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Hemmes, Kas

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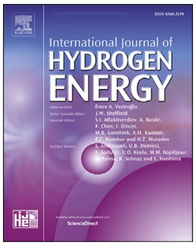

A personal retrospect on three decades of high temperature fuel cell research; ideas and lessons learned

Kas Hemmes

Delft University of Technology, the Netherlands

HIGHLIGHTS

- Do not try to fight thermodynamics in Fuel Cells; make use of it!
- MCFC's and SOFC's suffer from high Nernst loss due to anion conduction.
- Cation (proton) conducting fuel cells are thermodynamically more favourable.
- DCFC's including electrochemical gasification are thermodynamically superior.
- IR-FC's can enable the energy transition using their unique characteristics.

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ABSTRACT

In1986 the Dutch national fuel cell program started. Fuel cells were developed under the paradigm of replacing conventional technology. Coal-fired power plants were to be replaced by large-scale MCFC power plants fuelled by hydrogen in a full-scale future hydrogen economy. With today's knowledge we will reflect on these and other ideas with respect to high temperature fuel cell development including the choice for the type of high temperature fuel cell. It is explained that based on thermodynamics proton conducting fuel cells would have been a better choice and the direct carbon fuel cell even more so, with electrochemical gasification of carbon as the ultimate step. The specific characteristics of fuel cells and multisource multiproduct systems were not considered, whereas we understand now that these can provide huge driving forces for the implementation of fuel cells compared to just replacing conventional combined heat and power production technology.

Introduction

Several accounts have been written on the history of fuel cell research dating back to the early experience of Sir William Grove and the German scientist Christian Friedrich Schoenbein e.g. Ketelaar in Blomen ed [1]. Fuel cell research got a huge stimulus from the USA space program. That research focused on low temperature fuel cells: polymer exchange membrane fuel cell in the Gemini program and the alkaline fuel cell (AFC) in the Apollo program. In the space shuttle program the polymer fuel cell came into the picture again but the alkaline fuel cell seemed to be able to withstand the

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E-mail address: ijzrkhemmes@gmail.com.

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competition of the PEM fuel cell, unlike on earth where the PEM fuel cell is the number one choice for mobile applications. The focus of this article however, is on high temperature fuel cells from a personal and a Dutch perspective. At the start of the Dutch national fuel cell program in 1986 worldwide two types of high temperature fuel cells were investigated; the Molten Carbonate Fuel Cell (MCFC) and the Solid Oxide Fuel Cell (SOFC), which still are the main types in the temperature range of roughly 600–1000 °C. The Dutch national research program was first and foremost focused on the molten carbonate fuel cell, later also solid oxide fuel cell research has been started followed by low temperature fuel cell research on the polymer fuel cell. The main part of the program was carried out at ECN The Energy Research Centre in Petten in the Netherlands, while the more fundamental research in the program was performed at TU Delft. The author has been involved in leading the Molten Carbonate Fuel Cell research at TU Delft as of 1987 in the group of late Prof. Dr. J.H.W. de Wit.

Although there are critical remarks to be made and I do make some myself, remarkable progress has been made. Looking at the Dutch program they delivered what they promised: a 10 kW MCFC pilot plants operated successfully. Moreover a lot of technological knowledge and know-how on materials, components and fuel cell systems was developed, which including its IP was transferred to the USA at the end of the Dutch fuel cell program. Personally I still remember the flexible lithium aluminate porous matrix produced by tape casting that was so strong and flexible that it could be rolled up like an old parchment paper. It was demonstrated by an ECN employee to students following my fuel cell course.

What were the ideas behind the research policy choices that were made in those period? Would we have chosen differently with the knowledge of today? And if so what can we learn from that and how would or should that influence our present day research policy choices? These and other questions will be addressed. Rather than aiming for a precise historical review, which has been written [in Dutch] by D. van der Hoeven [2], I take the liberty here to reflect on the more than three decades of fuel cell research that has passed since the start of the Dutch fuel cell research program in 1986 from a more personal perspective based on my personal experience and a little knowledge obtained on fuel cell thermodynamics.

Deciding on the type of fuel cell

Making the choice for the MCFC

In the Netherlands it was Prof. Barendrecht of Eindhoven Technical University who initiated the idea for a national research program on fuel cells. Based on progress in the US and Japan and appealing to the fear of missing out while in the Netherlands impact full research on the molten carbonate fuel cell took place in the past by pioneers Prof. Ketelaar and GHJ Broers at the university of Amsterdam in the nineteen fifties [3]. Later in the sixties GHJ Broers continued the work at the research institute TNO. After that Broers became professor at University Utrecht. Personal connections sometimes can speed up technology development. In this respect it is interesting to note that Prof. Broers was one of the professors of JHW de Wit who became professor himself at TU Delft in the area electrochemistry and corrosion and who then subsequently hired me as fuel cell coordinator to run the fundamental fuel cell research. This personal connection with Broers allowed us (the PhD students Robert Makkus, Ricardo Weewer and me) to pay one or two visits to his home in Alkmaar to learn from Broers about his molten carbonate research. Also in the beginning of the national fuel cell program we paid a visit to Prof. Selman at IIT Chicago which enormously boosted our knowledge and gave us a head start. The coincidence that Prof. Selman was originally Dutch proved to be very helpful in that initial process where we as newcomers in the field had to start from scratch.

Prof Barendrecht convinced the Dutch government to start the Dutch national fuel cell program, which was effectuated in 1986. An historic account has been given in Dutch by D vd Hoeven [2]. A technical state of the art with a review on early history by prof Ketelaar and also a contribution from prof Barendrecht on electrochemistry and fuel cell fundamentals can be found in the excellent book Fuel Cell Systems by Blomen ed [1]. From the fuel cell types developed at the time the molten carbonate fuel cell; MCFC was chosen partly for these historical reasons. However it was also seen as the most reasonable and logical choice based on the argument that the alkaline fuel cell; AFC was not really suitable for large-scale terrestrial applications due to corrosion problems and the constraint to avoid CO_2 in gas supplies to the anode as well as cathode, making air an unsuitable oxidant and a fossil hydrocarbon an unpractical fuel. Due to the high cost of the PEMFC polymer electrolyte membrane fuel cell, caused by a monopoly of Dupont on the proton conducting membrane the PEMFC was only considered for niche applications such as in space flights, where money was less of an issue. The phosphoric acid fuel cell; PAFC was considered to be already reasonably developed and (semi-) commercial. It would have been hard to catch up with that development and make a significant contribution. The solid oxide fuel cell; SOFC on the other hand was certainly an option, but the developments were not that far at the time, so it was considered the option for the far future. And indeed later at ECN (Netherlands Energy Research Centre now called ‘ECN part of TNO’) solid oxide fuel cell research was also started next to the MCFC research. In terms of development the MCFC was in between the phosphoric acid fuel cell and the SOFC. There was no commercial development yet, but the research abroad, mainly in Japan and the USA, was strong and promising.

All in all the choice for the MCFC was justified by good rational arguments that coincided with historical developments in the Netherlands and some national feelings for those who were sensitive to that. For a clear understanding it is good to recall that mobile applications in transport e.g. fuel cell vehicles or portable electronics were not considered at the time. The vision of the policy makers was to replace large-scale coal and gas fired power plants by fuel cells. In this future vision the MCFC's were essential components in a hydrogen economy and therefore to be fuelled by hydrogen. It is clear that as long as the hydrogen economy had not developed the large quantities of hydrogen needed for the MCFC had to come from reforming natural gas which was and to a certain extent still is, abundantly available in the Netherlands.

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Yet the 10 kW MCFC stack developed at ECN was not an internal reforming fuel cell. Pallets with 200 bar hydrogen cylinders were placed outside the building to fuel the stack. It was common sense that this was not a commercial solution but just put in place for the purpose of testing the 10 kW stack.

In the initial vision of the Dutch Fuel Cell program MCFC's were not yet seen in the light of distributed generation. I find this typical for innovation. It is apparently hard to imagine other systems than the existing one and go more than one step of change beyond the existing system. However, the vision of replacing existing power plants by fuel cells totally ignores the different characteristics of these fuel cells compared to conventional power plant technologies. We now much better understand these characteristics such as the modularity of fuel cells that allows for cost reduction by mass production, in contrast with the economies of scale concept that holds for conventional technology. As is well-known the modularity means that fuel cell efficiency is basically independent of the size and therefore fuel cells are particularly suited for distributed generation. Also if the goal was to replace coal-fired power plants by a more efficient technology why not opt for the Direct Carbon Fuel Cell (DCFC) which was also known at the time see e.g. Ketelaar in Blomen [1], but as far as I know the DCFC never was considered or even discussed. More on the DCFC below in Section Direct carbon fuel cell.

On the other hand, if the DCFC would have been considered it would probably rapidly have been set aside because hardly any development on this type of fuel cell had taken place at the time. And even if it would have developed further, it did not fit in the vision of a hydrogen economy in which hydrogen would be the dominant energy carrier in connection to renewable energy from solar and wind. Consequently hydrogen was envisioned as the fuel of choice also for the high temperature fuel cells in the long run.

Hydrogen; a suboptimal fuel for high temperature fuel cells

Although it is true that most fuel cells actually run on hydrogen and hydrogen is the reactant with the highest electrochemical reaction rate, hydrogen as a fuel in these high temperatures lead to large thermodynamic losses due to the entropy term in the well-known thermodynamic equation relating the Gibbs free energy and the enthalpy change of the overall fuel cell reaction [4,5]:

$$\Delta G = \Delta H - T.\Delta S \tag{1}$$

$$H_2 + 1/2\ O_2 <=> H_2O\ (\Delta H \sim -250\ \text{kJ/mol},\ \Delta S \sim -50\ \text{J/mol.K}) \tag{2}$$

For illustrative purposes, easy to remember order of magnitude values of the enthalpy change and entropy change of the reaction have been given as well. More exact thermodynamic values can be found in Table 1. Because of the negative sign of the entropy change for the overall hydrogen fuel cell reaction and the large value of T.ΔS at higher temperatures (T) the OCV of high temperature fuel cells (being proportional to the Gibbs free energy change) is significantly lower than the theoretical value of about 1.25 V relating to the hypothetical open cell voltage at a temperature of absolute zero. Here assuming that the enthalpy change is temperature independent and so also ignoring the phase changes of water at 0 °C and 100 °C and approximating Faraday's constant by ~10^5 J/C. Only at the extreme low temperature of absolute zero all the chemical energy ΔH in the hydrogen fuel - at least in theory-could be converted into electricity: $\Delta G = \Delta H$ and $E = \Delta G/2F$ at $T = 0$ would be around; 250 10^3 J/mol: 2 × 10^5 C/mol = 1,25 V.

Table 1 – Thermodynamic data for carbon, carbon monoxide, carbon dioxide and oxygen.

	h_0 (kJ/mol)	s_0 (J/mol.K)
C	0	6
CO	111	198
CO_2	394	214
O_2	0	205

As stated this is just an order of magnitude calculation with easy to remember approximate numbers.

Consequences for efficiencies

Using practical fuel and cathode gas compositions the OCV's of MCFC's and SOFC's are around 1 V, hence the theoretical conversion efficiency has decreased for this reason alone from 100% to ~80%.

It becomes even worse if one includes Nernst loss [see separate frame] which accounts for another 100–200 mV thereby reducing the maximum available conversion efficiency to about 65–70% [6,7]. On top of this we of course have the irreversible losses due to ohmic resistances, slow diffusion of reactants and slow kinetics of the electrochemical reactions of also about 100–200 mV depending among others mainly on current density. Therefore the cell voltage is roughly between 600 and 800 mV henceforth the efficiency is only 50–65%. When we include the fact that the hydrogen cannot be fully converted; u_f ~0.9, in practical fuel cell systems another 10% of the fuel is not being converted into electricity. So in this very rough order of magnitude calculation total efficiency is reduced to 45–60%. In the course of the national program more and more the combined cycle gas turbine power plant was mentioned, because of its high efficiency of also around 60%. So what was the point of developing MCFC's for central power plants? This comparison was not quite fair because for internal reforming FC's fuelled by natural gas efficiency is better due to the heat integration with the endothermic steam reforming reaction. Moreover, in the combined cycle two thermodynamic cycles are combined and this can also be done for high temperature fuel cells when a so-called bottoming cycle is included to convert the high temperature waste heat via a steam turbine in the additional power. Alternatively an integrated gas turbine fuel cell system is even better and much higher efficiency can be achieved up to 75% with natural gas as the fuel of choice [8]. Downside of the hybrid system is the larger and more complex and costly system. I remember discussions on these rough efficiency calculations with staff from BCN ("Fuel Cell the Netherlands") the organization to commercially exploit the molten carbonate fuel cell research by ECN. Their idea was to build the molten carbonate fuel cell into a standard ship container for

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Frame 1
Nernst loss and fuel cell modelling.

We note that in most fuel cells the gas composition changes locally due to utilization of the reactant gas(es) and mixing with product gas(es). Therefore locally the entropy term increases (in absolute sense) and more heat is dissipated (as $T\Delta S$). Consequently the local Nernst potential difference between anode and cathode is lowered. This effect decreases overall fuel cell efficiency and is known as Nernst Loss.

Because the fuel(gas) is consumed its partial pressure, or in general its chemical potential, becomes gradually lower towards the outlet. At the same time reaction products are formed diluting the fuel (or oxidant). Both phenomena lead to a decrease in the local Nernst potential difference between anode and cathode as a function of gas utilization.

Since the gas flows of oxidant and fuel can be controlled independently, the local utilization of oxidant and fuel in general are not the same. In fact often a large oxidant flow is applied for cooling purpose, hence oxidant utilization is low and for sake of simplicity we will discard that in the further discussion.

The Nernst loss is defined as the decrease in cell voltage relative to OCV due to utilization of the fuel. It is equal to the area between the OCV and the local equilibrium potential difference V(u) between anode and cathode plotted as a function of utilization, or in formula:

$$\Delta V_{Nernst} = V_{eq}(0) - \frac{1}{u_{tot}} \int_{0}^{u_{tot}} V_{eq}(u)du$$

When the inlet fuel composition is known, the Nernst loss can be simply calculated as the difference between OCV (V_{eq} (0))and the averaged Nernst potential calculated by the integral in the equation above with u the gas utilization.

So Nernst loss is a fundamental loss term NOT similar to ohmic, kinetics and diffusion losses. The latter are irreversible losses that can be minimized by technological development; better materials etc. and since they are non-equilibrium thermodynamic process losses they are minimized by lowering the flow; in our case the current density (see a.o. Bedeaux et al. [64]).

Nernst loss is fundamental in the sense of equilibrium thermodynamics and can therefore be formulated in an abstract equation based fashion; the above formula in this frame. Nernst loss is expressed as an integral with fuel utilization as the integration variable and not the position x indicating the relative distance between inlet and outlet ! Therefore Nernst loss does not depend on scale and micro flow design and other spatial parameters as suggested e.g. by one of the reviewers, it is only a function of fuel utilization; by definition I would almost say notwithstanding the fact that u itself is a function of x: u(x).

As shown in the NETL DOE fuel cell handbook it is possible to split the fuel cell (stack) in several subcells (substacks) by cutting the stack like a cake in slices each with their own cell voltage approaching the reversible cell voltage belonging to the local gas composition [5]. This is indeed possible (in theory as in a “gedanken experiment”), however the reversible cell voltage can only be approached at very low current density. In the Fuel Cell Handbook it is assumed that all cells are connected in series and are of the same size hence current density is the same for the whole stack, but very low! Henceforth one cannot obtain the same power of the stack let alone an increased power as implicitly assumed by the claim of minimized losses. The advantage obtained by “cutting the cake in slices” is that at the same average current density the irreversible losses are minimized (by a few percent) because of a more homogeneous distribution of the current density. This finds it roots in the mathematical inequality $<f(x)>^{2} \leq <f(x)^{2}>$ where $<f(x)>$ means the average of the function f(x) over a certain range. For further reading I referred to my chapter in Modern Aspects of Electrochemistry [65], the theoretical modeling work of F.R.A.M. Standaert a.o. in his PhD thesis [66] and the experimental verification of that modeling work by S.F. Au [67,70,71].

Which brings me to one final point; fuel cell modeling including Nernst loss. In literature one often finds detailed mathematical modeling based on the electrochemistry and physics in the fuel cells including Butler-Volmer for the kinetics and equations for diffusion polarization which in principle is of course correct. However, inspired by Leo Machielse of ECN who as a MCFC researcher always measured linear dependencies of cell voltage on current density and fuel utilization and tried to model that by linearizing all nonlinear equations that he encountered in deriving a formula for the cell voltage. my PhD student Frans Standaert did the detailed mathematical fuel cell modeling including approximations of correction terms when linearizing the exact mathematical expression he found for the cell voltage. In his exact expression for the cell voltage below one recognizes the Nernst loss term:

$$V_{cell} = \frac{1}{u_{tot}} \int_{0}^{u_{tot}} V_{eq}(u)du - \frac{1}{i_{tot}} \int_{0}^{1} r(x)\{i(x)\}^{2}dx$$

The irreversible polarization losses are a similar integral in which a nonlinear resistance term accounts for all kinetic, diffusion and ohmic losses. Note r is a function of x the position in the cell !

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My PhD student Siu Fai Au [70,71] verified the linearized equation by experiments finding small deviations that could be covered by the approximations for the correction terms as derived by Standaert. Basically the exact equation above can be approximated by the simple expression below:

$$V_{cell}^{SM} \approx V_{eq}(0) - \frac{1}{2}\alpha_f.u_f - i_{tot}.r$$

If needed some correction terms in the order of a few mV can be added. So often detailed physicochemical models that only can be solved by using numerical computer programs and still tweaking the parameters is not necessary, depending on the purpose of the modeling of course. For example for detailed engineering of the stacks including heat balances etc. the detailed modeling would still be necessary. Otherwise the simple bi-linear equation above gives a very good approximation of the overall behavior of high temperature fuel cells relating cell voltage, current density and fuel utilisation with the second term on the right hand site accounting for the Nernst loss.

local combined heat and power applications. Not much later the national Fuel Cell program was stopped. I strongly belief the inherent (thermodynamic) efficiency limitations as explained above are an important factor in why MCFC (and SOFC) have such a hard time becoming commercially viable and why among many other reasons BCN stopped its commercialisation activities [2].

Methane/natural gas

As shown in Fig. 1 the use of methane leads to a cell voltage independent of the operating temperature. However, there should be made the remark that methane does not or very slowly react electrochemically on the electrode. There is evidence that direct oxidation is possible in particular in an SOFC with dedicated anodes made of alternative materials [9]. But in MCFC's and conventional SOFC's a reforming step is usually applied. In that reforming step the heat produced by converting the hydrogen electrochemically in the fuel cell is used in the endothermic process of steam reforming in which the hydrogen is produced. This requires a strong heat coupling between the reformer and the fuel cell. This can be done as is well known by external reforming but preferably by internal reforming in which internal heat coupling takes place even on a molecular level without the need for a heat exchanger. So using natural gas as a fuel improves the efficiency estimates, but using natural gas was not the original idea when starting the national Fuel Cell research program. More importantly MCFC's and SOFC's are still less suited in a hydrogen economy with hydrogen as the main energy carrier if we still and only see them as converters of hydrogen into electricity.

High temperature proton conducting fuel cells

High temperature proton conducting fuel cells have a great advantage over anion-based electrolytes, with anions such as the carbonate ion (MCFC) and oxide ion (SOFC). In the latter type of fuel cells a large Nernst loss is created due to the fact that reaction products like water (and CO_2 in case of the MCFC) are released on the anode side where they dilute the fuel gas. (See separate frame on Nernst loss). In a proton conducting fuel cell the reaction product (water) is formed at the cathode where it has hardly any influence on the partial pressure of

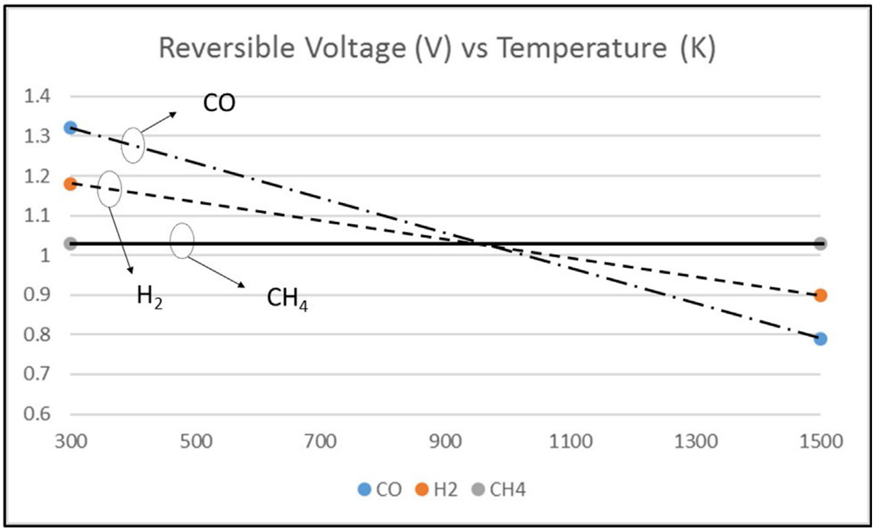

Fig. 1 – Reversible Cell Voltage as a function of temperature for a H2/O_2; a CO/O_2 and a CH_4/O_2 fuel cell.[1]

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[1] https://www.doitpoms.ac.uk/tlplib/fuel-cells/printall.php.

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the reactant (oxygen) because in conventional operation a surplus of air is supplied to cool the fuel cell. Therefore Nernst loss in these fuel cells will be in the order of a few tenths of a mV even at high temperatures, about ten times smaller than for anion conducting electrolyte fuel cells (MCFC and SOFC). Moreover, fuel utilization can be closer to 100%. In principle even hundred percent hydrogen fuel utilization and zero Nernst loss can be achieved if the Fuel Cell is operated on very pure hydrogen in so-called dead-end mode [10].

Similar to the DCFC the development of high temperature proton conducting fuel cells was not really considered at the start of the Dutch national Fuel Cell program, although both are to be preferred from a thermodynamic point of view. If the possibility of a proton conducting fuel cell was known at all it would have probably been set aside because of the higher specific ohmic resistance of the electrolytes compared to oxide conducting electrolytes. Also worldwide hardly any development took place in this area [11–14]. In hindsight this has been a suboptimal decision based on limited knowledge on the topic of all polarization losses including Nernst loss. Nernst loss was not (well-) known in these early days and did not enter the discussions on the choice for a type of fuel cell to further develop, whereas we know now that Nernst losses in MCFC and SOFC are almost of the same order of magnitude as all other polarization losses together including ohmic losses. One cannot just compare conductivities of oxygen and proton conducting electrolytes and claim one is better than the other if one ignores the final purpose in fuel cells and the difference in Nernst loss that would be experienced in the fuel cells based on anion or cation conductivity respectively. I will illustrate this with a simple order of magnitude calculation. Assuming a Nernst loss of 150 mV and a current density of 150 mA/cm2 at 1 Ω cm^2 total internal resistance including linearized kinetic, diffusion and ohmic losses each contributing 50 mV to a total polarization of 150 mV a cell voltage of 700 mV results when the OCV = 1V. When assuming only 50 instead of 150 mV or even zero Nernst loss, the ohmic losses of a proton conducting fuel cell are allowed to be 3 respectively 4 times higher than that of an MCFC or SOFC. All other parameters assumed equal, the proton conducting fuel cell would then also operate at 700 mV cell voltage.

Direct Carbon Fuel Cell

Full conversion of carbon

The thermodynamic advantages of the Direct Carbon Fuel Cell are well known nowadays and relate to the (near) zero entropy production in the overall reaction of carbon into carbon dioxide [15–17]. Relevant thermodynamic data can be found in Table 1. Again easy to remember order of magnitude values of the enthalpy change and entropy change have been added below to the reaction equation:

$$C + O_2 <=> CO_2 \ (\Delta H \sim -400 \text{ kJ/mol}, \Delta S \sim 0 \text{ J/mol.K}) \quad (3)$$

Therefore theoretically all chemical energy can be converted into electricity; so 100% efficiency if one excludes the irreversible losses. It is just to say that 100% efficiency is the thermodynamic starting point or upper limit for the DCFC in contrast to the MCFC and SOFC as argued in the previous sections.

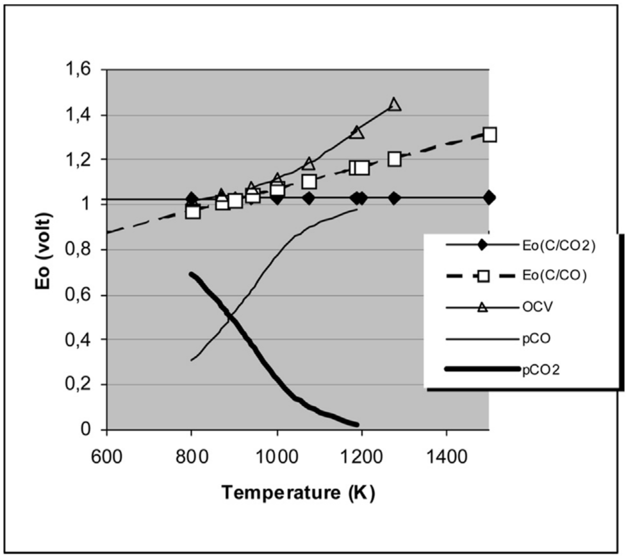

Fig. 2 – Standard potentials for the oxidation of carbon to CO and CO_2 and the Open Cell Voltage of a carbonate DCFC assuming $pCO + pCO_2 = 1$ atm at the anode and $pO_2 = pCO_2 = 1$ atm [From Hemmes & Cassir [18]].

Moreover there is no Nernst loss since independent of how little carbon remains available for electrochemical conversion, the activity of the carbon, being a solid, remains equal to 1. The same thermodynamic property allows us the advantage of hundred percent utilization of the carbon fuel. So there is no need to burn part of the carbon in a catalytic burner as is conventionally done in high temperature fuel cell systems with the remainder of the hydrogen. However, all that glitters is not gold. In the inevitable presence of carbon and the reaction product CO_2 the Boudouard reaction will take place and consume part of the carbon while releasing carbon monoxide:

$$C + CO_2 <=> 2\ CO$$

So part of the carbon fuel is reacted away without generating electrons, albeit under the production of a gaseous fuel; CO, which can easily be converted into hydrogen again.

The other downside of the DCFC is the technological difficulty in manifolding the solid fuel over the cells and constructing these cells in series to obtain practical voltages to transport and use the produced electric power. These technological problems are not yet solved. So in spite of the thermodynamic advantages the technological development path is not easy and then we have not even mentioned the fuel that is needed in terms of purity and structure. To make pure carbon from coal would require several purification steps. Because of this I was hesitant to publish on the DCFC however, sometimes solutions pop-up from unexpected areas. At the same time around 1998 that we published and presented the DCFC ideas on a conference [16] people in the US were working on the decarbonisation of natural gas by thermal decomposition [19–21]. In this vision large amounts of pure carbon would become available. They were looking for solutions and applications for this carbon. One suggestion was to put the

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carbon back under the ground to avoid CO_2 emissions; the original goal of the whole idea. However one has to realize that the carbon contains a large part of the energy from the national gas and in that sense that idea would be rather unfeasible, maybe just as unfeasible as a DCFC on coal. However combining the two unfeasible ideas might lead to a feasible solution. I compare this to a two photon process in physics. The energy of one photon is not enough to bring an electron into the next quantum orbit but if two photons hit the same electron rapidly after one another one can observe that the electron reached the next quantum level. This only is observed for very intense (laser) light beams, otherwise the quantum mechanical photo electric effect (for which Einstein received the Nobel prize) is observed. So sometimes two unfeasible ideas combined can bring about a feasible concept, at least in this case a concept worth studying further, as fortunately we can see happening now.

Sustainability of the DCFC can be further increase if the carbon fuel is not to be derived from fossil fuels, but from biomass. Several biomass sources have been studied in literature such as carbon from almond shells or olive wood [22–24].

Electrochemical gasification of carbon

There is yet another advantage of the Direct Carbon Fuel Cell that is less well known. That is the possibility of a DCFC to operate in such a way as to mainly produce CO instead of CO_2 [16].

$$C + 1/2\ O_2 <=> CO\ (\Delta H \sim -100\ kJ/mol,\ \Delta S \sim +100\ J/mol.K) \quad (4)$$

Because of the positive sign of the entropy change in the order of +100 J/mol.K the absolute value of the Gibbs free energy increases with temperature. Therefore the open cell voltage increases with temperature, meaning in fact that more electricity is produced than supplied by the ‘chemical energy in the fuel’; or better the enthalpy difference of the overall reaction of Eq. (4). The additional energy is the uptake of heat in the endothermic electrochemical reaction. So there is no violation of the first law of thermodynamics (energy conservation), but a very interesting fuel cell is at least theoretically possible in which, next to the conversion of carbon into CO and electricity, also heat is converted into electricity without the usual limitations of Carnot. This is reflected in the increase of the OCV with temperature as shown in Fig. 2. In the calculation for this figure we have taken the Boudouard equilibrium into account. The partial pressures of CO and CO_2 are also indicated in Fig. 2 assuming a total pressure of 1 atm at the anode ($pCO + pCO_2 = 1$). For simplicity of the calculation we assumed $pO_2 = pCO_2 = 1$ atm., hence 2 atm. total pressure at the cathode. If both CO and CO_2 can be produced what is the ratio between the two in a real DCFC and what parameters are of influence on this ratio?

As shown in the previous section the equilibrium is determined by the Boudouard equilibrium which depends on temperature and pressure. Fig. 2 illustrates the CO/CO_2 ratio for the equilibrium situation as a function of temperature. Clearly the formation of CO is promoted at higher temperatures with $pCO = pCO_2$ at around 900 K. What will happen if we start drawing current is that an overpotential will develop at the electrodes (or vice versa; a current will flow when we apply an overpotential). This overpotential is such that any CO at the electrode will want to react into CO_2. So the higher the overpotential the higher the change that a CO molecule will electrochemically react into CO_2. Therefor a low current density promotes the production of CO next to a high temperature. On the other hand any CO_2 can react chemically with the carbon fuel in the Boudouard reaction to CO. So if the partial pressure of CO_2 is above the equilibrium pressure at the specific operating temperature (as caused by the electrochemical reaction of CO into CO_2) this chemical back conversion of CO_2 with carbon particles into CO again will occur too. The kinetics of these (electro-) chemical reactions and the geometry of the anode and fuel chamber determining the residence time of the respective molecules at possible reaction sites, will determine the final CO/CO_2 ratio in the anode off-gas.

In spite of the complexity of the system with two ways of CO formation and many determining factors we again have obtained a Multi Source Multi Product energy system with very interesting properties. Carbon and high temperature heat are converted into electricity and CO.

Note that in the well-known shift reaction with steam CO can be converted into hydrogen. This chemical reaction is called a shift reaction because it is hardly endothermic nor exothermic and CO is just shifted to H2 under the coproduction of CO_2:

$$CO + H2O <=> CO_2 + H_2 \quad (5)$$

So CO can be considered to be more or less equivalent to H_2, therefore one could speak of a fuel cell producing hydrogen instead of consuming it and taking up heat instead of producing (waste) heat. Of course in practice there will be heat losses that will have to be taken into account and that will make performance less ideal as indicated by this theoretical, thermodynamic upper limit.

Note that Eq. (4) is in fact the gasification of carbon into CO with this difference that in a fuel cell it is accomplished by electrochemical reactions on an anode and a cathode whereas in ordinary gasification only chemical reactions take place. This makes a big difference; the first way is endothermic and co-produces electricity whereas the second route is exothermic and co-produces just heat. For a CO producing DCFC one could therefore also speak of ‘electrochemical gasification’. If we manage to operate the direct carbon fuel cell at very high temperatures and find sufficient high temperature heat to be supplied to the fuel cell, for example from concentrated solar, electrochemical gasification is a very promising option for the future where there most likely will be a high need for electricity and hydrogen. Further detailed studies are needed to verify this theoretical possibility by both experimental studies as well as by flowsheet simulations using Aspen or Cycle Tempo that include all the relevant thermodynamic data. The integration of fuel cell technology with high temperature heat form concentrated solar offers many new and interesting options of which a few will be discussed in the next section.

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DCFC and solar fuels

The energy carriers electricity and H2/CO described in the above section are produced in a MSMP (Multi Source Multi Product) system from both fossil and renewable energy (solar) sources [25,26]. The H2/CO can be seen as a solar fuel [27] in a double sense, when the production of carbon for the electrochemical gasification also involves heat from concentrated solar for the thermal decomposition of methane [28,29].

Upgrading high temperature heat from concentrated solar directly into electricity and H2/CO in electrochemical gasification is probably a process with higher (exergetic) efficiency and more economic than present practice of only electricity production in CSP [concentrated solar power] technology, but this needs further study.

In addition electricity is hard to transport over large distances, much harder than gaseous or liquid fuels. The CO/H2 can be transported in (natural gas) pipelines or first converted into liquid fuel. The solid carbon could be shipped all over the world as is now done with coal.

A conceptual design of the integration of fossil fuel with concentrated solar for the production of electricity and solar fuels is depicted in Fig. 3.

The application of concentrated solar for the thermal decomposition of methane into carbon and hydrogen and the further use of those energy streams in fuel cells is a promising option for integrating renewable energy and fossil energy and thereby also accelerating the development of concentrated solar as a renewable energy technology [30]. It provides a pathway for producing hydrogen without the need for gas separation in costly pressure swing adsorption machinery as instead an easy solid gas separation can be applied. The carbon formed in this thermal decomposition process is very reactive and suitable as fuel for the direct carbon fuel cell [30] or for that matter in a direct carbon fuel cell operated as an electrochemical gasification unit as depicted in Fig. 3. It should be noted that if one wants to convert the produced CO into hydrogen in a shift reaction one does need a gas separator to separate H_2 from CO_2 in contrast to the hydrogen produced by thermal decomposition.

The fact that these energy carriers and solar fuels are still partly derived from fossil energy is something that cannot be denied, but the emissions of CO_2 can be minimized due to the input of renewable (solar) energy. Moreover, due to the high efficiency, the CO_2 emissions are very low per unit of produced energy in the fuel or in the form of electricity.

Since global warming is a global problem, it doesn't make much sense to make a few systems hundred percent CO_2 emission free whereas on the other hand, we still need large amounts of energy from fossil fuels. Overall, it makes more sense to use the fossil fuels in a much more efficient way next to the development of renewable energy such as wind and solar not only as isolated technologies but preferably integrated in Multi Source Multi Product energy systems with many of them having some form of electrochemical conversion technology as their key component [25,26].

Discussion on the fuel cell of choice

What if we had known these theoretical possibilities and if these arguments had entered the discussion on the choice for the type of fuel cell to be develop in the Dutch national Fuel Cell program? We will never know. The fact that we did not immediately start with the development of the Direct Carbon Fuel Cell has set us back for several decades. Fortunately, nowadays researchers are catching up on its development in a rapid pace, in particular in China. Albeit three decades later

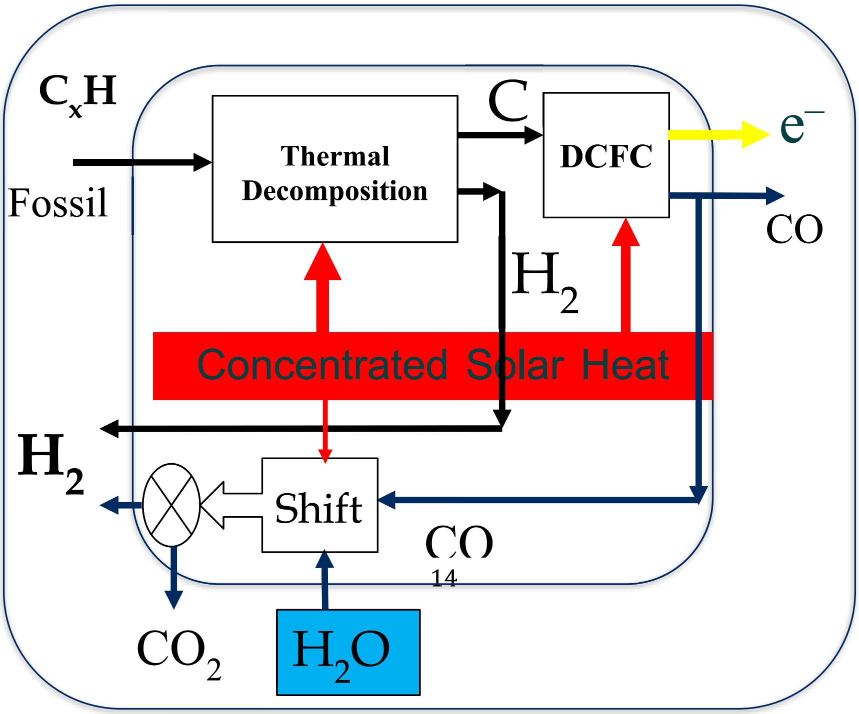

Fig. 3 – Conceptual scheme for the production of solar fuels and electricity.

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than might have been the case if we would have had better theoretical understanding of fuel cell thermodynamics and if that knowledge would have been known to the policymakers at the time. Or should we say that we are more than a century too late when considering the early experiments of Jacques [31] on the DCFC around 1900?

Nevertheless a disclaimer is in order here. In spite of the fact that high temperature fuel cells still have a hard time becoming commercially available products on the market partly for the reasons discussed in this paper above (see 2.2–2.4), they did show a successful technological development. It is not sure yet if the DCFC will reach the same maturity on a technological level given the difficulty among others of supplying a solid fuel. Moreover, present developments on the direct Carbon fuel cell cannot be seen independent of the development of the MCFC and SOFC's, since present types of Direct Carbon Fuel Cells are strongly based upon the latter types with the same electrolytes or combinations thereof, the same or similar cathodes and sometimes anodes as well [17,21,32,33]. Therefore, the technological developments and knowledge infrastructure on the MCFC and SOFC have strongly supported and still support the development of the DCFC.

Concerning DCFC development history seems to repeat itself. Again like for the MCFC and SOFC, in the development of the Direct Carbon Fuel Cell technology, not the specific characteristics of the technology are leading in its development, but the paradigm in which the technology is developed and in which, as is believed, the new technology has to fit. For example almost all research papers deal with the full conversion of carbon into CO_2 with the aim to produce as much electricity as possible and replace conventional power plants using the -in itself-valid arguments of higher efficiency and lower emissions (CO_2, NOx). But the specific characteristics and possibilities offered by the new technology such as electrochemical gasification and integration with concentrated solar are explored to a much lesser extent if at all. The lesson learned [and still to be learned] is that electrochemistry and fuel cell technology offer so much more than just the production of electricity. Although we no longer build our fuel cell innovation system around the paradigm of central power production we can do so much more taking into account the characteristics of fuel cells in electrochemical conversion in general. We do not need to restrict ourselves to the standard fuels and oxidant, but in general can look at all kinds of reactants for the production of valuable chemicals for the chemical industry and see to what extent we can possibly produce them in an electrochemical way under the production of electric power [34–38]. Some of these options have been explored in a paper together with the late Prof. G.P.J. Dijkema [39]. Moreover, one can also look at the application of existing type of fuel cells in the chemical process industry to leverage efficiency or otherwise improve the processes in a chemical factory [40]. Dijkema applies the concept of analysing all the functions of a certain conversion unit like a fuel cell not just its main function that it was designed for. In other words we can look at the specific characteristics of the fuel cell and try to use them in applications [41]. For example the cathode of a fuel cell works as a nitrogen concentrator since oxygen is taken from the air. Instead of expensive and energy intense air separation units one can apply a fuel cell to obtain nitrogen for further processing in for example an ammonia plant or adding it to natural gas as is done in the Netherlands on a large-scale to convert high-grade (imported) natural gas into lower grade standard Dutch quality gas for households.

Specific characteristics of the MCFC

We have seen that the choice for the MCFC and later the SOFC is unfortunate from the perspective that they fit poorly in a hydrogen economy that they originally were intended for while assuming hydrogen to be their main fuel. However, specific characteristics of fuel cells provide them a right of existence on their own, such as their modular design and suitability for distributed generation. In the next section we will touch upon a few of these characteristics and specific applications.

MCFC in distributed generation

Distributed generation of electricity and heat

It was soon realized that molten carbonate fuel cells could not be made on the scale of hundreds of megawatt for central power plants and that one has to start small. One realized that this is not necessarily a disadvantage and that the modular characteristics of fuel cells and the fact that their efficiency is more or less independent of size makes them very suitable for local generation of power and heat next to where the demand is. If one needs more power one can just place more of those modules. Instead of economics of scale as for conventional power generation technology, mass production could bring the cost down. Early applications of the MCFC included a pilot at a hospital (Kaiser Permanente CA, USA [42][2]) where another surprising characteristics of fuel cell technology was planned to be used. In spite of their early stage of development fuel cells proved to be very reliable. They can replace backup power; not one to one though, but replacing the grid as the main power supply and instead using the grid as the backup power.

Other advantages of local generation are of course the short distance between the production of waste heat in the Fuel Cell and the demand of heat in local applications. As is well known transport of heat is very difficult and costly. Moreover the local waste heat allows for the production of cold for air conditioning as well e. g. by means of absorption chillers [43].

Distributed generation of chemicals and fuels

MCFC's are capable of the coproduction of hydrogen and power [44,44,45]. The hydrogen is not pure but in the form of reformed natural gas; a gas mixture and a kind of syngas from which for example liquid fuel can be produced or pure hydrogen separated. One could envision MCFC's on natural gas near ‘gas stations' to fuel cars with electricity and/or locally produced liquid fuels and/or hydrogen provided a strong natural gas grid is locally available (as in the

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[2] In the end the pilot was not at the Kaiser P Hospital but at the Naval Air Station Miramar located in San Diego, California.

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Frame 2
The superwind concept.

In Fig. 4 a MSMP system is shown with as inputs natural gas and wind energy. Assuming that we keep the natural gas input constant (bottom left) it is shown how a peak in wind energy (indicated by the red square upper left) for which there is no demand (or just a very low price on the market) can be compensated by a lower electricity' production from the fuel cell unit. We also keep the electricity output of the system constant for sake of the argument. Surprisingly, flowsheet calculations have shown that by reducing electricity output from the fuel cell, while keeping the national gas input constant, an increase in hydrogen output in terms of energy per unit time is achieved that is three to four times higher than the wind energy peak that is being compensated to fulfil electric demand that is assumed to be constant in this example. Therefore it appears as if the peak in wind energy has been converted into hydrogen at an efficiency of 300%–400%. The word 'appears' is emphasized here because there is no real conversion of the electricity from wind energy. The electricity from the wind turbine just stays in the form of electricity and is still delivered to the grid or to a client fulfilling demand (as said assumed here to be constant). However, the peak is compensated by the reduced production of electricity from the fuel cell. This can be accomplished by changing the electric load to the fuel cell by electric control; decreasing the current or increasing the cell voltage. Since the current density is decreased also the irreversible losses are decreased (lower overpotential and higher cell voltage) and less heat is dissipated in the cell. Since the input of natural gas is assumed constant still the same amount of heat is used in the internal reforming reaction and still the same amount of hydrogen is produced and therefor the output of waste heat is decreased and the amount of hydrogen in the off gas increased. Since both outputs of waste heat and electricity (from the fuel cell) are decreased the amount of hydrogen can increase more than just the decrease in electric output from the fuel cell.

Producing hydrogen allows for operating the cell even at higher current densities and power densities since the extra heat than produced can be used to reform more natural gas. Note that in this case we do have to increase natural gas input. We have shown that power output from the same full cell can almost double while simultaneously producing that same almost double amount of hydrogen in terms of energy per unit time, thereby almost quadrupling useful output of the fuel cell in terms of hydrogen and power while not counting heat. As a consequence in the new situation the CAPEX in terms of \$/kW is decreased by a factor of 3 to 4 not because the fuel cell has become cheaper, but because the number of kW useful output has increased.

Moreover the added flexibility is key in a future with a large share of wind and solar electricity on the grid.

Netherlands) [46]. A pilot plant has been built in Fountain Valley California USA to demonstrate the feasibility of this tri-generation concept [47].

If we include developments in other areas new options might arise in the near future. We can think of a development like Process Intensification in the chemical process industry in which dedicated small scale chemical processes are designed to allow for local production of chemicals in efficient ways as to be able to compete with the economics of scale in large-scale chemical plants and avoid transport cost [48–50].

Flexible coproduction with an MCFC

Following the original paradigm of fuel cells replacing central power plants, there was no need to emphasize their dynamic behaviour and properties. They were and are still not designed to be operated in a flexible manner. However, they in principle could be designed to be able to operate dynamically, thereby compensating fluctuations in wind- and solar electricity production. Moreover, as shown in the Superwind concept [see Frame on Superwind] it is not balancing the power production from wind and solar by just producing more or less electricity with the fuel cell, but instead producing more hydrogen and less electricity at the same time when wind and solar are strong and put lots of electricity on the grid. Hereby the economic load factor is increased; the fuel cell is not standing idle when there is a surplus of electricity, but continues producing valuable economic goods (H2/CO).

One might expect that reducing power production with one unit might increase the H2/CO energy output also by one unit. However, flowsheet calculations have shown that instead, energy output in the form of H2/CO increases by 3–4 units [44,45]. This is reflected in Fig. 5. While going from right to left the utilization uf decreases from 95% to 60%) and electric efficiency decreases only little whereas gas efficiency increases more. Therefore total efficiency is increasing and the amount of waste heat decreasing.

The Superwind concept is explained in more detail in a separate frame to be found elsewhere in this article. Note that here use is made of the characteristics of fuel cells that they are a membrane technology with the membrane separating anode and cathode input flows as well as the output flows. Contrary to fuel cells a combustion chamber of a gas turbine for instance only has one output releasing the off gas.

With the development of wind and solar and their large-scale implementation, the need for flexible power production becomes more urgent. Whereas in the past, fluctuations in demand required a more a less flexible power production. Nowadays, the fluctuating character of wind and solar urges other production methodologies to be more flexible and dynamic and with shorter time constants than in the past. In economic analyses of fuel cells, the levelized cost of electricity (LCOE) for fuel cells had to match the price for electricity which was seen as a given, more or less fixed value, whereas nowadays we know that electricity prices fluctuate a lot. Even negative prices sometimes occur when the supply of wind and solar is so large that an overproduction on the electricity grid is established. There is a lot of talking about power to gas,

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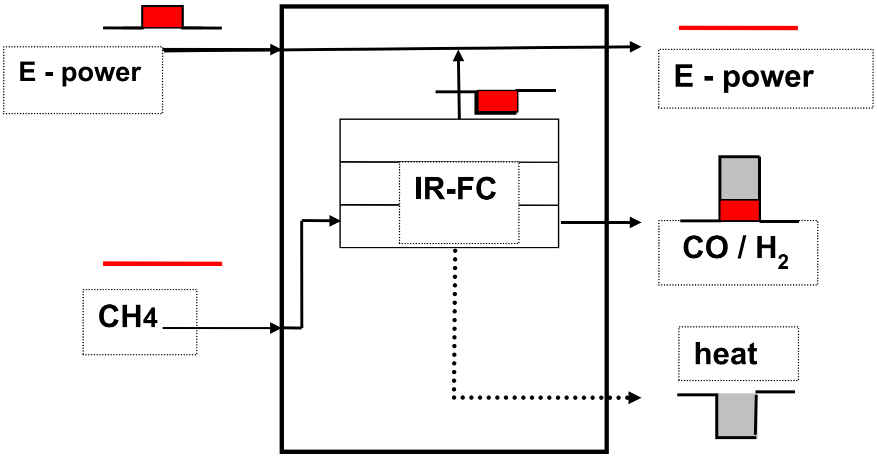

Fig. 4 – Superwind concept.

which is a marketing term for ‘ordinary’ electrolysis, but it makes more sense to first start to develop flexible production units and preferable flexible co-production units in which also hydrogen is produced when less electricity is needed. This can be perfectly well realized using a molten carbonate fuel cell or solid oxide fuel cell, as has been shown by simulations in literature [44,45] In order for fuel cells to fit in this shifted paradigm of flexible and dynamic production, fuel cells should be designed and built to withstand these dynamic conditions. The market asks for this change [51–53].

Fuel assisted electrolysis or depolarized electrolysis

In case flexible coproduction of electricity and hydrogen, or flexible production of electricity in general is not enough to cope with the fluctuations in wind energy and solar and the supply of those is so large that negative prices will occur and we really don't know what else to do with electricity -then and only then (!)- power to gas or electrolysis comes into the picture. One can opt for conventional electrolysis, but there is another option in electrolysis that for instance is also applied in Aluminium production in the well-known Hall-Heroult process. In conventional electrolysis oxygen production takes place, where often there is no need for that oxygen and it is just vented into the air. However, still electric power is needed for that and the electric energy needed for the production of 1 mol of hydrogen can be reduced by supplying some kind of cheap fuel to the oxygen producing electrode in an electrolyser. The electrolyser cell than more resembles a concentration cell. Or alternatively one can see it as a combination of an electrolyser and a fuel cell anode. In the Hall-Heroult process this is a carbon anode that can be seen as one half of a DCFC. The concept is called fuel assisted electrolysis [54] or depolarized electrolysis [55]. In this concept the formation of oxygen is prevented and thereby the electrochemical potential difference across the electrolyser is lowered. Hence, the electric power that is needed to produce a certain amount of hydrogen (respectively Aluminium) is lowered, because the amount of hydrogen (or Al) produced is directly proportional to the current flowing through the electrolyser cell and the power needed is the product of current and cell voltage.

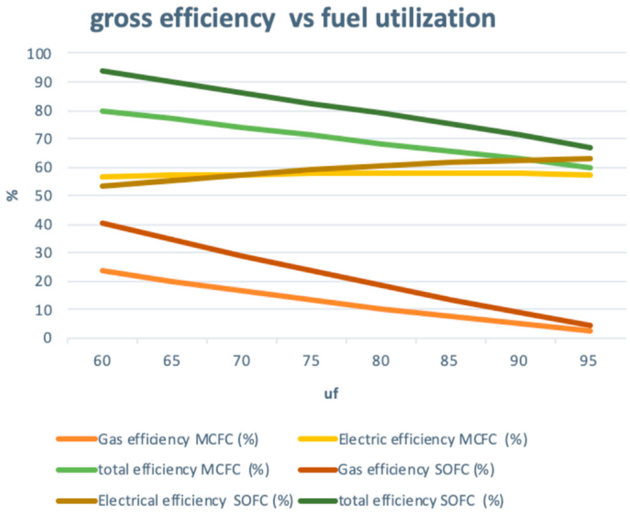

Fig. 5 – Efficiencies of an MCFC coproduction system as a function of fuel utilization compared with earlier published results on an SOFC system [44,45].

So in this way, another flexibility is introduced into the energy system. If there is really a large surplus of electricity than electrolysers could be operated as conventional electrolysers converting the power of electricity into hydrogen. In other circumstances, it can be meaningful and economic to supply a cheap and/or renewable fuel, for instance biogas, to the oxygen producing electrode to reduce the power needed for the production of hydrogen. Moreover, looking at the latter system using biogas it converts electricity and biogas into pure hydrogen, we sort of ‘upgrade’ the biogas into ‘electrolysis grade’ pure hydrogen. So, the hydrogen does not only come from the electricity of surplus renewable energy but also from the biogas. I sometimes call that biogas ‘dirty’ hydrogen defined as: “a gas mixture containing hydrogen”. So the ‘dirty’

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hydrogen is upgraded in this fuel assisted electrolyser process into pure hydrogen. Note that we are again dealing with a Multi SourceMulti Product energy system and that the gas mixture can be any fuel that is suitable for the anode of a high temperature fuel cell (SOFC or MCFC) including hydrocarbons if one provides internal reforming as well.

This process also enhances the economics of the electrolysers because under conventional circumstances the electrolysers have to stand idle in some periods. By using fuel assisted electrolysis, they can with a moderate supply of electricity still produce equal amounts of hydrogen and convert biogas into pure hydrogen at the same time. Meaning they have a higher load factor or utilization rate. Although solid oxide fuel cells were not designed for this purpose, they can be made suitable for fuel assisted electrolysis as has been shown for instance by Cinti et al. [54]. So the high temperature fuel cell technology can find different applications and we can observe a paradigm shift from; fuel cells being devices that convert hydrogen into electricity (and heat) to fuel cells being devices that produce hydrogen from hydrocarbons either under coproduction of electricity (Superwind concept in Section Flexible coproduction with an MCFC) or with the simultaneous input of electricity as in fuel assisted electrolysis. We recall that also electrochemical gasification is in fact a hydrogen producing fuel cell (albeit via CO).

MCFC in CCS

A particularly interesting characteristic of the molten carbonate fuel cell is its capability of capturing CO_2. This is because at the cathode oxygen and CO_2 are combined into a carbonate ion and the carbonate ion is subsequently transferred to the anode side where the CO_2 is released again. In their report on the status of MCFC development Moreno et al. report that [56], I cite: *During the 1980s, several studies showed considerable potential of MCFCs in terms of high efficiency, low emission, and the possibility of separating CO_2 for the exploitation of clean coal.* However, the awareness that CO_2 causes climate change was not dominant in 1985 the time that the choice for a molten carbonate fuel cell development in the Dutch national Fuel Cell program was made in the Netherlands. The large awareness of global warming in the policy arena appeared somewhat later [57–59]. However, this CO_2 capturing characteristic of the MCFC is a strong argument for its further development with global warming climbing higher and higher on the policy agendas of governments where it is translated into international agreements and CO_2 emission reduction goals, concrete action plans and research funding.

Integration of MCFC technology with existing infrastructure should not stop here. When the MCFC is near the fossil fuel power plant one can search for ways to integrate the waste heat of the MCFC with the power plant. Two Italian exchange students from the polytechnic of Milano have performed this exercise for the integration of an MCFC with a coal fired power plant under my supervision in Delft. High temperatures waste heat integration to superheat the steam in the steam cycle of the coal fired power plant is possible, but the students showed that also lower temperature heat can be integrated in lower temperature heat streams in the conventional power plant thereby increasing its efficiency [60].

Type of R&D

There is an important remark to be made on the R&D on MCFC and SOFC as it took place in the past decades in particular in the early phases. Since the research program was mostly designed by or at least in cooperation with researchers the research focused on performance and the fundamental aspects thereof, such as electrode polarization caused by slow reaction kinetics on poor electrochemical catalyst materials, slow diffusion and ohmic losses. Performance was key and a lot of research focused on minimizing electrode polarization by understanding the processes. In the Dutch national Fuel Cell program the fundamental part of the research was mainly assigned to TU Delft. ECN was more involved in technological development and upscaling of the MCFC technology up to a 10 kW MCFC pilot facility.

In a laboratory setting expensive laboratory grade components and chemicals are bought and although some care is taken about costs, not to the extent that the research has been cost driven. When fuel cell development in the much earlier phase would have been coupled to end-users we would have learned that next to high-efficiency it is predominantly about cost, endurance and footprint that the customer cares about. If those were the drivers of research probably we would have taken other research directions as a priority. Here we can learn form other R&D fields and R&D management literature [68,69].

Cost driven R&D

How would cost driven research be different from what we have been doing? What to say for instance, about the pure nickel that we use to prepare our nickel and nickel oxide electrodes? In a provocative thought we could imagine that we just take nickel ore, throw that into molten carbonate and since almost nothing is stable in molten carbonate we will be left with pure nickel, which is stable under a reducing environment. As said we have not done the test and it's probably not that easy, but it is an indication of the early research direction that we could have taken to produce cheaper electrodes. Just grinding nickel ore, mixing it with carbonate and tape casting it into thick electrodes that would become thinner when heating and reacting all its chemicals and constituents. Perhaps oxide and ceramic materials in the ore would provide sufficient creep resistance as a by-product so that we do not have to add laboratory grade aluminium(oxide) as a separate addition and what about the carbonate itself? Is it possible to just use limestone? Here we go back to the pioneering work of the Russian researcher Davtyan [61] who tested early fuel cell concepts with different electrolyte mixtures. As the Dutch MCFC pioneers Broers and Ketelaar [62] describe it, I cite:

Experimental work in these laboratories (note KH: of Broers and Ketelaar) on high temperature fuel cells was initiated by a thorough investigation of the type of cells described by Davtyan [61]*. Because neither the electrodes nor electrolyte were found to be stable, these cells are not suitable for long term operation. Therefore, work was directed toward developing a cell that would fulfil stability requirements.* end of citation.

Broers and Ketelaar found out that it was the carbonate ion in the electrolyte that was responsible for the conductivity of the electrolytes and allowed the operation of the cell as a fuel cell; the ancestor of the MCFC [3].

I continue citing: *Therefore, work was directed toward developing a cell that would fulfil stability requirements over long periods in the presence of reacting gases and their combustion products. The electrolyte selected was a mixture of lithium, sodium, and/or potassium carbonate, impregnated in a porous sintered disk of commercial magnesium oxide.* end of citation.

Henceforth all MCFC work is using these carbonates as electrolyte and all "of course" laboratory grade. Magnesium oxide was later replaced by lithium aluminate but what purity is really needed? And could researching that question eventually reduce cost?

It is not to say that ECN and others were ignorant of the cost. Along the way decisions were made for example to focus on removing the bubble barrier in the matrix that was deemed necessary to prevent gas crossover from anode to cathode or vice versa. And work on the Lithium cobalt cathode was stopped when realising that Cobalt was even more expensive than Ni and would probably become scarce in the future, albeit after already a lot of research had been performed on the material [63].

Discussion and conclusions

The high temperature fuel cells MCFC and SOFC are in a sense unfortunate choices due to:

1) the high operating temperature yielding a large term T.ΔS representing the amount of heat that has to be produced in order to not violate the second law of thermodynamics.
2) the utilization of the fuel that cannot be 100%.
3) A high Nernst loss next to, -and similar to-the term T.ΔS caused by
   i) a high operating temperature
   ii) reaction products diluting the fuel which is related to the conduction ion in the electrolyte being an anion (carbonate- and oxygen ion respectively)
   iii) The reactants are in the gaseous state; thereby activity is decreased as the partial pressure of the reactant is decreased contrary to solid state reactants that maintain their activity irrespective of the amount of reactant

Then how to avoid or minimize Nernst loss? The answer can be found in the reasons above:

1) Lowering the operating temperature. However, that is limited by the carbonate electrolyte that has to be molten and the conductivity of the solid oxide fuel cell electrolyte that exponentially decreases with lowering the temperature. Yet also for other reasons efforts are made to decrease the operating temperature of the SOFC. Of course there are low temperature fuel cells such as the polymer fuel cell which indeed suffer much less from Nernst loss, but they have other problems and fall outside the scope of this article.
2) Lowering fuel utilization. This option makes sense when methane or biogas is used as a fuel in internal reforming fuel cells. Than reformed methane is the anode off gas containing hydrogen that can be separated and commercialized next to electricity and heat.

More rigorous ways are to be found in new types of fuel cells.

4) Try to find and develop electrolytes based on cation conductivity such as proton conducting ceramics and develop fuel cells based on them.
5) Use a solid fuel like carbon in a DCFC.

In conclusion the lessons learned are to start from theoretical thermodynamic insights that give certain fuel cell types a head start over other types. In particular the DCFC and a high temperature internal reforming proton conducting fuel cell have such a head start.

Once a development has started one should also be aware of the dominant paradigm under which this development is taking place. The dominant paradigm for fuel cells is: fuel cells convert chemical energy into electricity and heat. And in a hydrogen economy vision the fuel of choice would be hydrogen.

In this paper arguments are given that the MCFC and SOFC could (or should) be seen as hydrogen production devices with electricity as a by-product next to heat. A DCFC operated as an electrochemical gasification unit would be able to produce hydrogen even under the uptake of heat. And a fuel assisted electrolyser can be seen as a mix of a fuel cell and an electrolyser also producing hydrogen. So in a future hydrogen economy fuel cells might more take the role of hydrogen production then of hydrogen consumption and conversion; a huge paradigm shift.

Another lesson learned would be to judge each new technology on its own merits and characteristics and make use of that rather than trying to fit the new technology in the old system replacing old technology one to one. Next to fuel cells as hydrogen production devices, fuel cells are nitrogen concentrators (remove oxygen from air) and the MCFC is even a CO_2 concentrator for application in CCS. Generalizing fuel cells as a shift from chemical reactions to electrochemical reactions, the production of some chemicals can be performed in an electrochemical device similar to a fuel cell producing less waste heat and electricity instead, next to the desired chemical product. With the introduction of more and more electricity from wind and solar on the grid we can observe the shift from a need from electricity to what I call 'flextricity'; electricity at the right place at the right time. This brings about the challenge for fuel cells to be operated dynamical without jeopardizing endurance. It is argued that preferably 'flextricity' should be produced in coproduction with hydrogen so that always valuable goods can be produced and the device is never standing idle.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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REFERENCES

[1] Blomen LJMJ, Mugerwa MN. Fuel cell systems. New York: Plenum; 1993.

[2] vanderHoeven. Een gedurfd bod: Nederland zet in op de brandstofcel. 2005.

[3] Broers GHJ. High temperature galvanic fuel cells. PhD thesis. University of Amsterdam UvA; 1958.

[4] Appleby AJ, Foulkes FR. Fuel cell handbook. New York: Van Nostrand Reinhold; 1989.

[5] Hirschenhofer JH, Stauffer DB, Engleman RR. Fuel cells, A handbook. P2-1 edn. 5th ed. US Department of Energy; 2000.

[6] Standaert FRAM, Hemmes K, Woudstra N. Nernst loss and multistage oxidation in fuel cells. Washington: Courtesy Associates Inc; 1998. p. 92–5.

[7] Standaert F, Hemmes K, Woudstra N. Nernst loss in fuel cells and fuel cell designs in dead-end mode. In: Proceedings of the fourth international symposium on carbonate fuel cell technology, vol. 97; 1997. p. 112–9 (4).

[8] Ghezel-Ayagh H, Walzak J, Patel D, Daly J, Maru H, Sanderson R, et al. State of direct fuel cell/turbine systems development. J Power Sources 2005;152(1):219–25.

[9] Shahid M, He C, Sankarasubramanian S, Ramani VK, Basu S. Co_3O_4-Impregnated NiO-YSZ: an efficient catalyst for direct methane electrooxidation. ACS Appl Mater Interfaces 2020;12(29):32578–90.

[10] Standaert F, Hemmes K, Woudstra N. Nernst loss in fuel cells and fuel cell designs in dead-end mode. In: Proceedings of the fourth international symposium on carbonate fuel cell technology, vol. 97; 1997. p. 112–9 (4).

[11] Ebbesen SD, Jensen SH, Hauch A, Mogensen MB. High temperature electrolysis in alkaline cells, solid proton conducting cells, and solid oxide cells. Chem Rev 2014;114(21):10697–734.

[12] Browning D, Weston M, Lakeman JB, Jones P, Cherry M, Irvine JTS, et al. Proton conducting ceramics for use in intermediate temperature proton conducting fuel cells. J N Mater Electrochem Syst 2002;5(1):25–30.

[13] Schober T. Tubular high-temperature proton conductors: transport numbers and hydrogen injection. Solid State Ionics 2001;139(1–2):95–104.

[14] Schober T. Protonic conduction in $BaIn_{0.5}Sn_{0.5}O_{2.75}$. Solid State Ionics 1998;109(1–2):1–11.

[15] Peelen WHA, Hemmes K, De Wit JHW. Carbon a major energy carrier for the future? Direct carbon fuel cells and molten salt coal/biomass gasification. In: Advances in molten salts: from structural aspect to waste processing; 1999. p. 478–89.

[16] Peelen WHA, Hemmes K, De Wit JHW. Carbon a major energy carrier for the future? Direct carbon fuel cells and molten salt coal/biomass gasification. High Temp Mater Process 1998;2(4):471–82.

[17] Hemmes K, Cooper JF, Selman JR. Recent insights concerning DCFC development: 1998-2012. Int J Hydrogen Energy 2013;38(20):8503–13.

[18] Hemmes K, Cassir MA. Theoretical study of the carbon/carbonate/hydroxide (electro-) chemical system in a direct carbon fuel cell. J Fuel Cell Sci Technol 2011;8(5).

[19] Cooper JF, Cherepy N, Upadhye R, Pasternak A, Steinberg M. Direct carbon conversion: review of production and electrochemical conversion of reactive carbons, economics and potential impact on the carbon cycle. CA, USA: Lawrence Livermore National Laboratory; 2000 Dec 12. Report No.: UCRL-ID-141818.

[20] Steinberg M. Conversion of fossil and biomass fuels to electric power and transportation fuels by high efficiency integrated plasma fuel cell (IPFC) energy cycle. Int J Hydrogen Energy 2006;31(3):405–11.

[21] Steinberg M, Cooper JF, Cherepy N. High efficiency carbon and hydrogen fuel cells for CO_2 mitigated power. Greenhouse Gas Control Technologies, Vols I and Ii. Proceedings 2003:1307–10.

[22] Elleuch A, Halouani K, Li YD. Investigation of chemical and electrochemical reactions mechanisms in a direct carbon fuel cell using olive wood charcoal as sustainable fuel. J Power Sources 2015;281:350–61.

[23] Elleuch A, Boussetta A, Yu J, Halouani K, Li Y. Experimental investigation of direct carbon fuel cell fueled by almond shell biochar: Part I. Physicochemical characterization of the biochar fuel and cell performance examination. Int J Hydrogen Energy 2013;38(36):16590–604.

[24] Elleuch A, Boussetta A, Halouani K, Li Y. Experimental investigation of Direct Carbon Fuel Cell fueled by almond shell biochar: Part II. Improvement of cell stability and performance by a three-layer planar configuration. Int J Hydrogen Energy 2013;38(36):16605–14.

[25] Hemmes K. (Towards) Multi-Source Multi-Product and other integrated energy systems. Int J Integrated Energy Syst 2009 Jun 1;1(1):1–15.

[26] Hemmes K, Zachariah-Wolff JL, Geidl M, Andersson G. Towards multi-source multi-product energy systems. Int J Hydrogen Energy 2007;32(10–11):1332–8.

[27] Romero M, Steinfeld A. Concentrating solar thermal power and thermochemical fuels. Energy Environ Sci 2012;5(11):9234–45.

[28] Maag G, Zanganeh G, Steinfeld A. Solar thermal cracking of methane in a particle-flow reactor for the co-production of hydrogen and carbon. Int J Hydrogen Energy 2009;34(18):7676–85.

[29] Meier A, Kirillov VA, Kuvshinov GG, Mogilnykh YI, Weidenkaff A, Steinfeld A. Production of catalytic filamentous carbon by solar thermal decomposition of hydrocarbons. J Phys IV 1999;9(P3):393–8.

[30] Cinti G, Hemmes K. Integration of direct carbon fuel cells with concentrated solar power. Int J Hydrogen Energy 2011;36(16):10198–208.

[31] Jacques WW, inventor; Method of converting potential energy of Carbon into electrical energy. US patent No. 555,511. Patented March 3rd (1896). https://patents.google.com/patent/US555511A/en. (26 jan 2021)

[32] Cooper JF, Selman J. Analysis of the carbon anode in carbon conversion cells. Int J Hydrogen Energy 2014;39(23):12361–8.

[33] Cooper J, Selman J. Kinetics of the carbon anode in molten salt. In: Energy Technology/Battery-Joint Session (General) - 224Th Ecs Meeting, vol. 58; 2014. p. 87–97 (36).

[34] Vayenas CG, Farr RD. Cogeneration of electric energy and nitric oxide. 208th ed. 1980. p. 593–4.

[35] Yentekakis IV, Vayenas CG. Chemical cogeneration in solid electrolyte cells - the oxidation of H_2S to SO_2. J Electrochem Soc 1989;136(4):996–1002.

[36] Neophytides S, Vayenas CG. Chemical cogeneration in solid electrolyte cells - the oxidation of CH_3OH to H_2CO. J Electrochem Soc 1990;137(3):839–45.

[37] Vayenas CG, Bebelis SI, Kyriazis CC. Cogeneration - electricity + chemicals .1. Solid electrolytes. Chemtech 1991;21(7):422–8.

[38] Vayenas CG, Bebelis S. Electrochemical promotion of heterogeneons catalysis. Catal Today 1999;51(3–4):581–94.

[39] Hemmes K, Dijkema GPJ, van der Kooi HJ. From chemical processes to electrochemical processes: the key to minimal entropy production. Russ J Electrochem 2004;40(11):1100–4.

[40] Dijkema GPJ. Fuel cells in the chemical industry. Electrochemical Society Series; 1999 Oct 18. p. 306–21.

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[41] Dijkema GPJ, Grievink J, Weijnen MPC. Functional modelling for a sustainable petrochemical industry. Process Saf Environ Protect 2003;81(B5):331–40.

[42] DOE. Molten carbonate fuel cell product development test. Final report. WASHINGTON: DoE; 1997. Report No.: DOE/MC/28065-1.

[43] Mehrpooya M, Sayyad S, Zonouz MJ. Energy, exergy and sensitivity analyses of a hybrid combined cooling, heating and power (CCHP) plant with molten carbonate fuel cell (MCFC) and Stirling engine. J Clean Prod 2017;148:283–94.

[44] Hemmes K, Patil A, Zachariah JL. Flexible co-production of hydrogen and power using fuel cells. 2004 Nov 1. Vancouver, Canada. 2004.

[45] Hemmes K, Patil A, Woudstra N. Flexible coproduction of hydrogen and power using internal reforming solid oxide fuel cells system. J Fuel Cell Sci Technol 2008;5(4). 041010-1-041010-6.

[46] Hemmes K, Kamp LM, Vernay ABH, de Werk G. A multi-source multi-product internal reforming fuel cell energy system as a stepping stone in the transition towards a more sustainable energy and transport sector. Int J Hydrogen Energy 2011;36(16):10221–7.

[47] DOE EERE. World's first tri-gen energy station-Fountain Valley. 2020. https://www.energy.gov/eere/fuelcells/downloads/tri-generation-success-story-worlds-first-tri-gen-energy-station-fountain.

[48] Hemmes K, Guerrero JM, Zhelev T. Highly efficient distributed generation and high-capacity energy storage. Chem Eng Process 2012;51:18–31.

[49] Hemmes K, Guerrero JM, Zhelev T. Highly efficient distributed generation and high-capacity energy storage [Chem. Eng. Process.: process Intensification 51] (pg 18, Jan, 2012). Chem Eng Process 2013;70:301.

[50] Hemmes K, Barbieri G, Lee YM, Drioli E, de Wit JHW. Process intensification and fuel cells using a Multi-Source Multi-Product approach. Chem Eng Process 2012;51:88–108.

[51] Verzijlbergh RA, De Vries LJ, Dijkema GPJ, Herder PM. Institutional challenges caused by the integration of renewable energy sources in the European electricity sector. Renew Sustain Energy Rev 2017;75:660–7.

[52] De Vries LJ, Verzijlbergh RA. How renewable energy is reshaping Europe's electricity market design. Econ Energy Environ Policy 2018;7(2):31–49.

[53] Maciejowska K. Assessing the impact of renewable energy sources on the electricity price level and variability - a quantile regression approach. Energy Econ 2020;85.

[54] Cinti G, Bidini G, Hemmes K. An experimental investigation of fuel assisted electrolysis as a function of fuel and reactant utilization. Int J Hydrogen Energy 2016;41(28):11857–67.

[55] Coughlin RW, Farooque M. Thermodynamic, kinetic, and mass balance aspects of coal-depolarized water electrolysis. Ind Eng Chem Process Des Dev 1982;21(4):559–64.

[56] Moreno A, McPhail S, Bove R. International status of molten carbonate fuel cell (MCFC) technology. Rome: ENEA, Rome, Italy & Joint Research Centre; 2008 Jan 1. Petten, The Netherlands.

[57] Discepoli G, Cinti G, Desideri U, Penchini D, Proietti S. Carbon capture with molten carbonate fuel cells: experimental tests and fuel cell performance assessment. Int J Greenh Gas Control 2012;9:372–84.

[58] Desideri U, Proietti S, Sdringola P, Cinti G, Curbis F. MCFC-based CO_2 capture system for small scale CHP plants. Int J Hydrogen Energy 2012;37(24):19295–303.

[59] Amorelli A, Wilkinson MB, Bedont P, Capobianco P, Marcenaro B, Parodi F, et al. An experimental investigation into the use of molten carbonate fuel cells to capture CO_2 from gas turbine exhaust gases. Energy 2004;29(9–10):1279–84.

[60] Auricchio R. The integration of high temperature fuel cells with fossil power plants as a topping cycle as well as for carbon capture. MSc thesis Politecnico di Milano. 2011.

[61] Davtyan OK. Bull Acad Sci USSR Class Sci Technol 1949;1:107–14.

[62] Broers GHJ, Ketelaar JAA. High temperature fuel cells. Ind Eng Chem 1960;52(4):303–6.

[63] Makkus RC, Hemmes K, deWit JHW. A comparative-study of Nio(Li), $LiFeO_2$, and $LicoO_2$ porous cathodes for molten-carbonate fuel-cells. J Electrochem Soc 1994;141(12):3429–38.

[64] Bedeaux D, Standaert F, Hemmes K, Kjelstrup S. Optimization of processes by equipartition. J Non-Equilibrium Thermodyn 1999;24(3):242–59.

[65] Hemmes K. Fuel cells. In: White RE, Conway BE, Vayenas CG, editors. Fuel cells; in modern aspects of electrochemistry, vol. 37. New York: Kluwer Academic/Plenum Publishers; 2004. p. 131–251. edn.

[66] Standaert FRAM. Analytical fuel cell modeling and exergy analysis of fuel cells. PhD thesis. Delft The Netherlands: Delft University of Technology; 1998.

[67] Au SF, Woudstra N, Hemmes K. Study of multistage oxidation by flowsheet calculations on a combined heat and power molten carbonate fuel cell plant. J Power Sources 2003;122(1):28–36.

[68] Berkhout AJ, Hartmann D, van der Duin P, Ortt R. Innovating the innovation process. Int J Technol Manag 2006;34(3–4):390–404.

[69] Kroon MC, Hartmann D, Berkhout AJ. Toward a sustainable chemical industry: cyclic innovation applied to ionic liquid-based technology. Ind Eng Chem Res 2008;47(22):8517–25.

[70] Au SF, Peelen WHA, Standaert FRAM, Hemmes K, Uchida I. Verification of analytical fuel cell models by performance testing at a 110 cm^2 molten carbonate fuel cell. J Electrochem Soc 2001;148(10):A1051–7.

[71] Au SF, Woudstra N, Hemmes K, et al. Verification of a simple numerical fuel cell model in a flowsheeting program by performance testing of a 110 cm(2) molten carbonate fuel cell. Energy Convers Manag Aug 2003;44(14):2297–307.