Thermodynamic analysis of direct internal reforming of methane and butane in proton and oxygen conducting fuel cells

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ABSTRACT

We present results of a thermodynamic analysis of direct internal reforming fuel cells, based on either a proton conducting fuel cell (FC-H$^+$) or an oxygen ion conducting fuel cell (FC-O^{2-}). We analyze the option of methane as fuel as well as butane. The model self-consistently combines all chemical equilibria in both the anode and cathode compartments with the proton or oxygen transfer rates through the membrane without predefining fuel utilization.

The highest efficiency for generating electricity is obtained in a FC-H$^+$ at a steam-to-carbon (SCR) ratio of around 2.5. In this case, the efficiency is 88% at 600 °C and 1 bar and increases when the temperature is decreased, or pressure increased. For an FC-O^{2-} the highest efficiency is obtained when no steam is added, and is always several %-points lower than for the FC-H$^+$. Important is that at the optimum SCR, coke formation is thermodynamically predicted not to occur in a FC-H$^+$, irrespective of the rate of proton transfer through the membrane, down to operating temperatures of 500 °C, both for methane and for butane as fuel. Likewise, in an FC-O^{2-} coke formation is thermodynamically not predicted to occur at the optimum oxygen ion transport rate (that is required for the highest efficiency). However, when the oxygen ion transport rate decreases, both for methane and for butane as fuel, we at some point enter the coke-forming regime. Thus, for direct internal reforming of methane or butane, we argue on thermodynamic grounds that a proton conducting fuel cell can be advantageous over an oxygen ion conducting fuel cell with respect to fuel cell efficiency and risk of coke formation.

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1. Introduction

Direct internal reforming of hydrocarbon fuels in (high temperature) fuel cells offers the possibility to generate electricity at a high efficiency [1–11]. Another advantage is that the anode off-gas is not diluted with nitrogen and thus, after condensing out the water, a pure stream of CO_2 is obtained. Because of its purity the CO_2 can be stored at relatively low costs, e.g., in geological formations or by mineral carbonation, without requiring an expensive CO_2/N_2-separation. Therefore electricity production using fuel cells opens up the possibility to use fossil fuels without releasing CO_2 into the atmosphere [12].

In this manuscript we will thermodynamically analyse both proton conducting fuel cells (FC-H$^+$) and oxygen ion conducting fuel cells (FC-O^{2-}), using either methane as fuel, or butane. In all cases air flows through the cathode compartment while gaseous fuel (premixed with steam) is fed to the anode compartment. In both compartments we assume that thermodynamic equilibrium will be reached and that compositions are constant throughout (ideal stirred tank behavior). An important element is that the transport of hydrogen or oxygen through the membrane feeds back into the equilibrium calculations in each compartment. Special attention will be given to fuel efficiency and the boundary of coke formation.

2. Theory

In this section a semi-analytical model is presented for a proton-conducting (high-temperature) fuel cell combined with internal reforming of methane in the anode compartment. Further on we

will discuss the modifications required when butane is used as fuel and/or when an FC-O^{2-} is considered. We assume that the entire fuel cell is isothermal, i.e., that heat transport from one compartment to the other is fast.

2.1. Fuel cell operation

We assume that in each compartment the gas phase mixture is at chemical equilibrium. Thus at the anode side, the methane steam-reforming (MSR) reaction as well as the water–gas-shift (WGS) reaction are both assumed to be at equilibrium, while at the cathode side the combustion of hydrogen with oxygen is at equilibrium. For a given kinetic rate for the gas phase reactions, this requirement can always be approached by increasing the gas phase residence time, for instance by reducing the flow rates into the anode and cathode compartments.

With respect to the transport of hydrogen from anode to cathode (in the FC-H$^+$), or oxygen from cathode to anode (in the FC-O^{2-}), we assume that the overall (or, membrane) transport rate is limited by the transport rate for electrons through the external circuit (by using a high resistance for electron flow, R_{ext}), or by Ohmic transport for protons (or, oxygen ions) through the electrolyte membrane (by using a high Ohmic electrolyte resistance, R_{ohm}), or by a combination of both. Mass transport from the gas phase bulk toward the electrodes, absorption/desorption on the electrodes, surface diffusion and electrochemical reactions are all assumed to be fast compared to these mass transport rates.

In that case, the generated electrical voltage, E, is given by [14,15]:

$$E = E^{oc} - iR_{ohm} \tag{1}$$

where the electrical current i is equal to $i = E/R_{ext}$, and the open circuit voltage E^{oc} is given by:

$$E^{oc} = \frac{RT}{2F} \ln \frac{p_{A,H_2}}{p_{C,H_2}} \tag{2}$$

where R, T and F have their usual meaning, where 'A' and 'C' refer to the anode and cathode compartments, and where the partial pressures are denoted by p and are expressed in units of the standard pressure of $P^* = 1$ bar. Combining Eqs. (1) and (2) results in:

$$E = \frac{RT}{2F} \cdot \frac{R_{ext}}{R_{ohm} + R_{ext}} \ln \frac{p_{A,H_2}}{p_{C,H_2}} \tag{3}$$

The current i is given after dividing E with R_{ext}, and the effective hydrogen molar flow through the membrane $\Phi_{H_2,mem}$ equals half the current i divided by F. Note that $\Phi_{H_2,mem}$ represents an effective flow of hydrogen molecules from the anode compartment to the cathode compartment, which in reality is accomplished via the simultaneous transport of electrons through the external circuit, and protons through the electrolyte phase. The electric power, P, that is generated in the fuel cell is given by $P = iE$.

From this point onward we assume that $R_{ohm} \ll R_{ext}$, thus $E = E^{oc}$. Thus we will describe an ideal fuel cell in which the generated voltage is not reduced by limitations due to (electro-)chemical reactions, hydrogen concentration gradients in the gas phase near the electrodes, or the proton transport through the membrane. Instead, the fuel cell voltage E is assumed to be only a function of the equilibrium gas phase hydrogen pressures in each compartment.

It must be remarked that though the ideal, open-circuit, voltage as given by Eq. (2) is not directly influenced by the exact value of R_{ext} (as long as it is high compared to the other membrane resistances), it is because we will consider situations where the membrane transport of hydrogen (or, oxygen) is not negligible compared to the flow rates into the anode and cathode compartments, that there is an indirect influence of R_{ext} via the relation $i = E^{oc}/R_{ext}$

and the mass balances, Eqs. (11) and (12) to be discussed below, on $p_{H_2,A}$ and $p_{H_2,C}$ and thus on E^{oc}. These effects are self-consistently considered in our model.

2.2. Oxygen-conducting fuel cell

To describe an FC-O^{2-}, we only need to replace Eq. (2) by:

$$E^{oc} = \frac{RT}{4F} \ln \frac{p_{C,O_2}}{p_{A,O_2}} \tag{4}$$

and realise that the effective molecular oxygen flow from anode to cathode, $\Phi_{O_2,mem}$ is one-fourth of the current i/F.

2.3. Thermodynamics

In the anode compartment methane steam reforming and the water–gas-shift reaction take place, and we assume that both are at chemical equilibrium. Thus:

$$K_{MSR} = \frac{p_{A,CO}p_{A,H_2}^3}{p_{A,CH_4}p_{A,H_2O}}, \quad K_{WGS} = \frac{p_{A,CO_2}p_{A,H_2}}{p_{A,CO}p_{A,H_2O}} \tag{5}$$

where $\ln K_i = -\Delta G_i^0/RT$ and

$$\Delta G_{MSR}^0 = 218422 - 246.16\,T, \quad \Delta G_{WGS}^0 = -36284 + 33.065\,T \tag{6}$$

These expressions for the standard state Gibbs energy of the respective reactions ΔG_i^0 (in J mol^{-1}) (and those presented further on) are based on the more complicated expressions for G_i^0 for each component, given as function of temperature in Ref. [16]. (The relations presented here for ΔG_i^0 and K_i are in close agreement with results obtained from the thermodynamic software "Gaseq 0.62".)

In the cathode compartment, hydrogen combusts with oxygen to gaseous water, described by:

$$K_{comb} = \frac{p_{C,H_2O}}{p_{C,H_2}\sqrt{p_{C,O_2}}} \tag{7}$$

where

$$\Delta G_{comb}^0 = -RT \ln K_{comb} = -245643 + 53.012\,T \tag{8}$$

2.4. Mass balances

We fix the total pressure in each compartment, P_i, thus:

$$P_A = p_{A,CO_2} + p_{A,H_2} + p_{A,CH_4} + p_{A,H_2O} + p_{A,CO},$$
$$P_C = p_{C,H_2O} + p_{C,H_2} + p_{C,O_2} + p_{C,N_2} \tag{9}$$

We assume that each compartment, i, has ideal-stirred-tank behavior, thus for each species, j, the ratio of partial pressure, $p_{i,j}$, to total pressure, P_i, equals the ratio of molar exit flow of component j, $\Phi_{i,j}^{out}$ to the total molar outflow, $\Phi_{i,tot}^{out}$:

$$\frac{\Phi_{i,j}^{out}}{\Phi_{i,tot}^{out}} = \frac{p_{i,j}}{P_i} \tag{10}$$

The molar outflows, $\Phi_{i,j}^{out}$, follow from atomic balances for each compartment. For the anode compartment this results in (balances for C, H and O)

$$\Phi_{A,CH_4}^{in} = \Phi_{A,CH_4}^{out} + \Phi_{A,CO_2}^{out} + \Phi_{A,CO}^{out}$$
$$2\Phi_{A,CH_4}^{in} + \Phi_{A,H_2O}^{in} = 2\Phi_{A,CH_4}^{out} + \Phi_{A,H_2O}^{out} + \Phi_{A,H_2}^{out} + \Phi_{H_2,mem} \tag{11}$$
$$\Phi_{A,H_2O}^{in} = \Phi_{A,H_2O}^{out} + 2\Phi_{A,CO_2}^{out} + \Phi_{A,CO}^{out}$$

and for the cathode compartment (balances for H, O and N):

$$\Phi_{H_2,mem} = \Phi^{out}_{C,H_2O} + \Phi^{out}_{C,H_2}, \qquad 2\Phi^{in}_{C,O_2} = \Phi^{out}_{C,H_2O} + 2\Phi^{out}_{C,O_2},$$

$$\Phi^{in}_{C,N_2} = \Phi^{out}_{C,N_2} \tag{12}$$

2.5. Modifications for butane as fuel and/or oxygen ion conducting fuel cell

When butane is fed to the fuel cell, we will assume full butane conversion (which for thermodynamic equilibrium is correct) and only need to make the following modifications, namely that in Eq. (11) we replace the first term by $\Phi_{inA,CH2.5}$ and in Eq. (11) the first term by $1.25\,\Phi^{in}_{A,CH2.5}$.

When we consider an FC-O^{2-}, the following modifications are required: a partial pressure of oxygen, p_{A,O_2} is added to Eq. (9)a, and p_{C,H_2O} and p_{C,H_2} are removed from Eq. (9)b; $\phi_{H_2,mem}$ is set to zero in Eqs. (11) and (12), while on the left-hand side of Eq. (11)c a term $2\phi_{O_2,mem}$ is added. Eq. (12)a is removed, while in Eq. (12)b Φ^{out}_{C,H_2O} is replaced by $2\phi_{O_2,mem}$; finally, we evaluate Eq. (7) in the anode compartment, and no longer in the cathode compartment.

2.6. Enthalpy balance

An overall fuel cell enthalpy balance is given by (Ref. [17], Eq. 3.56)

$$\sum \Phi^{in}_{i,j} H_j(T_{in}) = \sum \Phi^{out}_{i,j} H_j(T_{out}) + P + L \tag{13}$$

where i describes both the anode and cathode flows, and j runs over all molecular species. The generated power is P and heat losses are described by L. When the fuel cell is part of a system in which hydrogen, CO, and hydrocarbons are post-combusted, and which also includes heat exchange equipment, an enthalpy balance over this system can be set up which is given by:

$$\Phi^{in}_{A,CH_x} \cdot LHV = P + L \tag{14}$$

where LHV is the lower heating value of the fuel ($x = 4$ for methane; $x = 2.5$ for butane), which is the enthalpy that is released when the fuel is combusted with oxygen into gaseous water and carbon dioxide at 25 °C. Eq. (14) assumes that all feed and exit gases of the entire system are at 25 °C. The fuel cell system electrical efficiency can then be defined as:

$$\eta = \frac{P}{\Phi^{in}_{A,CH_x} LHV_{CH_x}} 100\% \tag{15}$$

For methane, $LHV_{CH4} = 803\,kJ\,mol^{-1}$, while for butane, $LHV_{CH2.5} = 663\,kJ\,mol^{-1}$ C-atoms (thus, the LHV per mole of butane is four times larger). Note that Eq. (15) differs from the definition of efficiency used in Ref. [8] where it is assumed that no fuel, CO or hydrogen leaves the anode compartment as off-gas. Finally, note that the efficiency in Eq. (15) is based on the lower heating value of the fuel, and can be modified to define efficiency with respect to the higher heating value (for methane as fuel, $HHV = 890\,kJ\,mol^{-1}$, and thus all values for η must be multiplied by 0.9) [18].

The enthalpy balance considers the full system consisting of heat-exchangers, fuel cell, and post-combustion (to convert CO and CH_4 remaining in the anode exhaust), and assumes incoming and outgoing gases to be at 25 °C and the water in the liquid state. As long as the calculated efficiency η is below 100%, the theoretical fuel cell-temperature can always be reached, with excess heat being produced in the system. This excess heat is lost either by venting the exhaust gases at temperatures above 25 °C, or because the

vented water is partially in the gaseous form, or because heat is lost otherwise (because of non-perfect isolation).

2.7. Coke formation

After solving the semi-analytical model we can check for coke formation in the anode compartment. As long as some coke (carbon, graphite) is present, equilibrium predicts that the gas phase concentrations of CO and CO_2 are related according to:

$$K_{CF} = \frac{p_{CO_2}}{p^2_{CO}} P^* \tag{16}$$

where

$$-RT \ln K_{CF} = \Delta G^0_{CF} = -171963 + 176.73\,T \tag{17}$$

As long as the right-hand side of Eq. (16) is larger than K_{CF}, coke formation will not occur. We can combine Eqs. (16) and (17) to derive the minimum temperature above which thermodynamics predicts that coke is not formed, given by:

$$T^{min} = 171963 / \left(176.73 + R \ln \left(\frac{p_{CO_2}}{p^2_{CO}} P^* \right) \right) \tag{18}$$

Eq. (18) can be used from 300 to 1300 K with a maximum error ~0.5%. Eq. (18) significantly extends a similar equation in Ref. [16] which can only be used above $T = 900\,K$. Note that even though Eqs. (16)–(18) are based on the Boudouard reaction only, for thermodynamic equilibrium this fully suffices to describe the thermodynamics of coke formation, as also noted in Ref. [4]. It would be equivalent to select another reaction leading to coke formation (between the molecules that are considered) because it will give the same prediction for T^{min}.

3. Results and discussion

In this section we first present calculation results for a proton-conducting fuel cell in which methane steam reforming occurs in the anode compartment, while air is fed to the cathode side (21% O_2 and 79% N_2). The overall pressure is set to $P_A = P_C = 1$ bar. The steam-to-methane ratio (SMR) is the molar ratio of H_2O-molecules to CH_4-molecules fed to the anode compartment, while the oxygen-to-methane ratio, O2MR, is the ratio of the molar flow of oxygen, O_2, fed to the cathode compartment, to the methane flow fed to the anode.

The calculation results will be presented in dependence of the dimensionless external resistance (or, 'load') R_{ext} which can be varied from zero (shorted circuit) to infinity (open circuit). The presented values for R_{ext} are dimensionless, and can be multiplied by RT/F^2 and divided by the molar fuel flow Φ^{in}_{A,CH_x} (in mol s^{-1}) to obtain the external resistance in Ω. We will not fix the fuel utilization, but calculate the fuel conversion self-consistently. In the calculation the transport of hydrogen (or, oxygen) from anode to cathode (or vice versa) is self-consistently calculated, and feeds back into all the chemical equilibria, including coke formation. Therefore, it is possible that the value of R_{ext} influences the coke formation limit, as will be discussed.

Fig. 1 shows for internal reforming of methane in a proton-conducting fuel cell the influence of the SMR and O2MR on the fuel efficiency, η. Fig. 1a shows that an optimum value exists for the SMR of SMR$_{opt}$ = 2.5, a value which is close to the value given by Demin et al. (Ref. [7]; SMR$_{opt}$ = 2.6). Below the optimum value for SMR, some methane remains unconverted, while at higher SMR the steam dilutes the hydrogen and thus reduces the partial pressure p_{H_2} and thus the electrical power P. In Fig. 1a at SMR = 1 a sharp transition can be observed which relates to the fact that up
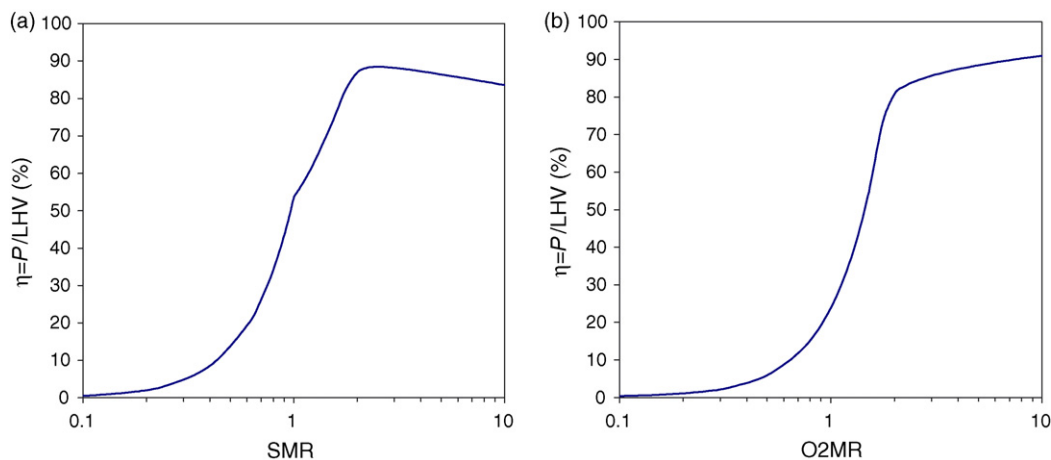
Fig. 1. Influence of SMR and O2MR on fuel cell efficiency in a proton-conducting fuel cell running on methane ($T = 600\,°C$, $R_{ext} = 1.65$). (a). O2MR = 5. (b) SMR = 2.5.

to SMR = 1 we have (based on pure stoichiometry) always some methane unconverted, a restriction which is removed from SMR = 1 onwards. With increasing O2MR, the electrical efficiency η continuously increases. However, above O2MR∼5 the effect of further increasing O2MR becomes small. At low O2MR the strong influence of O2MR on η is due to the fact that in the cathode compartment the hydrogen conversion is not very high and thus the hydrogen partial pressure is not yet very low. Above O2MR∼5, the hydrogen conversion in the cathode compartment is very high, and the effect of further increasing O2MR is mainly to dilute the cathode flow. At O2MR = 5 (SMR = 2.5, $R_{ext} = 1.65$, $T = 600\,°C$) the oxygen utilization in the anode compartment is 38.5%.

Based on optimized values for SMR and O2MR, Fig. 2a is constructed which shows the influence of the external load R_{ext} and temperature on fuel efficiency η. Interestingly, there is a very strong dependence on R_{ext}, with a very sharp maximum in electrical efficiency, η, for a certain value of R_{ext}.

How can we explain the strong influence of R_{ext} on η? In the case of $R_{ext} > R_{ext}^{opt}$ the hydrogen flow through the membrane is increasingly restricted, and significant amounts of hydrogen and CO leave with the anode exit gases. As an example, at the optimum value of R_{ext}, for each H_2 molecule that leaves the anode compartment in the off-gases, ∼42 molecules (>84 protons) diffuse through the fuel cell membrane, thus the hydrogen loss is only ∼2.5% ($T = 600\,°C$) (the CO slip from the anode compartment is ∼half of the hydrogen slip, while methane slip is almost zero, < 50 ppm unconverted). With increasing R_{ext}, the hydrogen (and CO) loss through the anode off-gas increases dramatically.

For $R_{ext} < R_{ext}^{opt}$ the electric power decreases because the generated voltage E starts to go down significantly. And that is because the hydrogen partial pressure in the anode compartment starts to decrease. As an example, we already have a >4.5 point decrease in $\ln p_{A,H_2}$ when R_{ext} decreases rather slightly from 1.6 to 1.3, which results in a generated voltage of 0.78 V instead of 0.96 V. The reason for the decrease in hydrogen partial pressure at lower R_{ext} is a depletion effect, namely it is directly due to the increased hydrogen flow through the membrane at the lower R_{ext}.

The influence of temperature on the efficiency at the optimum R_{ext} is similar to that predicted by Demin et al. (Ref. [7]) who also predict a decrease in efficiency of ∼15% upon increasing the temperature by 400 °C.

For the FC-O^{2-} a similar calculation was made as in Fig. 1 for methane as fuel, by varying SMR and O2MR at the optimum R_{ext}-value of 1.55. The maximum efficiency is obtained for SMR = 0

($\eta = 82.8\%$ at O2MR = 5) which is 5.6 percent-points below the optimum value for the FC-H$^+$. With increasing SMR the fuel efficiency decreases further, to $\eta = 80.0\%$ at SMR = 2.5 and $\eta = 76.1\%$ at SMR = 10. The influence of O2MR on efficiency is very similar to that in the FC-H$^+$, increasing steadily with increasing O2MR, and therefore also in this case we fix O2MR = 5.

Results of the calculation for the FC-O^{2-} for the influence of R_{ext} are given in Fig. 2b. Similar curves are obtained for η vs. R_{ext} as for the FC-H$^+$ though efficiencies are somewhat lower, e.g., 5.6% lower at $T = 600\,°C$ when we compare efficiencies in each case at the optimum R_{ext}.

Next we analyse the robustness of the system towards coke formation. For the FC-H$^+$ running on methane, we have no coke formation at all at the optimum R_{ext} at each temperature considered. At the optimum R_{ext} at each temperature the minimum temperature required to remain free of coke, T_{min}, remains below the actual temperature. ($T_{min} = 376\,°C$ at $T = 400\,°C$, $R_{ext}^{opt} = 2.2$, $\eta = 95.1\%$; $T_{min} = 480\,°C$ at $T = 600\,°C$, $R_{ext}^{opt} = 1.65$, $\eta = 88.4\%$; $T_{min} = 521\,°C$ at $T = 800\,°C$, $R_{ext}^{opt} = 1.25$, $\eta = 80.3\%$). At the highest temperature we are very far from the coke regime, but even at $T = 400\,°C$ there is a margin $\Delta T = T - T_{min}$ of $\Delta T = 24\,°C$.

How does the margin ΔT increases when R_{ext} changes? In all cases T_{min} increases as well because with a higher load, less hydrogen is extracted from the anode compartment, thereby shifting the WGS-equilibrium back toward CO and thereby making coke formation more likely. However, with increasing R_{ext} it is only at $T = 400\,°C$ that we actually reach the coke limit with increasing R_{ext} (namely beyond $R_{ext} = 2.42$). This critical value is rather close to $R_{ext}^{opt} = 2.25$ and thus operating a FC-H$^+$ efficiently at $T = 400\,°C$ might not be possible without running the risk coke formation. Still, it is interesting to find that in a FC-H$^+$ it is theoretically possible to operate without coke formation at steam-to-carbon ratios and temperatures for which in the limit of $R_{ext} = \infty$, i.e., in standard methane steam reforming, coke formation would occur. This positive influence of the extraction of hydrogen in an FC-H$^+$ on coke formation was also noted in Ref. [3].

At $T = 500\,°C$, where $R_{ext}^{opt} = 1.9$ ($\eta = 92.3\%$), we have $T_{min} = 440\,°C$, and thus a temperature margin of $\Delta T = 60\,°C$ at R_{ext}^{opt}. With increasing load, T_{min} first increases (to ∼496 °C at R_{ext}∼3) and then slightly decreases again (to $T_{min} = 485\,°C$ at $R_{ext} = \infty$). Thus, theoretically, even at high R_{ext}, e.g., during start-up, at an operating temperature of $T = 500\,°C$ we remain outside the coke formation-regime (though the margin is very small). At $T = 600\,°C$ and higher temperatures the margin is always much larger. E.g., at $T = 600\,°C$ we have a margin at R_{ext}^{opt} of $\Delta T = 120\,°C$, and with increasing R_{ext} we always remain at
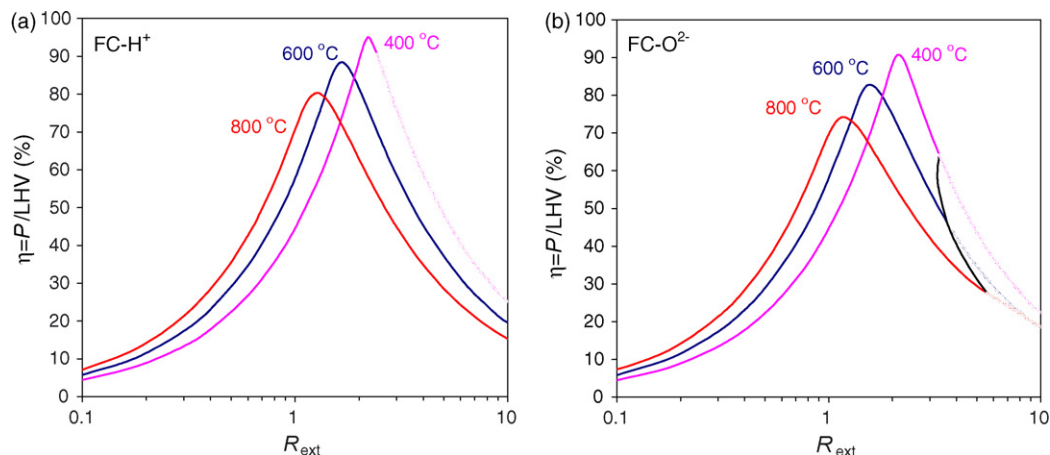
Fig. 2. Fuel cell efficiency η as function of external load and temperature. Fuel: methane; (a) proton-conducting fuel cell (SMR = 2.5, O2MR = 5); (b) oxygen conducting fuel cell (SMR = 0, O2MR = 5). Dashed lines show conditions for coke formation.

least ΔT = 24 °C on the safe side (minimum ΔT = 72 °C at T = 700 °C, and minimum ΔT = 150 °C at T = 800 °C).

How is the situation for an FC-O^{2-}? Similar to the FC-H$^+$, at the optimum external load, $R_{\text{ext}}^{\text{opt}}$, and the optimum SMR (namely zero for a FC-O^{2-}) in all cases operation is in a free-from-coke regime (T = 400 °C: $R_{\text{ext}}^{\text{opt}}$ = 2.15, η=90.9%: ΔT = 43 °C; T = 600 °C: $R_{\text{ext}}^{\text{opt}}$ = 1.55, η=82.8%, ΔT = 177 °C; T = 800 °C: $R_{\text{ext}}^{\text{opt}}$ = 1.20, η = 74.1%, ΔT = 312 °C). At low temperature, such as T = 400 °C, and at the optimum R_{ext}, operation in an FC-O^{2-} is thermodynamically further away from forming coke than in an FC-H$^+$.

Let us next consider how for an FC-O^{2-} the temperature margin ΔT changes upon an increase in external load R_{ext}, i.e. upon a reduction of the oxygen transport from the cathode to the anode. Interestingly, in this case, we find that ΔT rapidly decreases with increasing R_{ext}, and at all temperatures at some point we will arrive at a condition where the methane/oxygen mixture in the anode tends to form coke (from R_{ext} = 3.32 at T = 400 °C to R_{ext} = 5.58 at T = 800 °C). This is a fundamental difference with the FC-H$^+$ and is important, e.g., in case the system needs to operate temporarily at a non-optimal R_{ext}. This problem can be remedied by also operating with steam in the anode compartment, but then the maximum efficiency (of 82.8% at SMR = 0) decreases further, to, e.g., 80.0% at SMR = 2.5.

Interestingly, our calculation results that fuel cells with a proton-conducting electrolyte can be run free from coke, and may have in this respect advantages over oxygen-conducting membranes, are strongly at odds with statements made in Sangtongkitcharoen et al. [4] and Assabumrungrat et al. [3].

Sangtongkitcharoen et al. [4] compare direct internal methane reforming in proton-conducting and oxygen-conducting fuel cells, and conclude 'SOFCs with the hydrogen-conducting electrolyte. were observed to be impractical for use, regarding to the tendency of carbon formation' and 'From the study, direct internal reforming with the oxygen-conducting electrolyte seems to be the promising choice for operation.' Also, their remark 'the disappearance of hydrogen from the anode side by electrochemical reaction favors the carbon formation' is at odds with our results.

Similarly our results do not support the statements by Assabumrungrat et al. [3] (for methanol as fuel) that. 'The hydrogen-conducting electrolyte is impractical for use given the tendency for carbon formation' and 'Therefore, the formation of carbon is less likely in the oxygen-conducting electrolyte system [compared to the proton-conducting electrolyte].' Calculation results (Fig. 5) in Assabumrungrat et al. [3] show that with increasing hydrogen transport out of the anode compartment, coke formation becomes

more likely and they write: 'For the hydrogen-conducting electrolyte, an increase in the electrochemical reaction of hydrogen significantly demands a higher steam/methanol ratio to prevent coke formation.'

However, the hydrogen extraction rates (for a FC-H$^+$) considered in Refs. [3,4] are rather low (no more than 2 moles of hydrogen extracted per mole of methane fed to the anode compartment) whereas we find that at optimum conditions 3.85 moles of hydrogen are extracted per mole of methane fed to the anode compartment (T = 600 °C, SMR = 2.5). At these conditions we have a methane conversion of >99.99% and 0.15 mol of CO + H$_2$ slipping away in the exhaust of the anode compartment. However, the extraction of only 2 moles of hydrogen at SMR = 2 (in Refs. [3,4] values beyond this are not considered) results in a methane conversion of 85% and a CO + H$_2$ slip of 1.4 mol. Thus, operating conditions in Refs. [3,4] are very different from the conditions that we identify as being optimal for hydrogen-conducting fuel cell operation. It is indeed true that at the extraction rate considered in Refs. [3,4] hydrogen extraction has a negative effect on operation free from
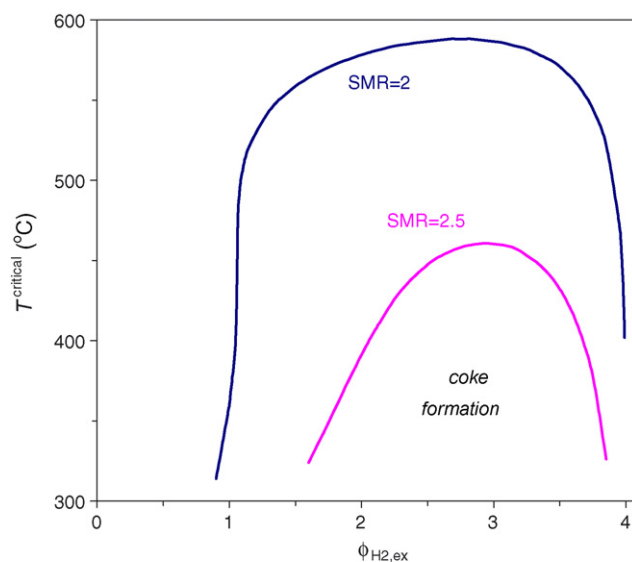

Fig. 3. Minimum temperature for coke-free operation for a methane/steam mixture, as function of hydrogen extraction rate and steam-to-methane ratio, SMR ($\phi_{\text{CH}_4,\text{in}}$ = 1).

coke. However, for extraction rates that correspond to optimal fuel cell operation, an increase in the hydrogen extraction rate improves the robustness to coke formation.

This is elucidated in Fig. 3 where we show for a methane–steam mixture the minimum, critical, temperature (as function of hydrogen extraction rate and SMR) required to operate free from coke. A first important point is the effect of SMR. At the value of SMR = 2.5 that we identify as an optimum condition for the FC-H$^+$ the minimum temperature for coke-free operation is much lower than at SMR = 2 (the maximum value for SMR considered in Ref. [4]). Furthermore, we see that T^{critical} does not monotonically increase with hydrogen extraction rate, but actually sharply drops at values of the hydrogen extraction rate $\phi_{\text{H}_2,\text{ex}}$ close to 4 ($\phi_{\text{CH}_4,\text{in}} = 1$). Interestingly, the conditions that we find for optimum efficiency are located on the right-hand side of the curve and thus, at a given temperature, increasing the hydrogen extraction rate can bring us from a coke-forming regime into a free-from-coke regime. This is exactly opposite to the regime considered in Refs. [3,4] where values for $\phi_{\text{H}_2,\text{ex}}$ of a maximum of 2 are considered. Indeed in that regime increasing the hydrogen extraction rate can bring the system into a range where coke is formed. This difference in operating regime is the reason for the different conclusions drawn in Refs. [3,4] compared to our results.

Next we analyze the same fuel cells, but operated on butane, C$_4$H$_{10}$. Butane conversion is assumed 100%, but significant amounts of methane can be formed. In the FC-H$^+$, the optimum steam to carbon ratio (H$_2$O-molecules per carbon atom of the fuel) is just as for methane as fuel equal to SCR = 2.5. At SCR = 2.5 and O2CR = 5 fuel efficiency is 87.3% at 600 °C, with a margin for coke formation of ΔT = 126 °C. With increasing external load R_{ext}, ΔT goes down but always remains at least 25 °C. At decreasing temperature the efficiency goes up (T = 500 °C: η = 91.2% at R_{ext} = 2.35, ΔT at that condition: 66 °C) but with increasing load, the margin to stay away from coke goes down, to only ΔT = 4 °C. Clearly, operation with butane as fuel at T = 500 °C will be complicated if the hydrogen extraction rate from the anode compartment is not high enough. At an operation temperature of T = 400 °C, fuel efficiency is even higher (η = 94.0% at R_{ext} = 2.75) but now the margin for coke formation becomes rather small, at the optimum R_{ext} it is ΔT = 22 °C; and beyond R_{ext} = 3.05 we run into coke. In conclusion, from a thermodynamic point of view, an FC-H$^+$ can successfully run on butane, with high fuel efficiencies and safe margins with respect to coke formation, certainly for an operating temperature of 600 °C or above.

How does an FC-O^{2-} operate on butane? Similar results are obtained as for methane and/or in a proton-conducting fuel cell, with values for maximum efficiencies very close to those for the FC-O^{2-} running on methane, at values of R_{ext} that are ~25% higher. The temperature margins for coke formation ΔT are again very similar to the values for methane as fuel in the same fuel cell type. And finally, again we find at all temperatures similar value for R_{ext} above which we run into coke.

Finally, we briefly discuss the influence of the total compartment pressure, P_i. We make calculations for an FC-H$^+$ running on methane. When we increase the pressure in both compartments from the value of P_i = 1 bar as used before, we find a significant influence. At P_i = 10 bar, the efficiency η has increased to 91.7% (from 88.4% at P_i = 1 bar, R_{ext} = 1.65, SMR = 2.5, O2MR = 5, T = 600 °C), an increase of 3.3%. Increasing R_{ext} to 1.70 optimizes η to 92.2%. At T = 400 °C and at the optimum R_{ext} for that temperature (R_{ext} = 2.2),

and the same values for SMR and O2MR, the increase is less dramatic, by only 0.8%, from 95.1% at 1 bar to 95.9% at 10 bar.

4. Conclusions

A thermodynamic analysis is made of direct internal reforming of hydrocarbon fuels both in proton-conducting and in oxygen-conducting fuel cells, in which fuel utilization and ion transport rate are self-consistently obtained. The model assumes fully mixed and equilibrated gas phase mixtures and the calculations show that both for methane and for butane as fuel, high fuel efficiencies, close to and beyond 90%, can be obtained without running the risk of coke formation. It must be noted that because of local deviations from this fully mixed state, e.g., near the electrodes, coking might still be possible, but this requires a more detailed analysis of flow patterns.

In a proton-conducting fuel cell, efficiencies are higher than in an oxygen-conducting fuel cell. In a proton-conducting fuel cell at high enough operating temperature the system remains free from coke even when the ion transport is (temporarily) decreased (at a high load). This is in contrast to the oxygen-conducting fuel cell where at the optimum steam-to-carbon ratio (namely zero) and for too low oxygen ion transport rates from the cathode compartment we always run into a regime where coke is thermodynamically predicted. The behavior in case of butane as fuel is very comparable to the situation with methane as fuel. In all cases, the efficiency increases when the temperature is lowered, but simultaneously the system runs more risk of coke formation.

In conclusion, direct internal reforming of hydrocarbon fuels in both hydrogen-conducting and oxygen-conducting fuel cell is a very promising technology to produce electricity at a high conversion efficiency, while simultaneously producing almost pure CO$_2$ (mixed only with water, and small amounts of CO, H$_2$ and CH$_4$).

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