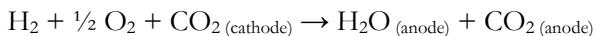


Molten Carbonate Fuel Cell - solution

The electrochemical half-reactions in an MCFC are:

- Cathode: $\frac{1}{2} \text{O}_2 + \text{CO}_2 \text{ (cathode)} + 2 \text{e}^- \rightarrow \text{CO}_3^{2-} \text{ (electrolyte)}$
- Anode: $\text{H}_2 + \text{CO}_3^{2-} \text{ (electrolyte)} \rightarrow \text{H}_2\text{O} \text{ (anode)} + \text{CO}_2 \text{ (anode)} + 2 \text{e}^-$

The sum of both half-reactions gives the total reaction:



Although CO_2 appears on both sides of the reaction, it is important to keep it! Indeed, it is not on the same side of the membrane (cathode vs. anode), so that its partial pressure will be different and influence the results.

1. Standard redox potential E^\ominus

Despite the fact CO_2 is transferred from cathode to anode in addition to the usual oxidation of hydrogen, the standard redox potential still corresponds only to $\text{H}_2 + \frac{1}{2} \text{O}_2 \rightarrow \text{H}_2\text{O}$. Indeed, using Hess' law, the formation of enthalpy and the entropy of CO_2 appears on both sides, so that it cancels out (thermodynamically speaking).

Since the cell operates at 637°C , a temperature correction must be applied to the standard Nernst potential. A linear approximation can be used, with -0.23 mV/K as temperature coefficient.

The value at 637°C can be computed in one step, from $25^\circ\text{C} \text{ (g)} \rightarrow 637^\circ\text{C} \text{ (g)}$:

$$E_{637^\circ\text{C}}^\ominus = 1.184 - 230 \cdot 10^{-6} \cdot (637 - 25) = 1.043 \text{ V}$$

2. Redox potential at inlet E_{inlet}

The redox potential is computed with the Nernst equation, which account for the gases' composition and pressure.

Nernst equation:

$$E(T, p_k) = E^\ominus(T) - \frac{RT}{\nu_e \mathcal{F}} \ln(Q_r)$$

The quotient of a redox reaction with gases is:

$$Q_r = \frac{\prod_j \left(\frac{p_j}{p^\ominus} \right)^{\nu_j}}{\prod_i \left(\frac{p_i}{p^\ominus} \right)^{\nu_i}} = \frac{\prod_j \left(\tilde{c}_j \frac{p_{\text{mix } \ominus j}}{p^\ominus} \right)^{\nu_j}}{\prod_i \left(\tilde{c}_i \frac{p_{\text{mix } \ominus i}}{p^\ominus} \right)^{\nu_j}}$$

The MCFC is operated at atmospheric pressure. Therefore, the term measuring the influence of mixes' pressure cancels out (pressure drop can also be neglected).

$$E(T, p_i) = E^\ominus(T) - \frac{RT}{\nu_e \mathcal{F}} \ln \left(\frac{\prod_j (\tilde{c}_j)^{\nu_j}}{\prod_i (\tilde{c}_i)^{\nu_j}} \right) = E^\ominus(T) - \frac{RT}{\nu_e \mathcal{F}} \ln \left(\frac{\tilde{c}_{\text{H}_2\text{O}}^{\text{an}} \tilde{c}_{\text{CO}_2}^{\text{an}}}{\tilde{c}_{\text{H}_2}^{\text{an}} \tilde{c}_{\text{CO}_2}^{\text{cat}} \sqrt{\tilde{c}_{\text{O}_2}^{\text{cat}}}} \right)$$

Gases at cathode are considered dry in this exercise. In reality, humidity (steam) may be present. However, at cathode, H₂O is not involved in the reaction.

Replacing by the molar fractions that were given for the inlet:

$$E_{\text{inlet}} = E_{637^\circ\text{C}}^\ominus - \frac{RT}{2F} \ln \left(\frac{0.3 \cdot 0.1}{0.5 \cdot 0.3 \sqrt{0.7 \cdot 0.21}} \right) = 1.043 + 0.026 = 1.069 \text{ V}$$

Remark:

The expression of the redox potential could also be developed considering each electrode separately (i.e., each half-reaction), and then “assemble” them. In that case, the activity of the molten carbonate salt in solution $a_{\text{CO}_3^{2-}}$ would appear in both cases. Since it is not gaseous, its activity would be measured as its concentration. Anyway, it cancels out during the assembly.

3. Redox potential at outlet E_{outlet}

The Nernst equation has the same form as above, but this time, with molar fractions at the outlet. Note the presence of CO₂, which is transferred from cathode to anode. The absolute quantity of N₂ remains constant at anode and at cathode.

Remark:

For simplicity, it is considered that the 10% of “other gases” at anode (CO, CH₄, and N₂) are *inert* (i.e., it can be assumed that the part of CO and CH₄ is negligible with respect to N₂). Otherwise, it should be considered that the following (overall) chemical reactions will occur:

- Water-gas-shift: $\text{CO} + \text{H}_2\text{O} \rightleftharpoons \text{H}_2 + \text{CO}_2$
- Methane steam reforming: $\text{CH}_4 + 2 \text{H}_2\text{O} \rightleftharpoons 4 \text{H}_2 + \text{CO}_2$

Observe especially that the reforming of 1 mole of methane with 2 mole of steam produces 4 moles of hydrogen and 1 mole of carbon dioxide. Therefore, even a small molar fraction of methane can modify sensibly the resulting molar fractions of steam and hydrogen. Assuming these reactions are at equilibrium, the effective values could be computed using the equilibrium’s constant (depending on temperature). It typically results in a non-linear system of equations.

a) The following definitions are used in the next developments:

- $\dot{N}_k^{\text{out}} = \dot{N}_k^{\text{in}} - \dot{N}_k^{\text{c}} + \dot{N}_k^{\text{p}}$, with “c” for consumed and “p” for produced species k
- Fuel utilization γ_f : $\dot{N}_{\text{H}_2}^{\text{c}} = \gamma_f \dot{N}_{\text{H}_2}^{\text{in}}$
- Air excess ratio λ_a : $\dot{N}_{\text{O}_2}^{\text{in}} = \lambda_a \dot{N}_{\text{O}_2}^{\text{st}}$
- Molar fractions \tilde{c}_k : $\dot{N}_k^{\text{x}} = \tilde{c}_k^{\text{x}} \dot{N}_{\text{mix}}^{\text{x}} \quad \& \quad \sum \tilde{c}_k = 1, \quad \forall k \in \text{mix, at location } \text{x}$

As for example, at anode inlet: $\dot{N}_{\text{an}}^{\text{in}} = \frac{\dot{N}_{\text{H}_2}^{\text{in}}}{\tilde{c}_{\text{H}_2}^{\text{in}}} = \frac{\dot{N}_{\text{H}_2\text{O}}^{\text{in}}}{\tilde{c}_{\text{H}_2\text{O}}^{\text{in}}} = \frac{\dot{N}_{\text{CO}_2}^{\text{in}}}{\tilde{c}_{\text{CO}_2}^{\text{in}}}$

In addition, it is known from the electrochemical reaction that:

- At anode: $\dot{N}_{\text{H}_2\text{O}}^{\text{p}} = \dot{N}_{\text{H}_2}^{\text{c}}$ $\dot{N}_{\text{CO}_2}^{\text{p,an}} = \dot{N}_{\text{CO}_2}^{\text{c,cat}} = \dot{N}_{\text{H}_2}^{\text{c}}$
- At cathode: $\dot{N}_{\text{O}_2}^{\text{st}} = 0.5 \dot{N}_{\text{H}_2}^{\text{in}}$ $\dot{N}_{\text{O}_2}^{\text{c}} = 0.5 \dot{N}_{\text{H}_2}^{\text{c}}$ $\dot{N}_{\text{CO}_2}^{\text{c,cat}} = \dot{N}_{\text{CO}_2}^{\text{p,an}} = \dot{N}_{\text{H}_2}^{\text{c}}$

b) Molar fractions at anode outlet

The denominators and numerators are expressed as factorization of $\dot{N}_{\text{an}}^{\text{in}}$, which can then be cancelled out.¹

Pay attention that *the molar rate at anode outlet is not equal to that of inlet*. In the case of MCFCs, steam and carbon dioxide are generated on the anode-side, so that the amount of mole is *increasing* at anode (idem for mass).

$$\dot{N}_{\text{an}}^{\text{out}} = \dot{N}_{\text{an}}^{\text{in}} - \dot{N}_{\text{H}_2}^{\text{c}} + \dot{N}_{\text{H}_2\text{O}}^{\text{p}} + \dot{N}_{\text{CO}_2}^{\text{p,an}} \equiv \dot{N}_{\text{an}}^{\text{in}} + \dot{N}_{\text{H}_2}^{\text{c}} = \dot{N}_{\text{an}}^{\text{in}}(1 + \tilde{c}_{\text{H}_2}^{\text{in}} \gamma_f)$$

Hydrogen is consumed according to the fuel utilization (rate), so that its molar fraction becomes:

$$\tilde{c}_{\text{H}_2}^{\text{out}} = \frac{\dot{N}_{\text{H}_2}^{\text{out}}}{\dot{N}_{\text{an}}^{\text{out}}} = \frac{\tilde{c}_{\text{H}_2}^{\text{in}} \dot{N}_{\text{an}}^{\text{in}}(1 - \gamma_f)}{\dot{N}_{\text{an}}^{\text{in}}(1 + \tilde{c}_{\text{H}_2}^{\text{in}} \gamma_f)} = \frac{\tilde{c}_{\text{H}_2}^{\text{in}} (1 - \gamma_f)}{1 + \tilde{c}_{\text{H}_2}^{\text{in}} \gamma_f} = 3.4\%$$

In addition to the amount of steam already present, H_2O is produced at the same rate as H_2 :

$$\tilde{c}_{\text{H}_2\text{O}}^{\text{out}} = \frac{\dot{N}_{\text{H}_2\text{O}}^{\text{out}}}{\dot{N}_{\text{an}}^{\text{out}}} = \frac{\dot{N}_{\text{H}_2\text{O}}^{\text{in}} + \dot{N}_{\text{H}_2\text{O}}^{\text{p}}}{\dot{N}_{\text{an}}^{\text{out}}} = \frac{\dot{N}_{\text{an}}^{\text{in}} (\tilde{c}_{\text{H}_2\text{O}}^{\text{in}} + \tilde{c}_{\text{H}_2}^{\text{in}} \gamma_f)}{\dot{N}_{\text{an}}^{\text{in}} (1 + \tilde{c}_{\text{H}_2}^{\text{in}} \gamma_f)} = \frac{\tilde{c}_{\text{H}_2\text{O}}^{\text{in}} + \tilde{c}_{\text{H}_2}^{\text{in}} \gamma_f}{1 + \tilde{c}_{\text{H}_2}^{\text{in}} \gamma_f} = 51.7\%$$

Carbon dioxide is transferred from cathode to anode at the same rate as H_2O (and H_2), so that:

$$\tilde{c}_{\text{CO}_2}^{\text{out,an}} = \frac{\dot{N}_{\text{CO}_2}^{\text{out,an}}}{\dot{N}_{\text{an}}^{\text{out}}} = \frac{\dot{N}_{\text{CO}_2}^{\text{in,an}} + \dot{N}_{\text{CO}_2}^{\text{p,an}}}{\dot{N}_{\text{an}}^{\text{out}}} = \frac{\dot{N}_{\text{an}}^{\text{in}} (\tilde{c}_{\text{CO}_2}^{\text{in,an}} + \tilde{c}_{\text{H}_2}^{\text{in}} \gamma_f)}{\dot{N}_{\text{an}}^{\text{in}} (1 + \tilde{c}_{\text{H}_2}^{\text{in}} \gamma_f)} = \frac{\tilde{c}_{\text{CO}_2}^{\text{in,an}} + \tilde{c}_{\text{H}_2}^{\text{in}} \gamma_f}{1 + \tilde{c}_{\text{H}_2}^{\text{in}} \gamma_f} = 37.9\%$$

Caution:

- $\tilde{c}_{\text{CO}_2}^{\text{out,an}} \neq 1 - \tilde{c}_{\text{H}_2}^{\text{out}} - \tilde{c}_{\text{H}_2\text{O}}^{\text{out}}$
- Although the absolute quantity of the inert gases stays constant, their molar fraction is decreasing, since the total number of moles is increasing! $\tilde{c}_{\text{inert g.}}^{\text{out}} = 1 - \sum \tilde{c}_{\text{others}}^{\text{out}} = 7.0\%$

c) Molar fractions at cathode outlet

Denominators and numerators will be expressed with a common factor ($\dot{N}_{\text{H}_2}^{\text{in}}$).

$$\dot{N}_{\text{cat}}^{\text{in}} = \frac{\dot{N}_{\text{O}_2}^{\text{in}}}{\tilde{c}_{\text{O}_2}^{\text{in}}} = \frac{\dot{N}_{\text{H}_2}^{\text{in}} \lambda_a}{2 \tilde{c}_{\text{O}_2}^{\text{in}}}$$

Pay attention that *the molar rate at cathode outlet is not equal to that of inlet*. Indeed, according to the electrochemical reaction for MCFC, carbon dioxide and oxygen are consumed at the cathode side, so that the amount of mole is *decreasing* at cathode (idem for mass).

$$\dot{N}_{\text{cat}}^{\text{out}} = \dot{N}_{\text{cat}}^{\text{in}} - \dot{N}_{\text{O}_2}^{\text{c}} - \dot{N}_{\text{CO}_2}^{\text{c,cat}} = \dot{N}_{\text{cat}}^{\text{in}} - 1.5 \dot{N}_{\text{H}_2}^{\text{c}} = \frac{\dot{N}_{\text{H}_2}^{\text{in}}}{2 \tilde{c}_{\text{O}_2}^{\text{in}}} (\lambda_a - 3 \tilde{c}_{\text{O}_2}^{\text{in}} \gamma_f)$$

$$\dot{N}_{\text{O}_2}^{\text{out}} = \dot{N}_{\text{O}_2}^{\text{in}} - \dot{N}_{\text{O}_2}^{\text{c}} = 0.5 \dot{N}_{\text{H}_2}^{\text{in}} (\lambda_a - \gamma_f)$$

$$\tilde{c}_{\text{O}_2}^{\text{out}} = \frac{\dot{N}_{\text{O}_2}^{\text{out}}}{\dot{N}_{\text{cat}}^{\text{out}}} = \frac{\tilde{c}_{\text{O}_2}^{\text{in}} (\lambda_a - \gamma_f)}{\lambda_a - 3 \tilde{c}_{\text{O}_2}^{\text{in}} \gamma_f} = 10.1\%$$

¹ Note that in this exercise, it could also be possible to compute all the different molar rates, since enough data are given (see question 7). However, they are not requested and may be a source of calculation error.

$$\dot{N}_{\text{CO}_2}^{\text{out, cat}} = \dot{N}_{\text{CO}_2}^{\text{in, cat}} - \dot{N}_{\text{CO}_2}^{\text{c, cat}} = \tilde{c}_{\text{CO}_2}^{\text{in, cat}} \dot{N}_{\text{cat}}^{\text{in}} - \dot{N}_{\text{H}_2}^{\text{c}} = \frac{\dot{N}_{\text{H}_2}^{\text{in}}}{2\tilde{c}_{\text{O}_2}^{\text{in}}} (\lambda_a \tilde{c}_{\text{CO}_2}^{\text{in, cat}} - 2\tilde{c}_{\text{O}_2}^{\text{in}} \gamma_f)$$

$$\tilde{c}_{\text{CO}_2}^{\text{out, cat}} = \frac{\dot{N}_{\text{CO}_2}^{\text{out, cat}}}{\dot{N}_{\text{cat}}^{\text{out}}} = \frac{\lambda_a \tilde{c}_{\text{CO}_2}^{\text{in, cat}} - 2\tilde{c}_{\text{O}_2}^{\text{in}} \gamma_f}{\lambda_a - 3\tilde{c}_{\text{O}_2}^{\text{in}} \gamma_f} = 20.9\%$$

$$\tilde{c}_{\text{N}_2}^{\text{out}} = 1 - \tilde{c}_{\text{O}_2}^{\text{out}} - \tilde{c}_{\text{CO}_2}^{\text{out, cat}} = 69.0\%$$

Remark:

It is not a coincidence that CO_2 at cathode inlet amounts to 30% molar. Indeed, when mixed with air, O_2 then amounts to $\sim 15\%$ molar. Since CO_2 is consumed twice w.r.t. O_2 in the MCFC, one is not limiting the electrochemical reaction more than the other. Note also that if the amount of CO_2 was lower, then a CO_2 -excess ratio should be defined rather than an air-excess ratio.

d) Replacing molar fractions at outlet in the Nernst equation

$$E_{\text{inlet}} = E_{637^\circ\text{C}}^\ominus - \frac{RT}{2F} \ln \left(\frac{0.517 \cdot 0.379}{0.034 \cdot 0.209 \sqrt{0.101}} \right) = 1.043 - 0.175 = 0.868 \text{ V}$$

4. Ohmic loss

The ohmic loss *within the electrolyte* depends on its resistance to electrical current (flow of charge). The electrical resistance [ohm, Ω] is the inverse of electrical conductance [siemens, $\text{S} = 1/\Omega$]. Similarly, resistivity ρ (Ωcm) is the inverse of conductivity σ (S/cm). The electrical resistance R of a conductor (or resistor) of resistivity ρ , length l , and cross-surface S , is given by $R = \rho l/S$. For a unit surface, the electrical resistance of the electrolyte is then $\rho \cdot l = l/\sigma = 0.375 \Omega\text{cm}^2$. Note that here, the length l corresponds to the thickness of the electrolyte (0.15 cm).

At $j = 0.25 \text{ A}/\text{cm}^2$, the ohmic voltage drop is hence $\eta_{\text{ohmic}} = j \cdot \rho \cdot l = 0.094 \text{ V}$.

Note that ohmic losses are also dissipated within the interconnectors of cells in a stack.

5. Non-ohmic (non-linear) losses

The voltage of the cell is known (e.g., measured). It corresponds to the Nernst potential *of the cell* minus the ohmic and non-ohmic losses (i.e., voltage drops, or over-potentials):

$$U_{\text{cell}} = 0.75 \text{ V} = E_{\text{cell}} - \eta_{\text{ohmic}} - \eta_{\text{non-ohmic}}$$

The Nernst potential *of the cell* can be approximated as the average of the Nernst potential between inlet and outlet (linear approximation):

$$E_{\text{cell}} = (E_{\text{inlet}} + E_{\text{outlet}})/2 = 0.969$$

$$\eta_{\text{non-ohmic}} = E_{\text{cell}} - U_{\text{cell}} - \eta_{\text{ohmic}} = 0.969 - 0.75 - 0.094 = 0.125 \text{ V}$$

6. Electrical power

The electrical current is $I = j \cdot S = 0.25 \text{ A}/\text{cm}^2 \cdot 5'000 \text{ cm}^2 = 1'250 \text{ A}$

Hence, the electrical power that is generated is simply: $\dot{E} = U_{\text{cell}} \cdot I = 0.75 \text{ V} \cdot 1'250 \text{ A} = 938 \text{ W}$

7. LHV-based electrical efficiency

The electrical efficiency is computed according to the usual definition:

$$\varepsilon_{\text{el}} = \frac{\dot{E}}{\dot{Q}} = \frac{I \cdot U_{\text{cell}}}{\dot{N}_{\text{H}_2}^{\text{in}} \cdot \Delta_r \tilde{h}_{\text{H}_2, 25^\circ\text{C}}^\ominus (g)}$$

The LHV of hydrogen at 25°C is 241'800 J/mol. The molar rate of hydrogen that is injected in the fuel cell is given by Faraday's law, without forgetting to account for the fuel utilization of 90%.

$$\dot{N}_{\text{H}_2}^{\text{in}} = \frac{I}{90\% \nu_e \mathcal{F}} = 7.2 \cdot 10^{-3} \text{ mol/s}$$

Replacing in the expression for the electrical efficiency:

$$\varepsilon_{\text{el}} = \frac{0.9 \nu_e \mathcal{F} \cdot U_{\text{cell}}}{\Delta_r \tilde{h}_{\text{H}_2, 25^\circ\text{C}}^\ominus (g)} = 53.9\%$$

8. Amount of water (liquid) produced each day

For each mole of hydrogen that is oxidized (converted), one mole of water is produced, so that:

$$\dot{N}_{\text{H}_2\text{O}}^{\text{p}} = \dot{N}_{\text{H}_2}^{\text{c}} = 90\% \dot{N}_{\text{H}_2}^{\text{in}} = 6.48 \cdot 10^{-3} \text{ mol/s} \equiv 560 \text{ mol/day}$$

Using the molar mass and density of water (18 g/mol and 1 kg/L, respectively), it gives ~ 10 kg/day or ~ 10 L/day.