1

Altered Perspectives

> The man who makes no mistakes, does not usually make anything.
> Edward John Phelps, 1822–1900

In what follows we are building on the work of Sir William Groves, who made much, but committed one major sin of omission.

The introduction in this book of the equilibrium isothermal oxidation theory of **complete** fuel cells with isothermal circulators (concentration cells) imposes on the industry changes of perspective relative to existing non-equilibrium, Groves-type, **incomplete** fuel cells without circulators, and dependent on gas movement by irreversible diffusion in a concentration gradient. Equilibrium isothermal oxidation is in stark contrast to fundamentally irreversible combustion. The irreversibility of combustion is an overlooked, neglected, phenomenon, which the reader must from hereon retain in mind. The high-speed products of combustion are slowed down in the combustion gas, their speed being non-recoverable. They heat the gas and cool themselves in an irreversible process. A large irreversible entropy growth occurs. The kinetic exergy of the high-speed product molecules is destroyed. This destruction is ignored in traditional engine analysis, to produce efficiencies which are far too high, but do enable each engine to be compared with any other.

The modified perspectives in the sections below relate to fuel cells (liquid and gaseous), engines, fuel cells integrated with engines, hydrogen sources and the hydrogen economy.

Fuel Cells, Engines and Hydrogen – An Exergy Approach Frederick J. Barclay

Would tae God, the Giftie Gie Us,
tae see Oor'sels, as Ithers see us!
Robert Burns

This second quotation seeks a refreshed sense of proportion about things, exactly the mission of the chapter to come.

In the author's introduction, the history of this book is explained, and initial stage-setting technical remarks are made. The history is expanded below, and new topics added, which make clearer the very large effect on the fuel cell industry of the new isothermal oxidation thermodynamic treatment using the equilibrium diagram, Figure A.1. The figure is the basis for detailed calculations of the fuel chemical exergy, in Appendix A.

As is common sense, the results of the performance calculations are dimensionless numbers, W/W, for actual power/ideal power. That cannot be said for calculations based on the calorific value, which are in units of $\mathrm{W\,J^{-1}}$. The use of 'fuel chemical exergy' in W s, a large number compared with 'calorific value' in joules, as the basis of fuel cell and engine efficiency calculations, greatly lowers the numerical efficiency of both systems, a realistic event. The unavoidable lesson is that all existing means of power generation based on heat cycles are woefully inefficient. Only complete fuel cells offer high efficiency, and that in the future after some problem solving.

The fuel cell development potential, when the necessary circulators and membranes are added, becomes very much larger than that of the engine, a greatly encouraging realisation and a spur to intense future development to improve upon the low efficiencies of the last sentence.

Comprehension of the difference between compressible gases as reactants and incompressible liquids gives an illuminating new sense of proportion about the overweening relative merit of power storage by redox battery in ESS-RGN versus the older, doubtful, Groves proposal for a hydrogen economy – doubtful because Groves uses inefficient and incomplete electrolysers and fuel cells dependent on irreversible gas diffusion for gaseous reactant and product movement.

1.1 POWER STORAGE

The one and only fuel cell being manufactured, which makes use of circulators, as in Figure A.1, is the power storage system ESS-RGN, formerly Regensys, which features liquid reactants which are incompressible in contrast to the gaseous reactants of all other fuel cell systems.

The circulators for liquid reactants are mere pumps, which elevate the liquid level in storage tanks. A full description of Regenesys, now owned by VRB Power Systems of Vancouver, Canada, is given in Chapter 2 so that the reader can compare and contrast this 'complete' system with the gaseous and 'incomplete' systems of later chapters. From the terminology, it is doubtful if VRB itself has grasped the underlying reason for the superiority of its two power storage systems. VRB speaks of energy storage, when (based on Joule's experiment), it should really speak of power storage. VRB is silent on the subject of incompressible liquid reactants and products.

1.2 CIRCULATORS

Figures A.1 and A.2, and the equilibrium calculations of Appendix A, lead to huge pressure ratios for the required isothermal concentration cell circulators. These are not existing, developed devices, but are ideas made necessary by Figures A.1 and A.2. The incorporation of fully developed circulators in a practical non-equilibrium gaseous cell, distinct from Figure A.1, would involve their operation at a reduced, more practical pressure ratio, relative to the operating point of the cell on its V/I characteristic, Figure 6.5, rather than relative to the zero-current point of equilibrium at the top of the figure. The initial steep slope of the figure results from readjustment from zero-flow equilibrium at the zero point to irreversible gas diffusion at the operating point. The latter explanation is unique to the author.

Mechanical circulators are probably not usable as they require intercoolers/heaters to achieve isothermal performance, and have a very limited pressure ratio.

1.3 INCOMPLETENESS

Incompleteness in Chapters 4–6 is of two kinds, lack of circulators and lack of a 'hydrogen mine', or cheap source of hydrogen. Both of these represent major development problems, as do semi-permeable or permselective membranes, which must accompany circulators and feature in the flow sheet of the hydrogen mine, Figure A.4.

The ICI Billingham plant (Barclay, 1998), and its more modern successors operated by Methanex and by Air Products, provide expensive hydrogen from natural gas reform via combustion heat. The elimination of combustion-heated reformers is needed, since they involve large combustion irreversibilities. Such plants are optimised using the technique of 'process integration', which gives the best arrangement of irreversible heat exchanger networks, having a sequence of temperature changes.

1.4 THE HYDROGEN MINE

The author asserts that an isothermal plant arrangement (process integration therefore not applicable) is essential for greater thermodynamic efficiency, and hopefully for cheapness. An equilibrium diagram for such a plant is shown in Figure A.4. The plant is arranged so that exergy is supplied as electrical power and not by combustion heat, an entirely theoretical concept, and therefore a difficult development problem, for Methanex, Air Products and Ballard.

An efficient plant must be based on making an approach, as near as is practical and economic, to the perfect processes of an equilibrium diagram, such as Figure A.4, which was initially composed as a calculation route for methane chemical exergy, and then realised to have larger implications. Methane had to be consumed in an isothermal equilibrium reversible process.

The process of the calculation involves a reformer which gets its exergy not from combustion, but as electrical power generated by supplying CO and H_2 to separate fuel cells which are able to create an excess above the need of the reformer. The invaluable JANAF thermochemical tables (Chase *et al.*, 1985) provided the thermodynamic data. The excess is the chemical exergy of methane.

Viewing Figure A.4 as a potential hydrogen mine, the change would be made that the excess hydrogen would be stored, and converted to power in separate stationary or mobile fuel cell power plants rather than in the fuel cells of the diagram. Such a hydrogen mine is both a major development problem (involving circulators, fuel cells with some fuel in their exhausts, as well as a new kind of reformer) and a pressing need. The hydrogen mine **must** somehow be realised to conserve the large fuel cell development and international investments of Ballard Power in the fuel cell vehicle. Note that the internal, fuel-cell-based power generation of the hydrogen mine would be very much more efficient than any combustion-based heat cycle. The way forward is for all non-nuclear power generation to be based on complete fuel cells with circulators and integrated with gas turbines.

Air Products, in its web site question and answer session, goes over the current status of hydrogen production by reforming natural gas, but predicts no future process change. But Fuel Cell Energy in its web site News Releases & Events discusses the prospect of a hydrogen energy station to produce power, heat and hydrogen simultaneously, in conjunction with Air Products: ‘The HES will integrate aspects of FCE Direct Fuel Cell (MCFC) Technology, with Air Products’ process and separation technology’. The HES sounds akin to Figure A.4, but no comparable flow sheet is given.

The Methanex Vancouver web site lays emphasis on methanol production and hopes for the direct methanol fuel cell (DMFC). Hydrogen is mentioned, but not the need for a hydrogen mine for the nearby Ballard Power Inc.

The hydrogen industry clearly needs to refresh its sense of proportion and begin to tackle its major new development problems. Likewise the fuel cell industry has much to reappraise and many new problems to tackle.

> And those behind cried forward, and those in front cried back!
> Baron MacAulay, 1800–1859

At such a juncture as the one covered here, the best way forward is not easy to establish.

1.5 COAL GASIFICATION

A large question, looked at below, is the future of gasified coal, supplying complete fuel cells, integrated with gas turbines and with greatly reduced carbon dioxide output, relative to present-day plants based only on heat cycles.

Coal gasification (Hotchkiss, 2003) to provide clean fuel for gas turbine power plants is an established competitive modern technology, with Spanish, UK and US examples. The fuel gas produced is largely carbon monoxide, but with a fraction of hydrogen. Enough coal is burnt to heat the remaining bulk of coal in a distiller closed to the atmosphere, and of such design that solid debris does not reach the gas turbine inlets.

The flow sheet of a Hotchkiss gasifier is given in Figure 1.1.

A future development would be to pass the fuel gases to the circulators of high-temperature complete SOFCs or MCFCs, integrated with gas turbines, that would result in a major gain in fuel efficiency. The

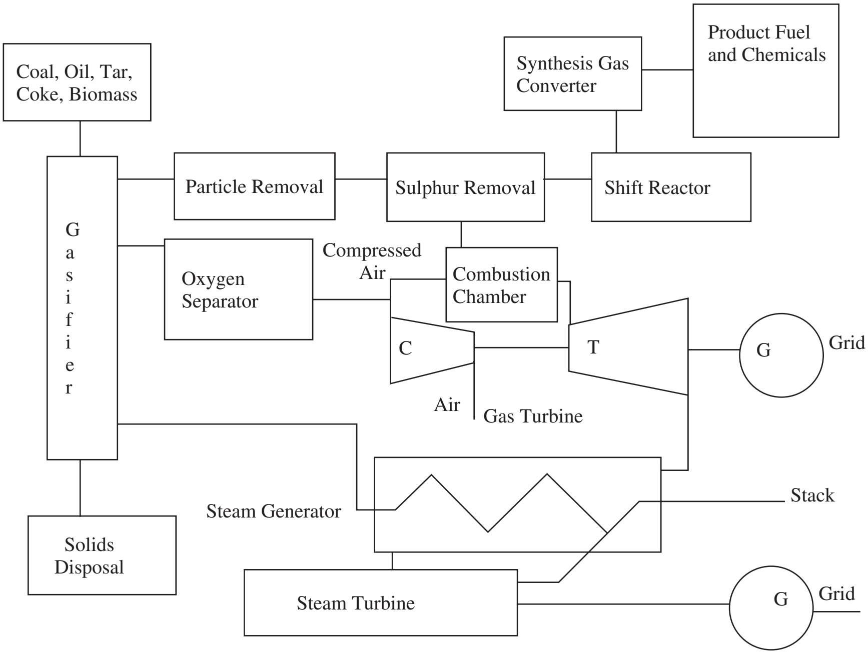


Figure 1.1 Coal distillation gasifier flow sheet

operating point of the fuel cells and the distiller operating point of the fuel cells would be interactive design variables.

In India and China, plentiful and cheap coal seems likely to be used to supply the power demands of these major populations. From the angle of the ocean acidification problem, and of the more complex greenhouse gas problem, a large economy in fuel consumption, by using fuel cells allied to coal gasification, would be a welcome new development. Both countries are also pursuing vigorous nuclear power programmes, which will, once operating, produce no carbon dioxide.

1.6 SOFCs

The designers of SOFCs have to face the new developments posed by the circulators of Figures A.1 and A.2. The letters SOFC denote a vigorous, diverse and expanding family of fuel cells based on the idea that at high temperature the thermal oscillations of the ions at the electrolyte/reactant/product interfaces lead to vigorous exchange current at equilibrium, and to usefully large ion conductivity at the selected operating point, some way from equilibrium. With the commonly selected electrolyte of yttrium-stabilised zirconia (YSZ), an operating temperature of 1000 °C lead to good ion conductivity.

However, 1000 °C leads to a very rapid reaction if anode reform is attempted and in many cases the result is excessive thermal stress of the ceramic electrolyte, so that conventional reformers must be used. As a consequence there has come about a class of intermediate-temperature SOFCs based on alternative ceramic formulations, 500 °C operation having been achieved by a metal/ceramic fuel cell by the company 'Ceres' (see Chapter 4) set up by Imperial College London.

The nascent ability of some SOFC versions to oxidise methane directly (Perry Murray *et al.*, 1999; Park *et al.*, 1999; Gorte *et al.*, 2000) using appropriate catalysts represents a major challenge to the rival MCFC, which cannot emulate the new technology. The direct isothermal oxidation of methane as in Figure A.5 means that the new system has no need for a 'hydrogen mine', although the need remains as an essential for vehicle fuel cells.

The SOFC exists in rectangular and circular form with flat plate membrane electrode assemblies (MEAs) and in tubular form with fat tubes and small tubes, the whole range being described in Chapter 4. An important variable is the thickness of the electrolyte layer, which is a manufacturing problem involving porosity if the layer is too thin. Losses are minimised if the layer is thin. The specialised small-tube SOFC must have relatively thick walls for tube strength, and sacrifices performance to achieve resistance to thermal shock and thermal stress due to anode reform. The Rolls-Royce design of the 50 W all-ceramic rectangular plate fuel cell, Section 4.3, was aimed from conception at mass production, and via ingeniously compact arrangement in large stacks for multi-megawatt power production. Gas turbine integration was and is intended.

An attempt by the author to forecast the design of a plant based on complete IT/SOFCs with concentration cell circulators, integrated with a gas turbine and consuming natural gas, is shown as Figure A.7.

1.7 MCFCs

The USA, Germany and Japan are large players in the business of the **incomplete** MCFC. Fuel Cell Energy, USA, its licensee MTU Friedrichshafn, and the Mitsubishi Materials Company all have to face up to the irreversibility caused by the lack of circulators. Details are in Chapter 5.

A strength of the system is its ability to undertake anode reform, with a comfortable reaction rate, and low thermal stress at 600 °C. The ability of the MCFC to achieve 40 000 h operating life is still being demonstrated by its protagonists. Moreover, changes to the molten carbonate formulation are under consideration. Observed mobility of the molten carbonate, within the matrix conceived as fixing it, has been ascribed by the author to the surface tension gradient associated with concentration and temperature differences.

The MCFC is suitable for integration with gas turbines, and Japanese studies of this topic are extensive. But there are no prototypes as for the SOFC (Siemens Westinghouse). Two figures taken from Chapters 4 and 5 are reproduced below for the reader's convenience. The first figure (Figure 1.2) is the Siemens Westinghouse SOFC/gas turbine integration scheme.

The second Figure (Figure 1.3) shows the author's thinking on MCFC/gas turbine Integration.

In brief the MCFC is somewhat less mature than its pressing competitor, the SOFC. The design of MTU Friedrichshafn is impressively compact and ingenious.

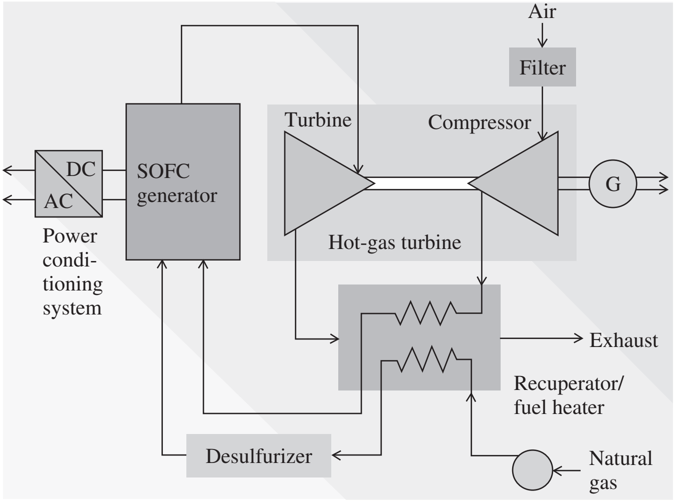
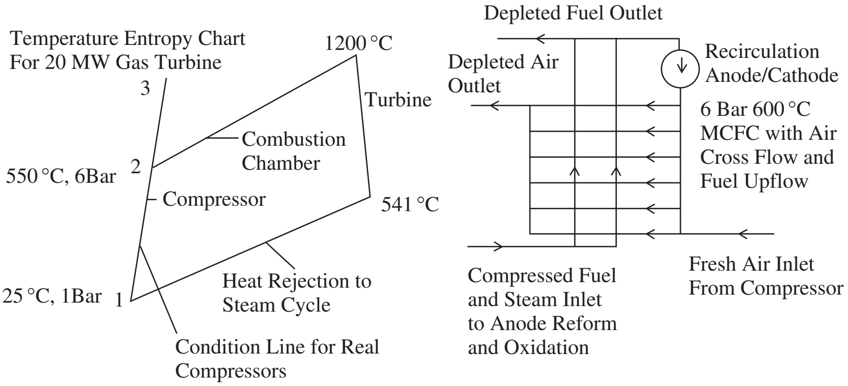


Figure 1.2 SOFC/gas turbine integration scheme



Notes

1] The temperature entropy chart is that of an existing 20 MW gas turbine.
2] An ideal machine would have a compressor outlet temperature equal to the MCFC, namely 600 °C.
3] The mismatch could be overcome by burning a little fuel at the combustion chamber inlet, and supplying the fuel cell with slightly depleted air, at 600 °C. Better to select, for simplicity, a matched gas turbinel.
4] The fuel cell would be large, way beyond anything currently contemplated.
5] There are no Published Test Data for MCFC installations. There are some mathematical models.

Figure 1.3 MCFC/gas turbine integration scheme

1.8 THE PEFC

The Ballard PEFC has been and is being developed in a well co-ordinated way. The basis is international. The MEAs are made in the UK by Johnson Matthey. The low-cost electrode structures/flow plates are formed from flexible graphite (Grafcell), from the US supplier Advanced Energy Products (formerly Graftech), but with catalyst platinum particles from Johnson Matthey Two lower cost alternatives to the classical proton exchange electrolyte, DuPont Nafion 112, are being developed in the UK by Victrex Ltd. The alternatives are Ballard Advanced Materials BAM3G and a Victrex material, Peek. See Chapter 6. These new materials are not available to competitors, who will have to purchase licences or do their own development as have the Japanese and Chinese.

In Xuezhong Du *et al.* (2001), Japanese ‘Aciplex’ and ‘Flemion’ and Chinese ‘Shanghai’ alternatives to Nafion are compared with Nafion in terms of their performance, and none is overwhelming. The latter alternatives have not yet caught on in the international scene. Price comparison is not made available.

Fuel cell stacks are assembled by Ballard and tested in application situations such as vehicles and stationary power. Operating experience is fed back. Bus demonstrations in many large cities displace the pollution from the vehicle to power plant stack. And not only displace but increase, since the hydrogen is produced in inefficient electrolysers without circulators.

The PEFC system itself will have to face the consequences of irreversibility due to lack of circulators. Crucially, the system must have a ‘hydrogen mine’. Perhaps Ballard will need to join with Methanex and Air Products to solve this major development and capital investment problem. There are no signs of that happening.

In order to minimise the sensitivity of the platinum catalyst to CO and CO_2 impurity in reformed fuel gas there has been a rise in PEFC operating conditions to 150 °C and corresponding pressure. A reason for favouring such a change is the response of the system to extreme climatic conditions such as 100% relative humidity, which the author has encountered in the Middle East, at 38 °C. Getting rid of steam water product in such conditions would be made easier by the operating temperature of 150 °C, compared with the usual 70 °C. Note that the idealised systems of Figures A.1 and A.2 exhaust to arbitrary standard 20% relative humidity. All extreme conditions need actual tests, and Ballard has done the tests on altitude by operating vehicles at 7000 ft (2130 m) in Mexico City. Reduced oxygen concentration does have an adverse effect, but not a disastrous one.

1.9 ENGINES

At the time of writing of the UK steam tables in the 1930s by Professor Callendar, he and other authorities on thermodynamics decided that widespread and thorough understanding of the work of Gibbs (see Gibbs, 1961) by engineers was unlikely. Such understanding has now become essential and indispensable to rational power production.

Accordingly, a formula was devised which enables comparison of the performance of one heat engine with another. The air flow through the combustion chamber of a gas turbine, for example, is heated by the experimentally determined calorific value of the fuel flow. That gives a heat input, to be compared with shaft power, to produce an efficiency. Dimensional analysis indicates, however, that such an efficiency is not a pure number, as an efficiency should be. The shaft output has to be compared with the chemical exergy of the fuel input, the latter being the maximum power theoretically available, calculated from Figure A.1. The exergetic efficiency so determined is very much lower than the conventional efficiency. Reiterating from above, the loss ignored by the conventional efficiency is the equilibration of the high-speed product molecules with their combustion air environment, a huge irreversibility.

The conventional efficiency has served the industry well, but cannot live on into a fuel cell era dominated by fuel cells integrated with engines (see Figure A.7). The fuel cell and the engine must share an identical efficiency basis. The integrated engine, operating in a low-efficiency cyclic way alongside a fuel cell stack, operating via efficient steady flow isothermal oxidation, must be seen as providing a marginal, but useful, increment of performance to the joint, fuel-cell-dominated, power production system. The gas turbine also provides an extremely useful stop/start capability, by the operation of the gas turbine and its compressor on mains power, to get the system up to ion conduction temperature and the commencement of isothermal oxidation.