Journal of Applied Electrochemistry (2005) 35:1277–1282
DOI 10.1007/s10800-005-9059-x

Electrical efficiencies of methane fired, high- and low- temperature fuel cell power plants

HARTMUT WENDT
TU Darmstadt, Darmstaedter Str. 65, D-64807 Dieburg, Germany
(e-mail: WendtIng.dieburg@t-online.de)

Received 19 January 2005; accepted in revised form 24 June 2005

Key words: cogeneration, energy efficiency, exergy, fuel cells, reformate, steam reforming

Abstract

The important system difference between power plants based on low temperature and high temperature fuel cells is that gas reforming and shift conversion is thermally decoupled from the cell in low temperature cell power plants whereas the gas process steps are performed at close to the elevated fuel cell temperatures in high temperature fuel cell power plants. This article elucidates the consequences: assuming equal electrical efficiencies for the respective cells (50%) it is shown that thermal decoupling leads to energy and exergy losses and sizably lower electrical system efficiencies because heat for the generation of the process steam necessitates the combustion of methane. Also hydrogen losses in the step for preferential oxidation of carbon monoxide (Selox process) and several heat transfer steps add to the lower efficiency of low temperature systems. Low temperature fuel cell power plants need 15–17% more fuel than high temperature fuel cell power plants for the same amount of electric energy. The theoretical comparison of an adiabatic LT and HT fuel cell process reveals that, with postulated electrical cell efficiencies of 50%, the theoretical electrical efficiency of the LT process is 6–7% points lower than that for the HT-process (35 vs. 41%). For exergy efficiencies also taking into account rejected heats, the numbers read 43 and 58%.

1. Introduction

For a decade fuel cells have been considered a promising innovative and, in principle, most efficient technology for electricity generation. Low temperature (LT) and high temperature (HT) fuel cells can convert only hydrogen directly. This cannot be said of hydrocarbons nor carbon monoxide. Therefore using other fuels like higher hydrocarbons or the lower alcohols as methanol and ethanol (for automobiles) and the more inert methane in the form of natural gas (NG) requires the conversion of these fuels to reformate gas. This gas mixture contains mainly hydrogen after shift conversion and preferential catalytic oxidation of trace amounts of carbon monoxide and one fifth carbon dioxide, some water vapour (and sometimes nitrogen). Therefore the gas process technology for reformate generation is a key technology for introducing fuel cells in the energy conversion business.

DaimlerChrysler demonstrated in 2003 that the technical problems of methanol reforming in cars can be solved but the costs involved are still a big problem for the time being. DaimlerChrysler and – to the knowledge of this author – all other motor companies have therefore ended their PEM-methanol programs. This underlines the importance of the gas process steps for complete fuel cell power plant systems.

It is well known, that Low Temperature FC (LTFC) power plants yield lower electrical efficiencies (30–35%) than high temperature fuel cell (HTFC) power plants (up to 50%). The reasons are the thermodynamics of the two different gas processes and not those of the different cells or their performance.

The principle difference of LTFC and HTFC power plants is the thermal decoupling of the gas process steps from the fuel cell process in LTFC power plants. In high temperature cells, however, the high operating temperature of the cell allows, in principle, to operate the gas process steps at the temperature of the cell. This means to couple the gas process and the fuel cell step thermally. Most frequently publications on gas process technology of fuel cell systems deal with catalysts, Peters [1], and much less on the thermodynamics of the process. In the Handbook of Fuel Cells [2] electrical efficiencies of fuel cells are dealt with but that of methane fired fuel cell power plants are not treated.

In 1979 Selman [3] and colleagues compared theoretically calculated and practically obtained electrical efficiencies of LTFC power plants. They concluded from the lower practical efficiencies, that the thermally decoupled gas process was the reason for energy and exergy losses.

Further work of Rosen [4], Joanides and Neophytides [5], Dovartzides Sontelieris and Tsiakaras [6], dealt with the problem. But none of the papers dealt with the detailed thermodynamics of the gas process steps nor did they compare the process thermodynamics for LTFC and HTFC systems. Only the last paper comes close to the intention of the present paper, although it treats only SOFC power plants.

It will be shown in this article that the thermodynamics of reforming gives HT cells an advantage with respect to LT cells, provided, the electrical efficiency of the cells, their technical reliability, the complexity of the different fuel cell systems and their costs are comparable.

This article does not deal with the electrochemical characteristics of the different types of fuel cells (compare Wendt, [7]). It is, however included in this collection of electrochemical and electrochemical engineering papers because the further fate of fuel cell technologies is to a great deal dependent and determined by chemical engineering and thermodynamic problems of the gas processes involved in FC power plants.

2. Comparing the flow sheets and electrical efficiencies of LT und HT fuel cell power plants

2.1. *The LTFC process*

The following assume adiabatic processes. As a first approximation no heat losses caused by heat transfer into the environment are considered. A second step will try to take account of heat and exergy losses by heat transfer within the process and into the environment.

Figure 1 depicts the flow sheet of a power plant constructed around a PEM-fuel cell. At the inlet natural gas and process steam with an S/C (steam to carbon) ratio of 3 is entering the catalyst bed in the reformer. There the process gas mixture is heated to 950 °C in externally methane – fired counter flow heat exchangers in order to convert in an endothermic reaction methane according to Equation (1) to a gas mixture containing mainly steam, carbon monoxide and hydrogen.

$$CH_4 + 3H_2O \rightarrow CO + 3H_2 + 2H_2O$$
$$\Delta H_{1200K} = +227\text{kJ (mol methane)}^{-1} \qquad (1)$$

(The stoichiometry $3H_2O$ at the left and $2H_2O$ at the right hand side refer to the stoichiometry of the S/C ratio equal to 3).

Two different shift gas reactors operating at two different temperatures, which may also be combined in one counter flow operated reactor vessel serve to perform the exothermic shift reaction (Equation (2))

$$CO + 2H_2O \rightarrow CO_2 + H_2 + H_2O$$
$$\Delta H_{650K} = -37\text{kJ (mol CO)}^{-1} \qquad (2)$$

At 200 °C (or 470 K) in the LT-shift reactor and the assumed S/C ratio of 3 the shift reaction can be performed almost to completion leaving only a rest of approximately 1% of CO unconverted. The respective assumed reaction temperatures are 1200 K for reforming and 650 K for high temperature and 470 K for low temperature shift reaction. The ambient temperature is taken to be 27 °C or 300 K.

The content of carbon monoxide in the reformate gas is still too high for PEM cells. For a cell temperature of PEMFCs of 60 to maximally 80 °C the CO content must be lowered by selective catalytic oxidation (SELOX) below some 10–15 ppm. Since the catalytic CO-combustion is not fully selective but consumes for any mol of oxidised CO 1 mol of hydrogen [8], one has to add oxygen in air in a stoichiometric ratio of 2 (related to 1 mol of CO one needs 1 mol of O_2). The purified reformate gas is then fed into the anode chamber of the cell where approximately 80% of the hydrogen is consumed electrochemically. The residual hydrogen is combusted in the burner of the reformer in order to provide the necessary heat for methane reforming which preserves the enthalpy of the non-combusted hydrogen of the anode exit. The air for the reformer burner is taken from the cathode gas outlet. Its oxygen content is depleted from 20 to 8%. This gas is already preheated to the cell temperature (between 60 and 80 °C). Figure 2 demonstrates the temperature path of the anode gas. The air which is needed for cathodic

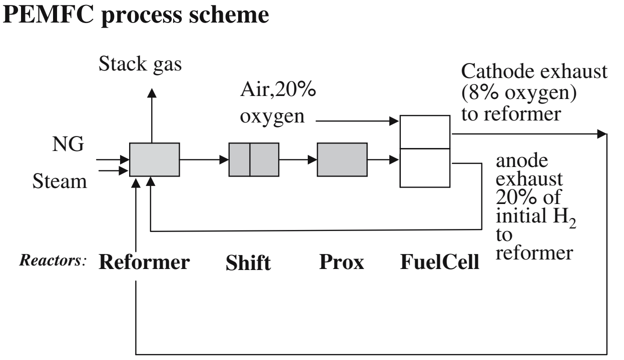

Fig. 1. Power plant process scheme of a typical NG – fired domestic energy supply with PEM – cells. Gas process technology comprises reformer, shift converters, and selective catalytic CO – oxidation (with added air).

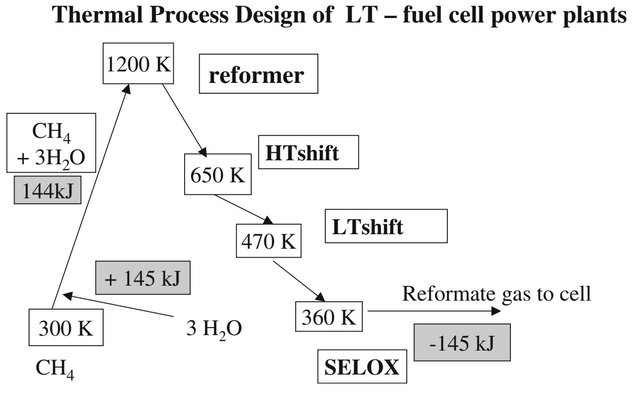

Fig. 2. Thermal process design of LT – fuel cell power plant.

oxygen reduction is heated from ambient temperature to the cell temperature. Heat exchange with the stack gas or internal circulation contributes to remove the waste heat, generated in the cell. Internal heat exchange in the high temperature process provides optimal conservation of heats and exergies (conservation according to first and second law), by heat exchange at lowest possible temperature differences. To give two examples:

The reformate leaves the reformer, with the target temperature of 1200 K. Its heat content is used to preheat the fresh process gas (the mixture of one part of methane and three parts of steam) in a counter current heat exchanger. Also the heat released by shift conversion is used for preheating the process gas. The heat balance in Table 1 is a simplified energy scheme of a LTFC process comprising the gas process technology and electricity generation for a LTFC power plant. Without any detailed consideration concerning the current voltage curve of the cell, the electrochemical process is assumed to proceed with a postulated energy efficiency of 50% with respect to the input heat of combustion of methane which amounts to −802 kJ (mol of methane)$^{-1}$.

The data are collected by joint evaluation of Janaf Tables, [9], and Barin and Knacke [10] and rounded to integer values of the different heat contributions. As already stated above the balance refers to the input of 1 mol of methane with a lower heating value of −802 kJ. The process steps correspond to data published in the internet by companies which develop domestic cogenerating (PEM) LTFC power plants [11, 12].

There are 14 different process steps, 12 of which are not connected to the electrochemical process but to physical heat inputs or outputs, to and from parts of the process gases. Only two contributions stem from electrochemical energy conversion in the cell: one is the electricity generation, the other the release of Joule heat in the cell (both assumed to be −400 kJ or approximately 50% of the input). All energy contributions are summing up to −802 kJ – the lower heating value of 1 mol methane, which equals the methane input.

Table 1. Heat balance of LT fuel cell power plant – first law balance for a fuel cell power plant with postulated 50% electric cell efficiency

Process step	Enthalpy change/ kJ per mol CH_4
01. 1 mol methane 27 → 127 °C	3
02. 3 mol H_2O 27 → 127 °C and steam generation	145
03. 3 mol 2 of H_2O(steam) and 1 mol CH_4 927 °C	162
04. Reforming	227
05. Cooling of reformate gas 927 → 427 °C	−102
06. HT steam shifting step	−37
07. Cooling of shift reacted gas to 327 °C and endshifting	0
08. Downcooling to 100 °C	−25
09. Electricity generation by cell reation	−400
10. Heat generation by cell reaction	−400
11. Heating of anode off-gas and air to 927 °C	136
12. Burning of off-gas in reformer	−227
13. Cooling of reformer stack gas to 100 ° C	−140
14. Condensing 3 mols of water from stack gas	−145

Therefore according to the first law, heat inputs equal heat outputs. But according to the second law this does not hold true. The flow sheet and the respective temperature niveaus show, that the HT heat with temperatures above 100 °C which is needed to produce 3 mols of process steam cannot be accounted for from internal heat sources.

Most important for our considerations and the comparison of LTFC and HTFC power plants is that with rejected heat of lower than 100 °C water can never be vaporized under ambient pressure.

To supply the process steam, additional heat of approximately 145 kJ must be added by combustion of methane. Therefore the readjusted process balance now needs an input of methane with an equivalent of 947 kJ instead of the initially assumed 802 kJ. This decreases the electrical efficiency from 50% to 42.3% – a difference of 7.7%. By selective oxidation of CO at least another percent point of electrical efficiency is lost due to cooxidation of hydrogen (result: approx. 41%), [8].

2.2. *The HT process*

MCFCs as well as SOFCs are the two established HT technologies for fuel cell power plants. Both technologies need NG or methane reforming – or at least prereforming as a step preceding the cell – though from different reasons. NG-reforming in SOFCs on the nickel anode at approx. 950 °C is too fast and would lead to local cooling of the cell due to heat consumption by the fast reforming reaction at its inlet.

At the cell temperature of 650 °C this reaction is too slow in MCFCs because of the relatively low cell temperature. In both HT – cells the larger part of the reforming reaction still proceeds in the cell. Considering both cell types from the thermodynamic point of view, they are comparable in so far, as in both cases, the gas process technology of prereforming and reforming are not thermally decoupled from the HT-cell. The chemical reactions proceed close to the working temperature of the cell, for instance in the fuel cell housing, where there is easy access to high temperature heat. In the following we will refer to the process scheme of the HOT MODULE of MTU because its details are relatively well known and documented by MTU, cfc-solutions [13].

Figure 3 demonstrates the temperature profile and Figure 4 the general design of the HOT MODULE whose particular properties are:

(a) direct cooling of the cell and simultaneous heating of the process air by direct heat exchange, by mixing the recirculated cathode gas together with the anode off gas with fresh, cold air.

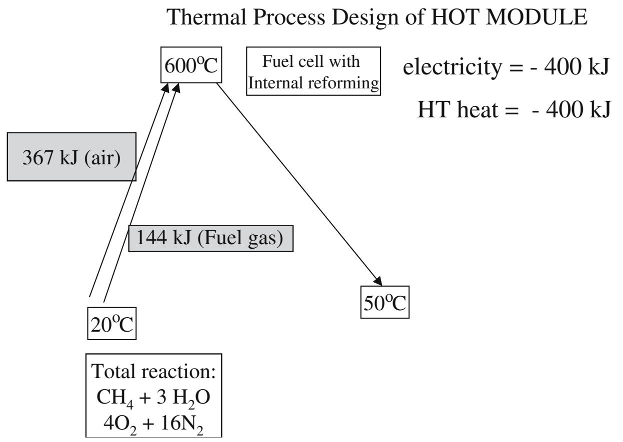

Fig. 3. Power plant process scheme for the HOT MODULE or any other HT – fuel cell power plant. Catalytic steps like reforming or prereforming and shift reaction are incorporated in the Hot box or the respective reactor is the cell proper – as for the shift reaction.

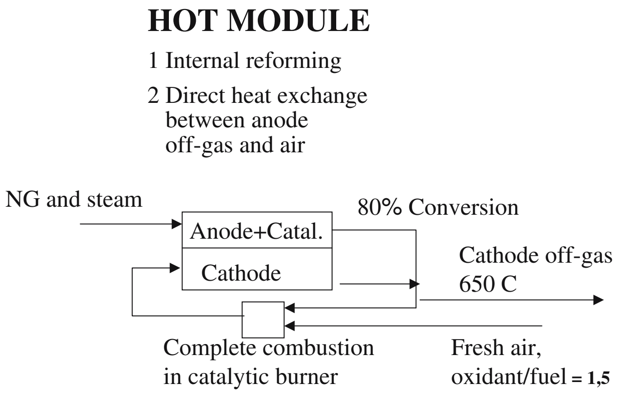

Fig. 4. Schematic of the HOT MODULE power plant of cfc-solutions MTU – technology. A cylindrical hot box of 2.5 m diameter and 3.5 m length houses the cell stack, heat exchanger for prereforming and the catalytic end – combustion. Reforming is performed in reformer boxes which are intercalated in the fuel cell stack. End – reforming and shift reaction is performed within the anode compartment of the cell.

(b) Mixing the anode off gas (which already contains CO_2 together with 20% non-combusted hydrogen and methane) with fresh air produces *in-situ* the cathode gas and, by completing the combustion, develops heat together with additional carbon dioxide. Carbon dioxide is needed at the cathode for O_2 reduction.

(c) Pre-reforming in the immediate vicinity of the cell. i.e. in the heat insulated HT-box containing the cell, facilitates the access of HT heat from the hot cell to the process gas.

(d) Rejection of almost all off-heats in the form of HT-heat of more than 100 °C provides thermal energy of sufficiently high temperature to produce the process steam. Only the final condensation of steam (−122 kJ) from the stack gas delivers low temperature heat.

(e) Water gas shift reactors are avoided because the catalytic exothermic shift reaction takes place in the anode chamber of the cell stack parallel to reforming and anodic conversion of hydrogen. It is catalysed by the catalytically active nickel anode.

The heat balance in Table 2 consists of only 8 steps. Most important is that in excess to the demand of high temperature heats for steps 01, 02 and 05 an excess of 214 kJ of high temperature heat is still available. That is more than one quarter of the primary energy. It can be exported to supply process heat for external processes or may be converted into electricity by a gas turbine process or a steam process. This yields under optimal conditions additionally 10% of the primary energy supply as electricity.

Without external heat losses the electrical efficiency is therefore in this first approach the same as initially assumed: 50% for the cell.

In industrial practice the efficiency of the HOT MODULE cell is 55%, but the effective efficiency is 50% because of the internal consumption of electrical power by blowers and auxiliaries and also due to heat losses to the environment.

3. Exergy losses

Heat transfer by heat exchangers produces exergy losses, which depend linearly on ΔT, the driving temperature difference for the heat transfer, and $T_h + \Delta T/2$ where T_h is the highest temperature of the heated process stream. Only isothermal electrochemical reactions coupled to direct heat exchange by mixing does not produce exergy losses. This latter principle is advantageously used in the HOT MODULE. For details see the appendix of this paper.

For all physical heating and cooling processes, which can be appropriately paired in the power plant processes and which are mediated by heat exchangers ΔT is taken to be 50 °C and for the reforming process 100°. The

Table 2. Heat balance of the HT Fuel cell power plant – first and second law balance for a cell with 50% efficiency producing 400 kJ electricity from 1 mol of methane

Process step	Heat/kJ per mol CH_4
01. [a]3 mol H_2O to 60–127 °C and steam production at 127 °C	122
02. 1 mol CH_4 and 3 mol steam to 650 °C	129
03. Electricity generation 50%	−400
04. HT – heat gen. in-cell and by combustion	−400
05. Heating combust. air, oxygen to fuel = 1.5 to 650 °C	288
06. Cooling of hot off-gases to 150 °C	−353
07. Cooling from 150 to 50 °C	−65
08. Condensing 3 mols of water	−122

[a] Only vaporisation, because hot condensate is vaporised.

vaporization is performed at 127 °C with ΔT equal to 27 °C. For all exergy calculations T_1, the lower temperature of the Carnot factor, is 27 °C. Four parts determine the exergy losses of LT process:

24 kJ for steam generation (heat transfer)
23 kJ for reforming (chemical reaction)
3.5 kJ for shift conversion (heat transfer)
15 kJ for paired heating and cooling (heat transfer)

The sum gives exergy losses losses of 65.5 kJ per mol of methane.

For the HT-process we have only 3 factors:

24 kJ from steam generation
11 kJ from heating/cooling 150–650 °C
5 kJ from heating/cooling below 150 °C

Summing up gives an accumulated exergy loss of 40 kJ (mol of methane). Obviously these exergy losses have to be accounted for by increased inputs of methane.

The lower heating values of the methane input for the LTFC power plant process sums up to (802 + 145 + 16 + 65.5) kJ yielding an electrical efficiency of approx. 39%. Accounting for all exergy losses of the HTFC power plant process, one would need a primary energy input of (802 + 40) kJ with an electrical efficiency of 47.5%. These considerations show from the thermodynamic point of view that the HT process is at a clear advantage because the efficiency for idealized adiabatic processes would be by 8% better for the HTFC than for the LTFC process at an assumed equal cell efficiency of 50%.

4. Real heat losses into the environment due to heat transfer from the hot parts of the process

By and large heat losses from the high temperature part of a LTFC power plants are comparable with those of HT fuel cell power plants. However, for the HTFC technologies SOFC and MCFC we have mainly information on 100 kW class power plants (see MTU cfc Solutions [13] and Siemens-Westinghouse [14]. For PEM based LTFC power plants rough data are only known for domestic heating units of the 3–5 kW class, for instance of Vaillant [11] or Viessmann, [12]. The size of HTFC and LTFC power plants are not comparable as the smaller units have a significantly higher surface to volume ratio, which at a power ratio of 50–100 is estimated to differ by just that ratio. So that they tend to have relatively higher heat losses than the bigger 100 kW class power plants. Better heat insulation for the smaller low temperature fuel cell power plants accounts for this difference in order to keep heat losses at bay.

For the HOT MODULE with a thermal input power of 500 kW (total) heat losses amount to 25 kW, i.e. 5% of the input power. For domestic fuel cell systems the losses are said (not published) to approach 10%.

Taking these differences into account, we calculate from the efficiencies above effective efficiencies of between 35 and 36% for LTFC- and 41–42% for HTFC-power plants. This result is summarized in Table 3, which collects the sum of the energies and exergies of all media entering and leaving the two different fuel cell power plants.

Table 3. Exergy efficiencies in LT and HT fuel cell power plants

	LT – process (3 to 5 kW el.)	HT – process (100 kW el.)
Lower heating value needed/kJ[a]	1029	922
Corrected for external losses/kJ	1131	968
Exergy content of fuel /kJ	1090	932
Amount of methane /mol	1.4	1.2
Electricity /kJ	400	400
Energy efficiency	35.40%	41.30%
Exergetic yield of electricity	36.50%	43.00%
Excess exit heat at 400 °C /kJ	0	214
Exergy attributed to 400 °C – heat	0	123
Exergetic yield of HT – heat	0	14%
Exit heat at 60 °C /kJ	560	71
Exergy of off heat at 60 °C /kJ	61	7.8
Exergetic yield of LT heat	6%	1%

[a] Minimum heat needed as lower combustion heat of methane to produce 400 kJ electricity.

5. Comparing exergy – efficiencies for LT- and HT-fuel cell power plants

The exergy of methane (free energy of the reaction $CH_4 + 2O_2 \rightarrow CO_2 + H_2O$) amounts to – 773 kJ (mol of methane)$^{-1}$ and is the reference for exergy efficiency calculations. The data of Table 3 refer to the production of 400 kJ of electricity which initially were attributed to the conversion of 1 mol of methane. The assumption in Table 3 concerning T_1, the environmental temperature, for exergy – calculations is 27 °C or 300 K.

The result of the data of Table 3 is clear: including the exergies of the different heats in the efficiency calculations LTFC power plants have a total exergy efficiency of roughly 43% whereas the exergetic efficiencies of HT cell power plants comes close to 58%. This is most convincing evidence for the advantages of HT over LT-fuel cell power plants.

6. Conclusions

HTFC power plants are shown to have sizably higher system efficiency as they make better use of the exergy content of the fuel by coupling electrochemistry and gas process technology thermally. In these considerations which deal with adiabatic LTFC and HTFC power plant processes, empirical data only were used, when the thermal losses of large HT and small LT-power plants were estimated and compared.

Therefore the results are indicative of fundamental differences and should be taken seriously. It is still too early to base a reliable prediction concerning the viability of the respective FC technology on these results. But in the long term this difference between LTFC and HTFC technologies is expected to bear upon their respective commercial progress and success. Also the simpler process design is an economic advantage.

Of the different types of fuel cells in the field of stationary cogenerating electricity generation, HT-cells – in contrast to LT-cells – have a heat to electricity ratio, which is rather 1:3 than the conventional 3:1 ratio. Only for domestic cogeneration does the ratio 3:1 come close to the existing demand. For all other cases a relatively higher amount of electricity is an additional commercial advantage, as making use of high temperature heat is less problematic the lower the amount of heat.

There exists one clear disadvantage: HT fuel cells demand continuous rather than discontinuous or variable load as they cannot sustain temperature shock or rapid cooling and heating. This, however, is not necessarily a drawback as HT-fuel cells can serve under base load conditions.

Appendix

Exergies and exergy losses

The definition of the exergy of heat Q is $\mathrm{Ex}(Q)=Q(T-T_{\mathrm{env}})/T$, T the actual, and T_{env} the environmental temperature.

(a) Exergy for isothermal processes as vaporiztion consuming heat Q at driving steady temperature difference ΔT:

$$\Delta \mathrm{Ex} = QT_{\mathrm{env}}\Delta T/(T_1 T_2)$$
$$T_1 - T_2 = \Delta T$$

(b) For heating a process stream in counter current heat exchange from T_1 to T_2 by exchanging the total heat Q under the constant temperature difference ΔT

$$\Delta \mathrm{Ex} = Q\Delta T(T_1^{-1} - T_2^{-1})$$

(this is a simplified solution for $T_2 - T_1 >> \Delta T$, for instance $T_2 - T_1 = 400$ K and $\Delta T = 50$ K).

References

1. R. Peters and J. Meissner, *Chem. Ing. Technik*. **76** (2004) 1555.
2. W. Vielstich, A. Lamm and H. Gasteiger, *Handbook for Fuel Cells, (4 Volumes)* (John Wiley and Sons, Heidelberg, New York, 2003).
3. T.G. Benjamin, E.H. Camera and J.R. Selman, *Proc. Intersoc. Energy Conversion Conf*. 14th, **1** (1979) 579.
4. M.A. Rosen, *Int. J. Hydrogen Energy* **15** (1990) 267.
5. T. Joannides and S. Neophytides, *J. Power Sources* **91** (2000) 150.
6. S.L. Dovartzides, F.A. Contelieris and P.A. Tsiakaras, *Int. J. Exergy* **1** (2004) 179.
7. H. Wendt and G. Kreysa, *Fuel Cells in Electrochemical Engineering, Science and Technology* (Springer, Berlin, Heidelberg, New York, 1999), pp. 386.
8. M.M. Schubert, V. Plzak, J. Garche and J.R. Behm, *Catal. Lett.* **76** (2001) 143.
9. Janaf Thermochemical Tables, D.R. Stull and H. Prophet editors. NSRDS – NBS 37 Nat. Stand. Ref. Data Series Nat Bur. Stand 37, June 1971.
10. I. Barin and O. Knacke, *Thermodynamic Properties of Inorganic Substances* (Springer Verlag, Berlin Heidelberg, New York, 1973).
11. www.vaillant.com.
12. www.viessmann.de.
13. http://www.mtu-cfc.com, Hot Module HM 300, data sheet, Das Brennstoffzellensystem Hot Module: Biogas und Sekundärgas – Anwendungen.
14. www.siemenswestinghouse.com.