows the effective cell voltage after internal resistance losses. At typical operating temperatures the Area Specific Resistance of a cell is 0.3 m Ω /m².

Fuel side Gas composition variation with temperature and pressure

Figure 3 shows the variation of fuel side flow composition with temperature with no electrochemical reaction term. 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. Varying the cell pressure was found to have little effect on gas composition above 800K despite the pressure term in the equilibrium composition equations

System Efficiency variation with temperature and fuel utilisation.

Figure 4 shows the variation in electrical, combined and net efficiency (after allowance for preheating of 35% of Carnot work output) 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 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 5 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 5atm. 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, not included here, which is overpotential decrease with increasing pressure that results in even greater benefits for high pressure operation. Pressure is unfortunately limited by materials properties – high pressured placing excessive stress on cell.

System efficiency variation with temperature and water inlet fraction

Figure 6 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.

2.7 Conclusions

- Fuel cell thermodynamic analysis suggests that, in theory, fuel cells derive the maximum amount of work possible from suitable fuels. However because existing fuel cells do not involve direct oxidation of methane they have reduced theoretical efficiencies.
- 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 simplistic 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.

3. References

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