UNIVERSITÀ DEGLI STUDI DI TRIESTE
Dipartimento di Ingegneria e Architettura

FUEL CELLS

THERMODYNAMICS, OPERATION, AND TRANSPORT PHENOMENA

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A.A. 2023-2024

OUTLINE

1. Fuel cells
2. Transport phenomena in fuel cells

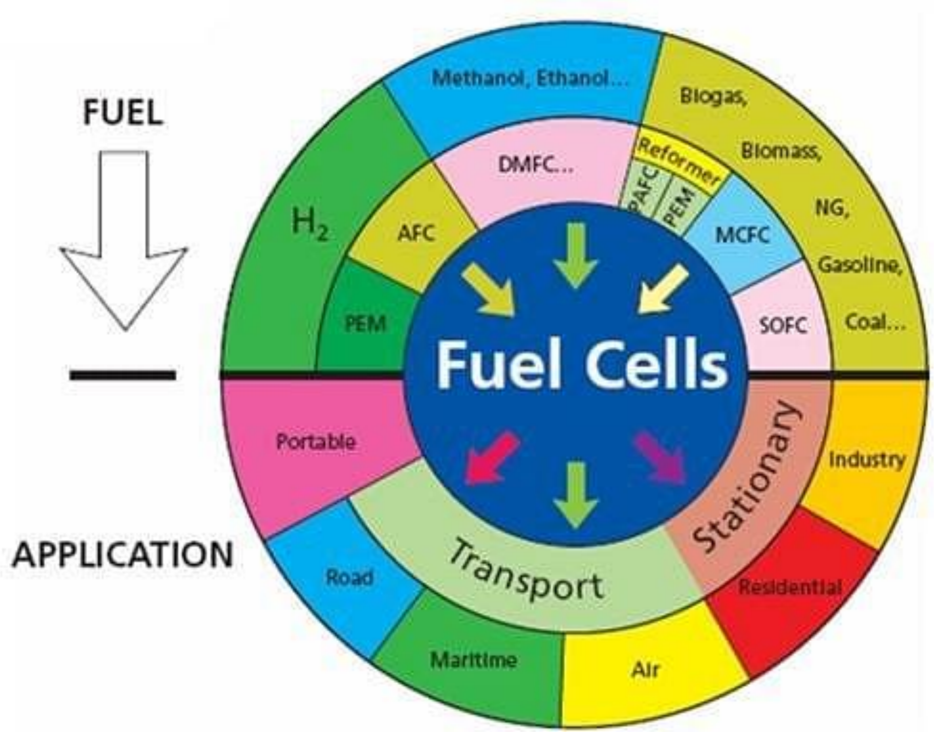
BIBLIOGRAPHY

Reference	Paragraph/Pages
Fuel Cell Systems Explained, Andrew L. Dicks, David A. J. Rand, (2018), Wiley	Ch. 2 and 3
Fuel Cell Engines, Mench M. M., (2008), Wiley	Ch. 5.1, 5.2, and 5.6

Insights		Pages
R1	Fuel Cell Engines, Mench M. M., (2008), Wiley; https://doi.org/10.1002/9780470209769	48-50
R2	Fuel Cell Engines, Mench M. M., (2008), Wiley; https://doi.org/10.1002/9780470209769	166-167

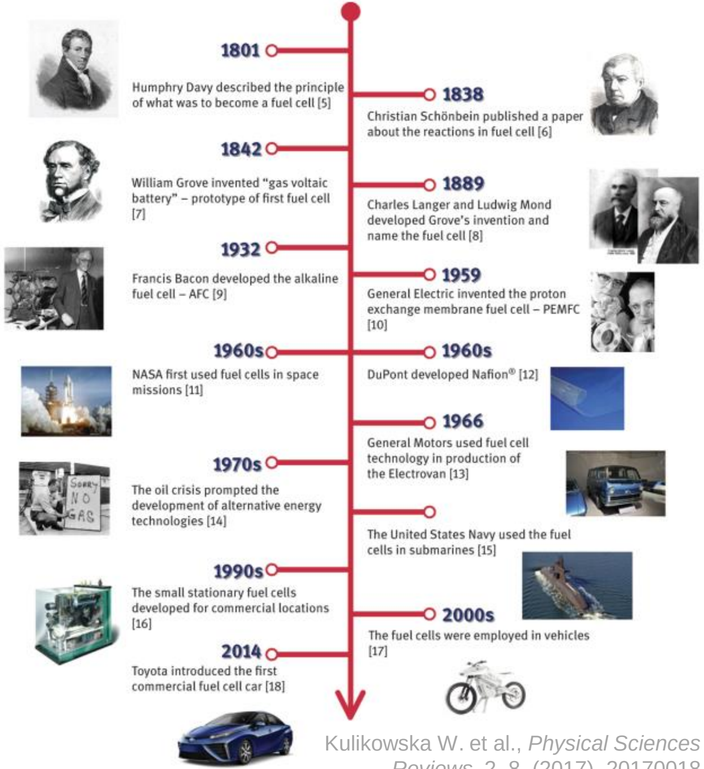
1. FUEL CELLS

INTRODUCTION



https://collegedunia.com/exams/fuel-cells-chemistry-articleid-152

INTRODUCTION



1801 Humphry Davy described the principle of what was to become a fuel cell [5]

1838 Christian Schönbein published a paper about the reactions in fuel cell [6]

1842 William Grove invented "gas voltaic battery" – prototype of first fuel cell [7]

1889 Charles Langer and Ludwig Mond developed Grove's invention and name the fuel cell [8]

1932 Francis Bacon developed the alkaline fuel cell – AFC [9]

1959 General Electric invented the proton exchange membrane fuel cell – PEMFC [10]

1960s NASA first used fuel cells in space missions [11]

1960s DuPont developed Nafion® [12]

1966 General Motors used fuel cell technology in production of the Electrovan [13]

1970s The oil crisis prompted the development of alternative energy technologies [14]

The United States Navy used the fuel cells in submarines [15]

1990s The small stationary fuel cells developed for commercial locations [16]

2000s The fuel cells were employed in vehicles [17]

2014 Toyota introduced the first commercial fuel cell car [18]

Kulikowska W. et al., *Physical Sciences Reviews*, 2, 8, (2017), 20170018

1839 The first fuel cell was invented by William Grove

1966 The first fuel cell powered vehicle, named Electrovan, was demonstrated by GM

1994-1996 NECAR 1 and NECAR 2 developed by Daimler were the first attempt to develop commercially viable fuel cell vehicles

2002 World's first limited leasing program of Toyota's fuel cell vehicles (FCHV) in Japan and the US

2003 Bush administration called for $1.2 billion in funding for fuel cell technology used for transportation

2005-2011 US DOE's $170 million Controlled Hydrogen Fleet and Infrastructure Validation and Demonstration Project. Four teams were involved: Hyundai-Kia/Chevron, Daimler Chrysler/BP, Ford/BP, and GM/Shell. A driving range target of 250 miles and fuel cell durability target of 2000 hours were met

2015 Toyota and Hyundai will begin the sale of world's first commercially available fuel cell vehicles

2017 Ford, Nissan, and Daimler will jointly develop technology to make "affordable, mass-market" fuel cell vehicles by 2017

2020 GM and Honda partnership is aiming to bring fuel cell vehicles to the public market by 2020

Qin N.. et al., FSEC report FSEC-CR-1987-14 (2014) US Dept. Transportation.

INTRODUCTION

Main advantages:

- **Efficiency.** Fuel cells are generally more efficient than (piston- or turbine-based) combustion engines. Moreover, efficiency is size independent: small fuel-cell systems can be just as efficient as large ones. In this extent, fuel cells are more suitable to be used in small-scale cogeneration plants (where nor turbine- nor engine-based systems can be used).
- **Simplicity**. Few, if any, moving parts are needed in FC systems. This can lead to highly reliable and long-lasting systems.
- **Low emissions**. When hydrogen is the fuel, pure water is the by-product of the main reaction of the fuel cell. Consequently, the power source is essentially 'zero emission', if green hydrogen is fed to the FC system. This is a particularly attractive for vehicle applications.
- **Silence.** Quietness is very important in both portable-power applications and for local power generation. The only sources of noise are related to the ancillary system.

INTRODUCTION

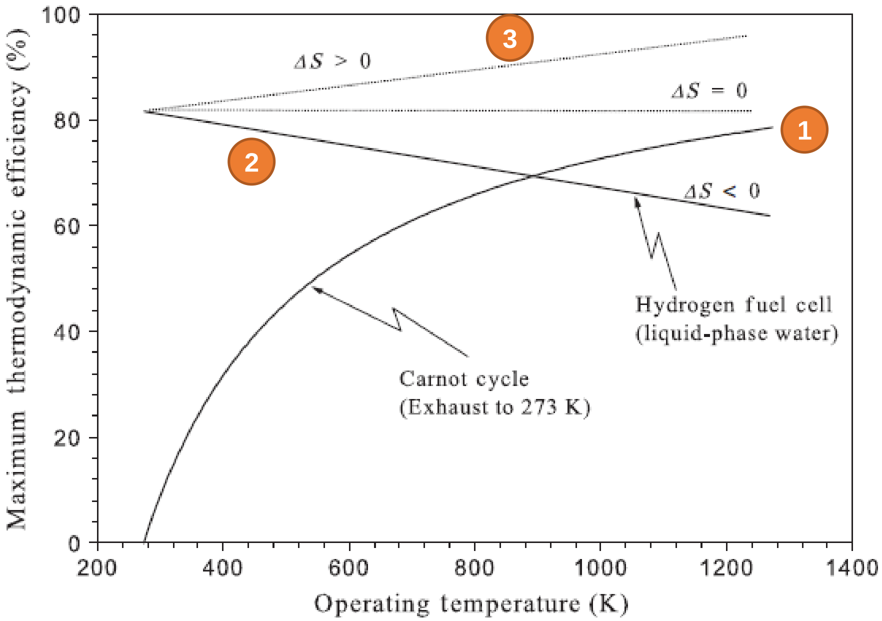
- **Efficiency**

In internal combustion engines the efficiency, given by the ratio among the generated work (W), and the heat of combustion of the fuel (ΔH), is limited by the operating temperatures at which the heat engine operates (T_1, upper temperature imposed by the engine specifications, and T_2, lower temperature, usually room temperature), according to the Carnot theorem:

$$\eta_{heat\ engine} = \frac{W}{\Delta H} = \frac{T_1 - T_2}{T_1}$$

Conversely, in fuel cells, efficiency is defined as the ratio among the energy converted into useful electric power over the chemical energy carried by the fuel, thus temperature dependence has a reduced impact over the efficiency.

INTRODUCTION



When comparing fuel cells and internal combustion engines (ICE) operating according to a Carnot cycle, the following observations can be made:

1. At high T, even if voltage losses are lower, the FC maximum thermodynamic efficiency can be lower than for ICE.

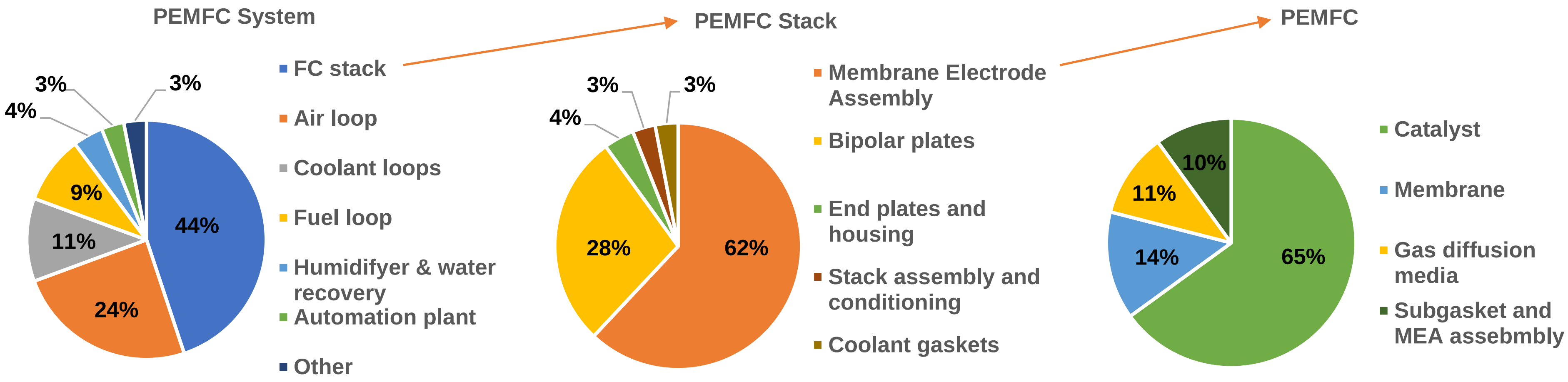
2. Losses are a strong factor reducing fuel cell losses and are not shown in this plot. Moreover, losses can be reduced when operating at higher temperatures.

3. Depending on ΔS (reaction-specific), some types of fuels show either almost no relationship, either increasing efficiency with T, due to different heats of reaction.

INTRODUCTION

Main drawbacks:

- **Capital cost.** Such technology is still expensive. Costs are There are, however, various advantages that feature more or less strongly for the different systems and lead to fuel cells being attractive for different applications.

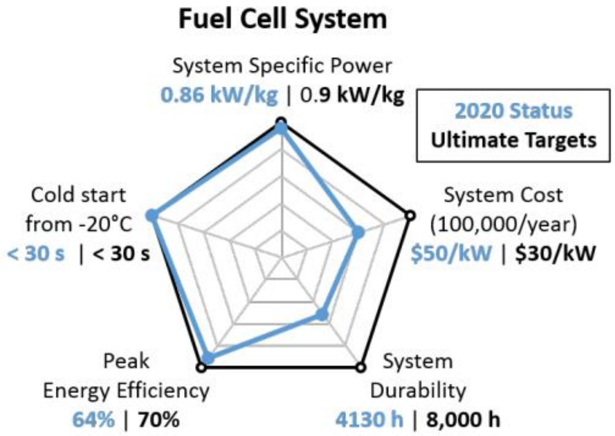


Adapted from:
DOE Hydrogen and Fuel Cells Program Record (2017)
Thompson *et al.*, J. of Power Sources, (2017)

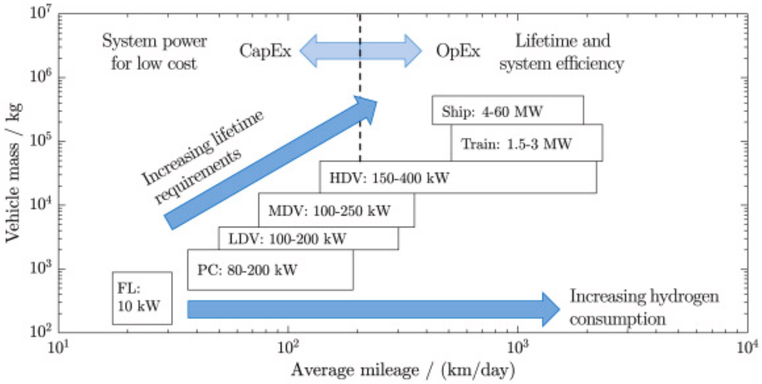
INTRODUCTION

Main drawbacks:

- **Lifetime.** The need is related in the framework of improving system autonomy, and consequently reducing their costs and shifting “*capex*-to-*opex*”.



https://www.hydrogen.energy.gov/pdfs/20005-automotive-fuel-cell-targets-status.pdf



Dirkes S. et al., Energy Conversion and Management, 277, 1, (2023), 116598

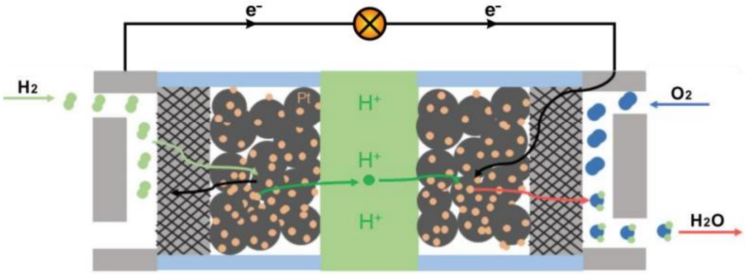
INTRODUCTION

As for electrolysers, fuel cell electrochemistry depends on the fuel cell architecture. As a reference point we are starting for simplicity analysing a fuel cells based on an acid electrolyte. At the anode electrode, the Hydrogen Oxidation Reaction (HOR) takes place: $2H_2 \rightarrow 4H^+ + 4e^-$

Conversely, at the cathode electrode the Oxygen Reduction Reaction (ORR) occurs:

$$4H^+ + 4e^- + O_2 \rightarrow 2H_2O$$

The overall reaction is: $2H_2 + O_2 \rightarrow 2H_2O + heat$



Guo H. et al., Materials 2022, 15, 8800

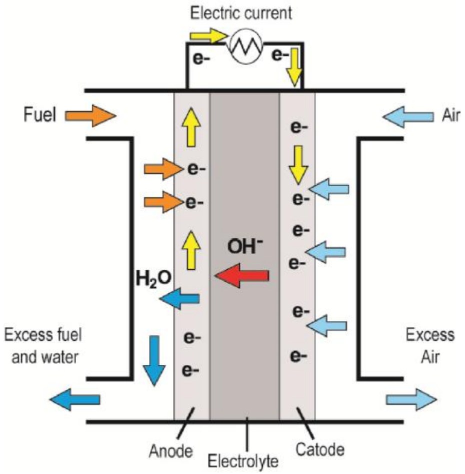
INTRODUCTION

On contrary, for fuel cells operating with an alkaline electrolyte, the interaction among hydrogen and hydroxyl atoms at the anode produces water as reaction product:

$$2H_2 + 4OH^- \rightarrow 4H_2O + 4e^-$$

On the other hand, at the cathode, water and oxygen react for producing hydroxyl ions:

$$O_2 + 4e^- + 2H_2O \rightarrow 4OH^-$$



Castañeda Ramírez S., Ribadeneira Paz R., New Trends in Ion Exchange Studies, (2018), Intech open

THERMODYNAMICS

The chemical energy of hydrogen usable in fuel cell systems for being converted into electrical one is defined by the Gibbs free energy, that is the energy liberated or absorbed in a reversible process at constant pressure and constant temperature. Put another way, it is the minimum thermodynamic work (at constant pressure) required to drive a chemical reaction and it can be used to determine weather the reaction is viable or not.

The difference of the Gibbs free energies of the reactants and the reaction products defines the change in Gibbs free energy:

$$\Delta G = \Delta H - T\Delta S$$

When normalized with respect the number of moles, the Gibbs free energy is written in lowercase letters.

THERMODYNAMICS

For a thermodynamically reversible systems (no energy losses), the Gibbs free energy released by the fuel cell equals the electrical work done:

$$\Delta G = -nFV^0$$

Where V^0 is the so-called Open Circuit Voltage (also known as reversible voltage) and represents the maximum possible voltage forming at the sides of a fuel cell without any losses.

At standard conditions $\Delta G = 237.2\ kJ\ mol^{-1}$, and:

$$V^0 = -\frac{\Delta G}{nF} = 1.229\ V \ \cong 1.23\ V$$

In the ideal case that all the potential chemical energy for a reaction is converted to electrical work ($\Delta G = \Delta H$), the so-called thermal voltage (V_{TH}) is defined as:

$$V_{TH} = -\frac{\Delta H}{nF}$$

And represents the maximum voltage for a reversible adiabatic system.

EFFICIENCY

It worth to pay attention to the fact that, according to the operating temperature, water can be produced either in liquid or in vapour phases and the change in enthalpy of formation corresponds to the molar enthalpy of vaporization of water.

Water phase	ΔH_f kJ mol^{-1}		**V_{TH} = - ΔH / nF**
Steam	- 241,83	LHV	1.35 V
Liquid	- 285.84	HHV	1.48 V
Difference	44.01		

For reactions involving water as a product, there is a choice in the calculation of thermodynamics voltages between a so called high heating value (HHV) and a low one (LHV): in the former case it is assumed as water is produced in the liquid phase, while in the latter one it is assumed that water is produced in the gas phase.

When expressing fuel cell efficiency, it should be stated the heating value of reference.

EFFICIENCY

Finally, fuel cell efficiency can be easily connected to its operative voltage (V_C), by recovering the definition of V_{TH}:

$$\Delta H = -\,n\,F\,V_{TH}$$

And by replacing the enthalpy change with either the HHV or the LHV:

$$\eta_{cell} = \frac{V_C}{1.48}$$

Due to the fact that not all of the fuel reacts within the cell, efficiency can be also expressed as:

$$\eta_{cell} = \mu_f \frac{V_C}{1.48}$$

Where the coefficient μ_f, known as Faradic efficiency, is given by:

$$\mu_f = \frac{mass\ (or\ flow\ rate) of\ the\ reacted\ fuel}{mass\ (or\ flow\ rate) of\ fuel\ supplied\ to\ the\ cell} \cong 0.95$$

and is a measure of the percentage utilisation of reactants in a galvanic process

EFFICIENCY AND STOICHIOMETRY

$$\mu_f = \frac{mass\ (or\ flow\ rate) of\ the\ reacted\ fuel}{mass\ (or\ flow\ rate) of\ fuel\ supplied\ to\ the\ cell}$$

Within the evaluation of the Faradic efficiency, the amount of reactant participating in current formation is given by the Faraday's law.

The inverse of μ_f is called stoichiometry (λ), which meaning differs from the analogous word used in chemistry. Due to the separation among cathode and anode electrodes, electrode stoichiometry is defined as:

$$\lambda_c = \frac{actual\ rate\ of\ oxidiser\ delivered\ to\ the\ cathode}{theoretical\ rate\ of\ oxidiser\ required} \qquad \lambda_a = \frac{actual\ rate\ of\ fuel\ delivered\ to\ the\ anode}{theoretical\ rate\ of\ fuel\ required}$$

Where the theoretical rates are calculated by the Faraday's law. Usually stoichiometric values are needed to be greater than one, as it is impossible to achieve complete reaction of reactants at the electrodes. This is the reason underneath the fact that Faradic efficiency is not 100%.

EFFICIENCY AND STOICHIOMETRY

Example.

Stoichiometry is useful when evaluations about gas consumption are needed to be done.

Let’s imagine a portable fuel cell (area: 20 cm^2) operating steadily at 0.75 V and 0.6 A/cm^2, characterized by a fuel utilization efficiency of 50% and cathodic stoichiometry of 2.3 (air is supplied at the cathode).

- Which is the volume of compressed hydrogen (20.26 MPa) required to guarantee three days of continuous operation at standard conditions?
    1. The total hydrogen required to sustain three days of operation can be calculated via the Faraday’s law:

$$\dot{n}_{H_2} = \lambda_a \frac{iA}{nF} = 2\frac{20 \cdot 0.6}{2 \cdot 96485} = 1.24\ 10^{-4}\frac{mol}{s}$$

$$n_{H_2} = \dot{n}_{H_2} \cdot 3600\frac{s}{h} \cdot 24 \cdot 3\ h = 32.24\ mol$$

$$m_{H_2} = n_{H_2} m_{W,H_2} = 32.24 \cdot 2.02 = 65.12\ g$$

EFFICIENCY AND STOICHIOMETRY

2. From the ideal gas law:

$$PV = n_{H_2}\mathrm{RT}$$

$$V = \frac{n_{H_2}\mathrm{RT}}{P} = \frac{32.24 \cdot 8.314 \cdot 298}{20.26\ 10^6} = 3.9\ 10^{-3}\ m^3 = 3.9\ L$$

- Which is the volume of compressed oxygen if pure oxygen would be wanted to be used within the same operating conditions?

$$\dot{n}_{O_2} = \lambda_c \frac{iA}{nF} = 2.3 \frac{20 \cdot 0.6}{4 \cdot 96485} = 7.46\ 10^{-5} \frac{mol}{s}$$

$$n_{O_2} = \dot{n}_{O_2} \cdot 3600 \frac{s}{h} \cdot 24 \cdot 3\ h = 19.34\ mol = 918.95\ g$$

$$V = \frac{n_{H_2}\mathrm{RT}}{P} = \frac{19.34 \cdot 8.314 \cdot 298}{20.26\ 10^6} = 2.4\ L$$

EFFECTS OF CONCENTRATION AND PRESSURE ON OPERATIVE CONDITIONS

By considering the general redox reaction:

$$v_A A + v_B B \leftrightarrow v_C C$$

And by considering the system in equilibrium conditions, it holds:

$$\Delta g_f = \Delta g_f^0 - RT \ln\left(\frac{a_A^{v_A} a_B^{v_B}}{a_C^{v_C}}\right)$$

Where a is the activity of the specimen involved in the reaction, and ΔG_f^0 is the variation of the Gibbs free energy of formation at standard conditions. For a hydrogen fuel cell:

$$\Delta g_f = \Delta g_f^0 - RT \ln\left(\frac{a_{H_2} a_{O_2}^{\frac{1}{2}}}{a_{H_2O}}\right)$$

By increasing the reactant (products) activity, the Gibbs free becomes more (less) negative and more (less) energy is released.

EFFECTS OF CONCENTRATION AND PRESSURE ON OPERATIVE CONDITIONS

By converting the expression of variation of the Gibbs free energy to voltage, it turns:

$$V = V^0 - \frac{RT}{2F}\ln\left(\frac{a_{H_2}a_{O_2}^{\frac{1}{2}}}{a_{H_2O}}\right)$$

Where V^0 is the cell OCV in standard conditions. The last equation is known as the Nernst equation and it describes how the activity of the reactants influences the difference of potential which is creating across the two poles of the electrochemical cell.

By considering ideal gases, activity can be considered as the ratio among , for an ideal gas it can be defined as the ratio among the partial pressure of the gas and the standard pressure (P^0 = 100 kPa), $a = p/P^0$, and the Nernst equation can be written as:

$$V = V^0 - \frac{RT}{2F}\ln\left(\frac{\frac{p_{H_2}}{P^0}\left(\frac{p_{O_2}}{P^0}\right)^{\frac{1}{2}}}{\frac{p_{H_2O}}{P^0}}\right)$$

EFFECTS OF CONCENTRATION AND PRESSURE ON OPERATIVE CONDITIONS

Nonetheless, in reality gases are usually a components of a mixture: hydrogen can present impurities due to the production method, oxygen can be fed by flowing air in the fuel cell. Consequently the partial pressures can be expressed as a fraction of the operating pressure (P), by means of constants depending on the molar mass and concentration:

$$p_{H_2} = \alpha P, \quad p_{O_2} = \beta P \quad p_{H_2O} = \delta P$$

And the Nernst equation can be expressed: as

$$V = V^0 - \frac{RT}{2F} \ln\left(\frac{\alpha \cdot \beta^{\frac{1}{2}}}{\delta}\right) + \frac{RT}{4F} \ln(P)$$

To underline the dependence of the voltage from the reactant activity and operating pressure

EFFECTS OF CONCENTRATION AND PRESSURE ON OPERATIVE CONDITIONS

$$V = V^0 - \boxed{\frac{RT}{2F}\ln\left(\frac{\alpha \cdot \beta^{\frac{1}{2}}}{\delta}\right)} + \boxed{\frac{RT}{4F}\ln(P)}$$

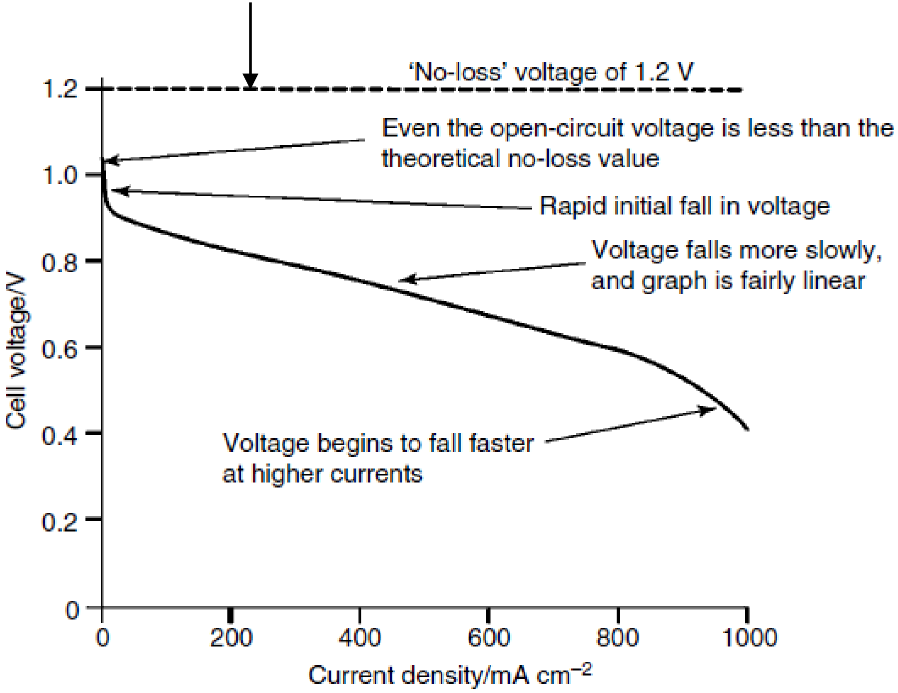
1. Once fuel and oxidant are consumed, partial pressure of the reactants (α and β) are reduced (while water partial pressure (δ) increases. This phenomenon is mostly observable in fuel cell stacks, reflected as a lower current density produced in correspondence of the gas outlets, where the fuel concentration is lower.

2. The operative pressure is directly influencing the developed voltage, and an increase of pressure (in example from P_1 to P_2, with $P_2 > P_1$) corresponds to a voltage variation equal to:

$$\Delta V = \frac{RT}{4F}\ln\left(\frac{P_1}{P_2}\right)$$

FUEL CELL OPERATION AND LOSSES

$V_{OCV} \propto \Delta G$ (theoretical upper limit)



The evolution of the polarization curve can be addressed to four different phenomena, which are leading to irreversibilities (or losses), leading to a reduction of the cell voltage. We will refer to them also as voltage losses.

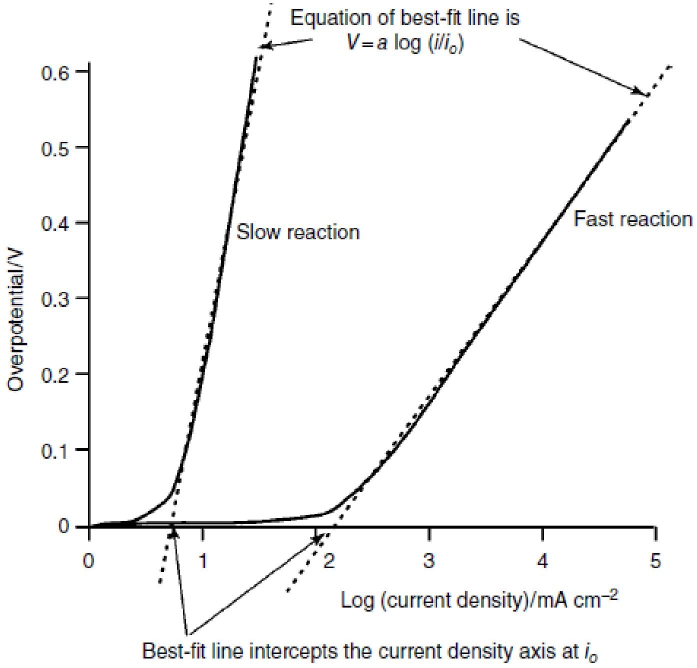
1. Activation losses
2. Internal currents and fuel crossover
3. Ohmic losses
4. Concentration (or mass-transport) losses.

FUEL CELL OPERATION AND LOSSES – ACTIVATION LOSSES

Activation losses are related to reaction kinetics taking place at the surface of the electrodes, more precisely to the fraction of energy which needs to be provided to the system to bring the system out of equilibrium and sustain the reaction.

$$\eta_{act} = E - E_{eq}$$

Where E is the (measured) electrode potential, and E_{eq} is the theoretical equilibrium potential of the electrode.



Fuel Cell Engines, Mench M. M., Wiley, 2008

Hydrogen and fuel cells
Prof. Marco Bogar

FUEL CELL OPERATION AND LOSSES – ACTIVATION LOSSES

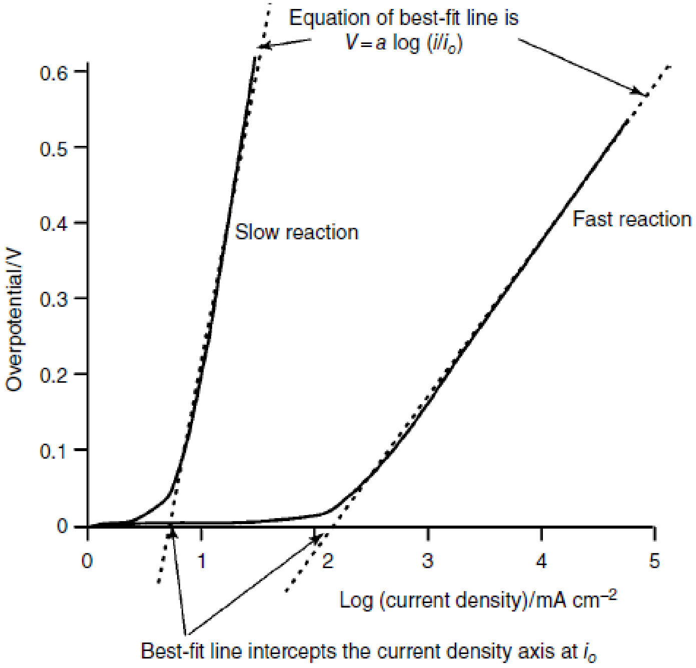
As previously introduced Tafel plots show as the overpotential is mostly linear with the logarithm of larger current densities. The relation of the overpotential with respect the exchange current density can be written as:

$$\eta_{act} = a \log\left(\frac{i}{i_0}\right) \qquad \eta_{act} = A \ln\left(\frac{i}{i_0}\right)$$

Where the constant *a* is known as the Tafel slope, and the constant *A* is equal to:

$$A = \frac{RT}{2\alpha F}$$

Here α is the charge-transfer coefficient ($\in [0,1]$), describing the fraction of the applied electrical energy which is involved in changing the reaction rate. It depends on both reaction chemistry and materials used. It can be considered equal to 0.5 for most of the hydrogen electrodes.



Fuel Cell Engines, Mench M. M., Wiley, 2008

FUEL CELL OPERATION AND LOSSES – ACTIVATION LOSSES

The Tafel equation can be rearranged to express the effects of the activation potential on the overall current. At an electrode level, the Tafel equation is expressed as:

$$i = i_0 \, e^{\frac{2\alpha F \eta_{act}}{RT}}$$

The Tafel equation holds when the $i \gg i_0$ and can be used for understanding and expressing the performance of most of the practical fuel-cell systems. Generalizing, the Butler-Volmer equation is obtained:

$$i = i_0 \left[e^{\frac{n\alpha_A F \eta_{act}}{RT}} - e^{-\frac{n\alpha_C F \eta_{act}}{RT}} \right]$$

Where n is the number of electrons involved in the reaction, and α_a and α_c are the charge transfer coefficients of the negative and positive electrodes. The Butler-Volmer and the Tafel equations can be used to directly investigate the activation overpotential in absence of other types of losses.

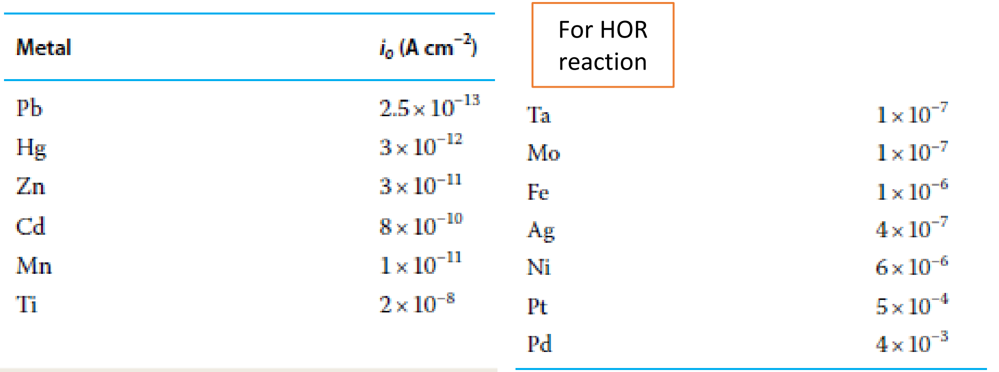
FUEL CELL OPERATION AND LOSSES – ACTIVATION LOSSES

By monitoring the voltage evolution of a FC not subjected to other losses than the activation losses, their influence on the fuel cell voltage develops in the left-most part of the polarization curve:

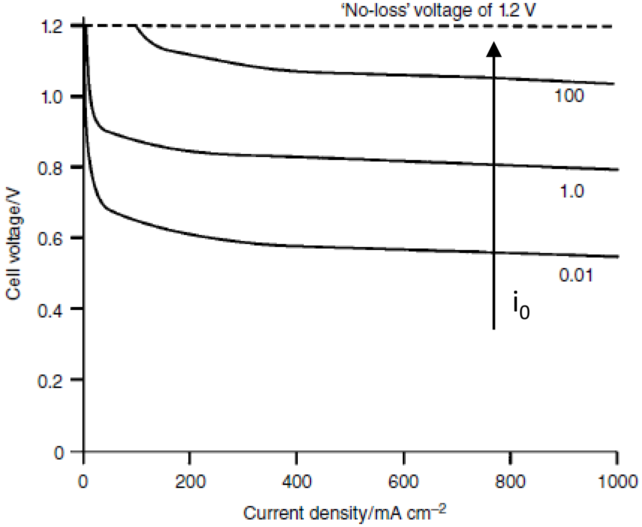
$$V_c = V^0 + \eta_{act} = V^0 - A\ln\left(\frac{i}{i_0}\right)$$

It is thus clear as the weight of the i_0 is predominant in reducing activation losses.

For HOR reaction



Metal	i_0 (A cm^{-2})
Pb	2.5×10^{-13}
Hg	3×10^{-12}
Zn	3×10^{-11}
Cd	8×10^{-10}
Mn	1×10^{-11}
Ti	2×10^{-8}
Ta	1×10^{-7}
Mo	1×10^{-7}
Fe	1×10^{-6}
Ag	4×10^{-7}
Ni	6×10^{-6}
Pt	5×10^{-4}
Pd	4×10^{-3}

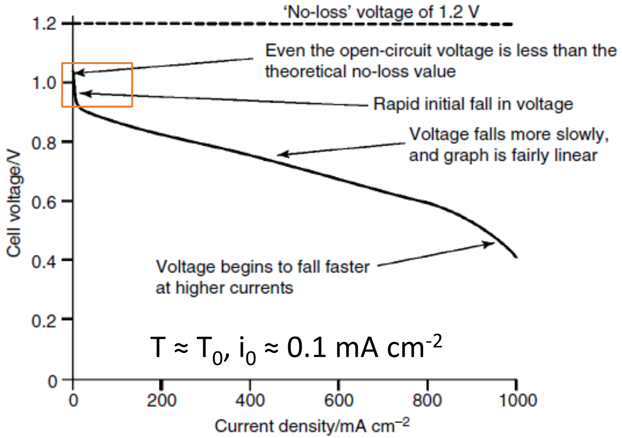


- i_0 is further reduced (about 10^5) for the ORR
- Porosity and roughness allow to increase i_0 of several (at least three) orders on magnitude

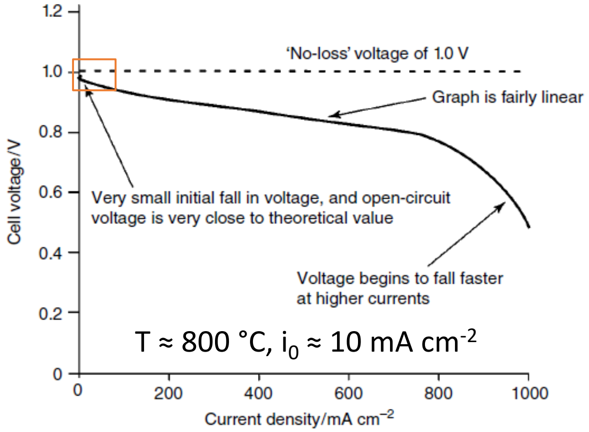
FUEL CELL OPERATION AND LOSSES – ACTIVATION LOSSES

As a general rule of thumb, fuel cells performances can be improved by optimizing exchange current density. This result can be achieved in several ways:

- **Raising the cell temperature**



$T \approx T_0$, $i_0 \approx 0.1$ mA cm^{-2}



$T \approx 800$ °C, $i_0 \approx 10$ mA cm^{-2}

FUEL CELL OPERATION AND LOSSES – ACTIVATION LOSSES

- **Optimise catalyst formulation.**

  In recent years, major efforts have been made to develop superior catalysts through the use of alloys.
- **Increase electrodes roughness.**
- **Increase reactant concentration.**

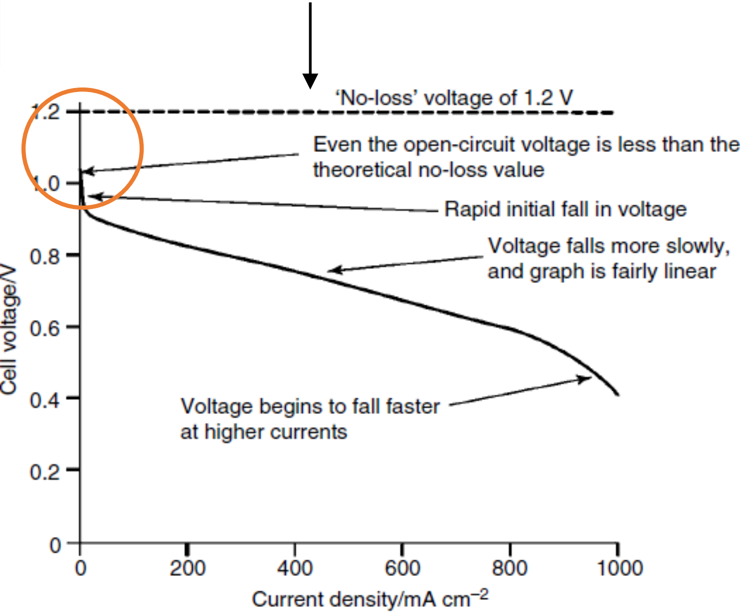
  In example, use pure oxygen instead of air. Such action enables the catalyst sites to be more effectively occupied by reactants, and to increase the open circuit voltage.
- **Increase the operating pressure.**

  This approach is also considered to be effective through enhancing the reactant occupancy of catalyst sites.

  Similar to enhancing the previous point, it allows to both enhance the reactant occupancy of catalyst sites, and increasing the open circuit voltage.

FUEL CELL OPERATION AND LOSSES – INTERNAL CURRENTS AND FUEL CROSSOVER

$V_{OCV} \propto \Delta G$ (theoretical upper limit)



By recalling the properties of electrolyte layers, it was shown as they need to be characterized by high resistance to electronic conduction and to gas permeation. Although electronic conductivity of electrolytes can be minute, it is not null, and leakage currents can develop inducing a slight reduction in the cell voltage. In addition, little amounts of hydrogen always permeate the electrolyte diffusing to the cathode electrode, where are directly reacting with oxygen, thus consuming a fraction of the fuel and reducing the current produced by the fuel cell (fuel crossover). The combination of these two effects produces an overall reduction of the number of electrons involved in the redox reactions. Such irreversibility is particularly evident in low-temperature fuel cells, causing a very noticeable voltage drop under open-circuit conditions (PEMFC ≈ 0.3 V)

FUEL CELL OPERATION AND LOSSES – INTERNAL CURRENTS AND FUEL CROSSOVER

Fuel crossover and internal current are not easily measurable, overall in fuel cell technologies in which the humidity of the operative environment is varying according to the fuel cell operation.

Indicatively, fuel crossover can be quantified by means of reactant consumption at open circuit. However, due to the low amount of gases, overall in single cells and small stack, regular flowmeters are not sensitive enough and highly sensitive techniques need to be used to quantify gas usage.

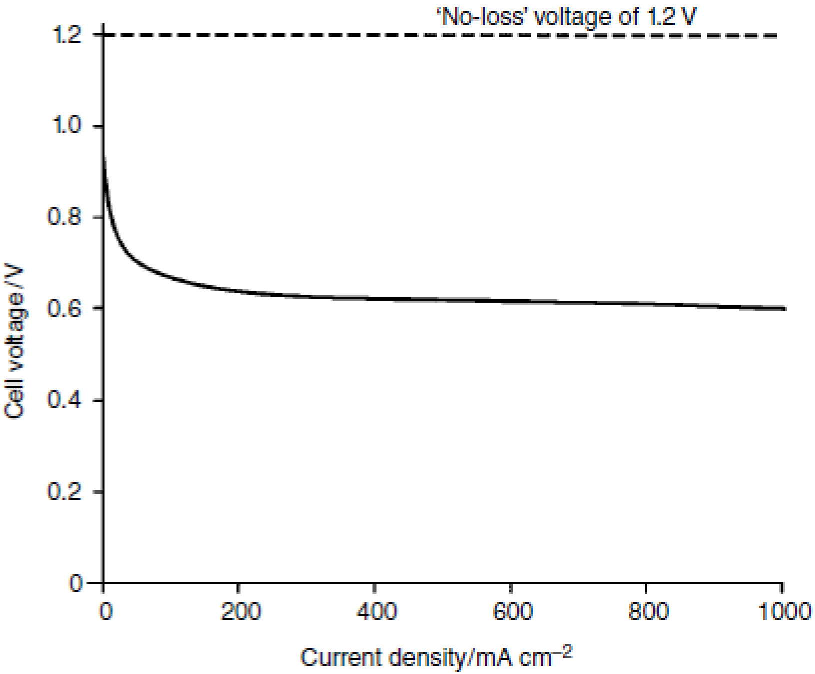
In example, for a single PEM FC mounting a MEA of 10 cm^2 hydrogen consumption at OCV was measured being equal to 3.4 10^{-9} m^3 s^{-1}, corresponding to 1.52 10^{-7} mol s^{-1} of hydrogen. Being: $\dot{n} = iA/2F \rightarrow i = 2.9\, mA\, cm^{-2}$. Such a current is large enough to induce a voltage drop about 0.1 to 0.3 V at open circuit voltage from the value of reversible voltage in PEM fuel cells.

FUEL CELL OPERATION AND LOSSES – INTERNAL CURRENTS AND FUEL CROSSOVER

To quantify the effects of internal currents and fuel crossover, from the equation previously seen expressing the cell voltage in function of activation losses, $V_c = V_r - A\ln\left(\frac{i}{i_0}\right)$, a correction term including the internal current density (i_n), can be added:

$$V_c = V^0 - A\ln\left(\frac{i + i_n}{i_0}\right)$$

The influence of internal currents is strongly reduced in high-temperature fuel cells because the exchange current density is much greater with respect low-temperature ones and the initial voltage drop is less pronounced.



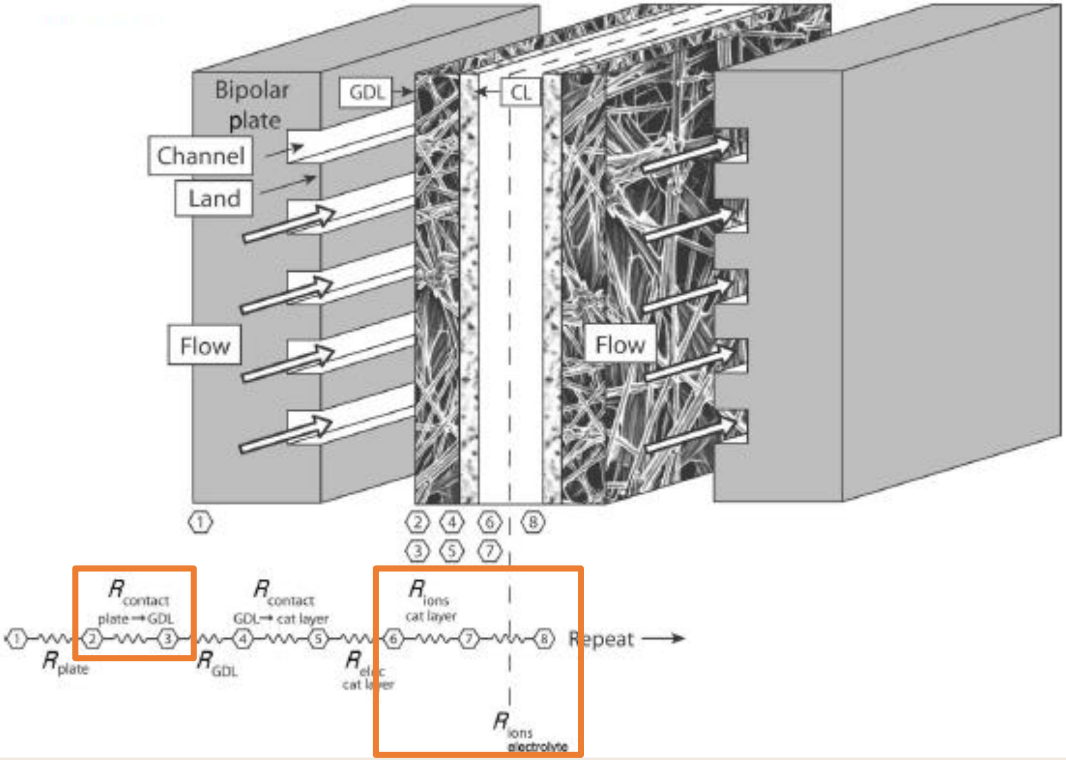
FUEL CELL OPERATION AND LOSSES – OHMIC LOSSES

They are related to the electrical resistance of the electrodes, and to the resistance to the flow of ions in the electrolyte. They can be modelled as a voltage drop according to the Ohm’s law:

$$\eta = IR = iAR = ir$$

Where *r* is a measure of resistance per unit area (or per cm^2, expressed in $\Omega\ cm^2$). In most fuel cells such resistance is mainly due to the electrolyte resistivity to ion conduction and to the charge transfer resistance among the catalyst layer and the bipolar plates. Ohmic losses are significant for all types of fuel cells and particularly affect solid-oxide technology.

FUEL CELL OPERATION AND LOSSES – OHMIC LOSSES



In first approximation, resistances related to electron transport across the catalyst layers and the GDLs can be neglected.

Thus the resistance to ionic conduction across the CCM, and contact resistance with the bipolar plates become the main contributions to be evaluated.

FUEL CELL OPERATION AND LOSSES – OHMIC LOSSES

They are three approaches which can be adopted to reduce the internal resistance:

- Using electrodes with the highest possible conductivity.
- Optimizing materials choice and bipolar plates design.
- Minimizing the electrolyte thickness.

Such a latter point is quite complicated to be dealt with because solid thin membranes are less mechanically resistant and reduce the shielding of reactant crossover. A trade off must be found also in technologies using liquid electrolytes where electrodes separation has to be enough for allowing electrolyte flowing.

FUEL CELL OPERATION AND LOSSES – MASS-TRANSPORT LOSSES

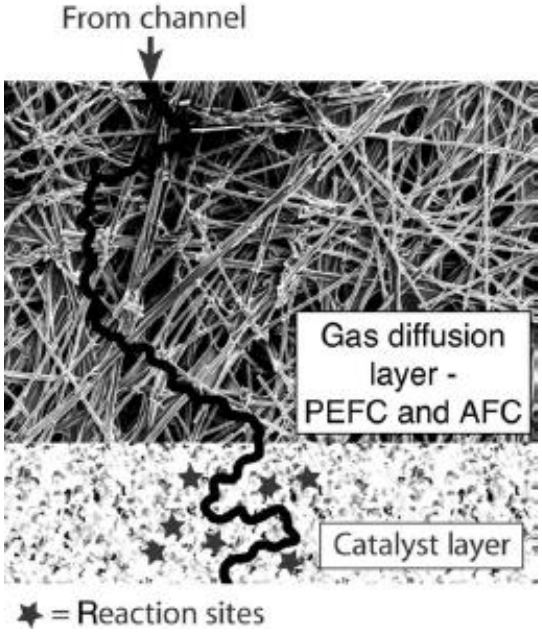
At the triple phase boundary, insufficient presence of reactants leads to the occurrence of mass transport losses. In fact, due to reactant consumption:

1. Reactant concentration decreases, and consequently, partial pressure.
2. Consequently, cell voltage reduction reduces, according to the Nernst equation:

$$\eta_{MT} = \frac{RT}{2F}\ln\left(\frac{P_2}{P_1}\right)$$

Limitations to the rate of transport to the electrode can be due to:

- Limitations due to the morphology of the gas diffusion layers
- Pore clogging by the produced water accumulating into MEA porosities
- Poisoning by impurities
- Clogging by formation and accumulation of inert gases (such as nitrogen from air)
- Insufficient mass transport across the electrolyte

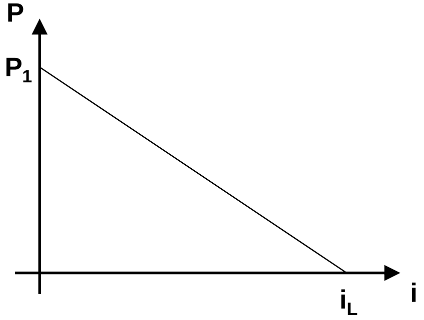


Fuel Cell Engines, Mench M. M., Wiley, 2008

FUEL CELL OPERATION AND LOSSES – MASS-TRANSPORT LOSSES

According to the operative conditions of the fuel cell, the so called **limiting current** (i_L) can be calculated. The limiting current is defined as the current in which the partial pressure of reactants falls to zero, and above which no more current density increase can be obtained.

By assuming that the reactant pressure drops linearly with the current increase:



$$P = -\frac{P_1}{i_L}(i - i_L) = P_1\left(1 - \frac{i}{i_L}\right) \rightarrow \frac{P}{P_1} = \left(1 - \frac{i}{i_L}\right)$$

Having seen as $\Delta V = f(\Delta P)$, mass transport losses (expressed via the Nernst equation) can be written as:

$$\eta_{MT} = \frac{RT}{2F}\ln\left(1 - \frac{i}{i_l}\right) = B\ln\left(1 - \frac{i}{i_l}\right)$$

Where the parameter B depends on the fuel cell technology and its operative state.

FUEL CELL OPERATION AND LOSSES – MASS-TRANSPORT LOSSES

The overvoltage due to concentration (mass-transport) losses is particularly important in cases where the hydrogen is supplied from a reformer or generator; as such an arrangement might have difficulty in adjusting the rate of supply of hydrogen sufficiently rapidly to meet changes in demand. The nitrogen left behind after oxygen is consumed at the air electrode can also hinder mass transport at high currents — it effectively blocks the oxygen supply.

FUEL CELL OPERATION AND LOSSES – COMBINING THE IRREVERSIBILITIES

$$V_c = V^0 - A\ln\left(\frac{i+i_n}{i_0}\right) - (i+i_n)r + B\ln\left(1-\frac{i+i_n}{i_L}\right)$$

Where:

V^0 is the (reversible) open-circuit voltage

i_n is the sum of equivalent current density from fuel crossover and the internal current density

A is the slope of the Tafel line

i_o is a function of both exchange current densities (or the exchange-current density at the positive electrode if the overpotential is much greater than that of the negative electrode one)

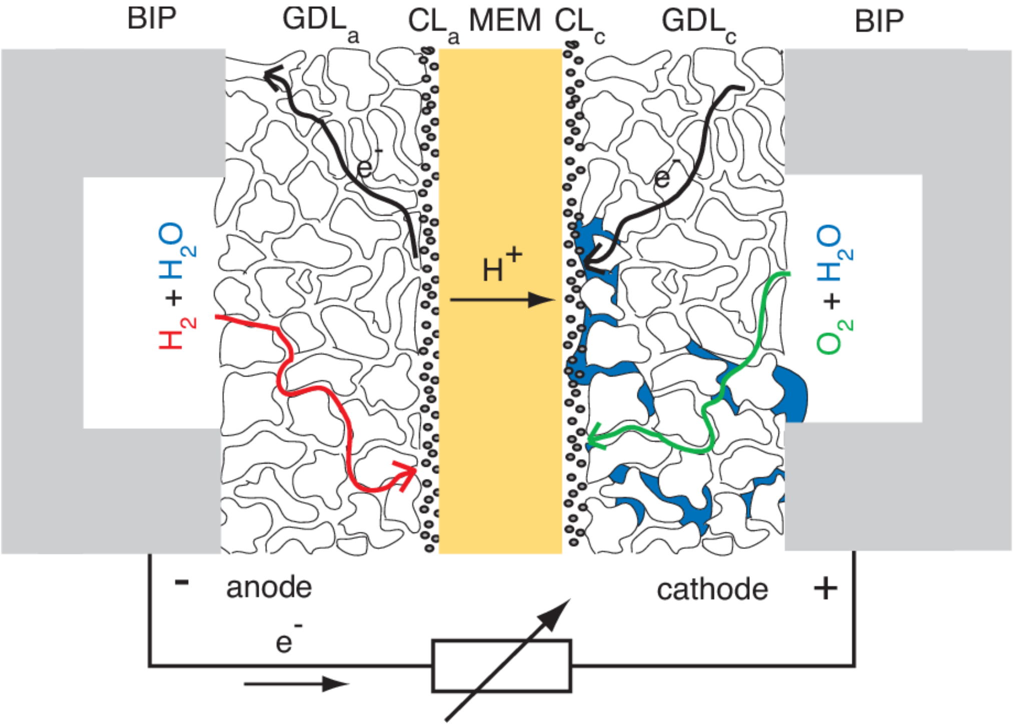
r is the resistance per unit area

B is the parameter in the mass-transfer overvoltage equation

i_L is the limiting current density at the electrode characterized by the lowest limiting current density

2. TRANSPORT PHENOMENA IN FUEL CELL SYSTEMS

TRANSPORT MATTERS



Flückiger, R. Doctoral thesis, (2009), ETH

- Ion transport
- Electron transport
- Heat transport

ION TRANSPORT IN AN ELECTROLYTE

In these class of electrochemical systems, ion transport is required for counterbalancing the charge transport sustained via the electrons. The net rate of ion transport can be directly related to the proportional to the current flow as:

$$i = \dot{n}_j z_j F$$

Where $\dot{n}_j$ is the molar rate of ion transfer through the electrolyte, and z_j is the charge number of the ion (z_j = 1 for H^+, -2 for O^{2-}).

Ion transport can be ruled by three phenomena:

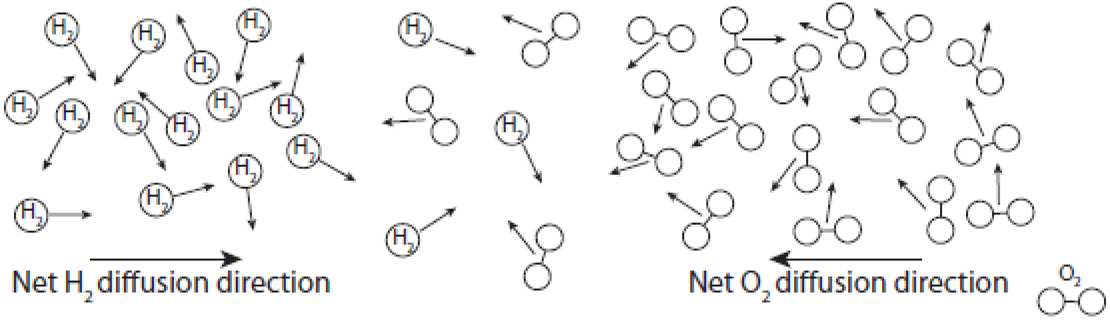
1. Diffusion
2. Convection
3. Migration

ION TRANSPORT IN AN ELECTROLYTE

Diffusion. It develops as a result of a concentration gradient of a specimen in a material (or an environment). It is described by the Fick's law; along a single direction of propagation:

$$\dot{n}_{j,x} = -D_{j,x}\frac{\partial C_j}{\partial x}$$

The negative sing represents the fact that the mass transport takes place in the direction of the decreasing concentration of the specimen j

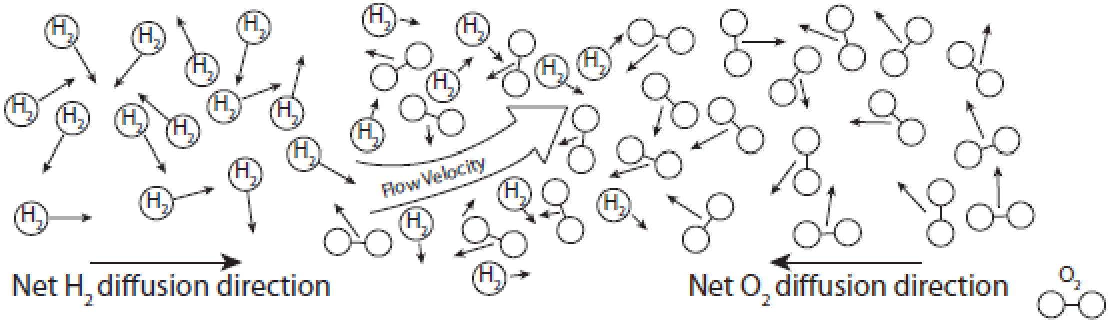


ION TRANSPORT IN AN ELECTROLYTE

Convection. It develops in result of a net motion of the electrolyte, and it is thus related to an externally controlled fluid motion. Natural convection is a result for buoyancy forces resulting from a density gradient. Along a single direction of propagation:

$$\dot{n}_{j,x} = C_{j,x} v_x$$

Where v_x is the velocity field along the x direction.

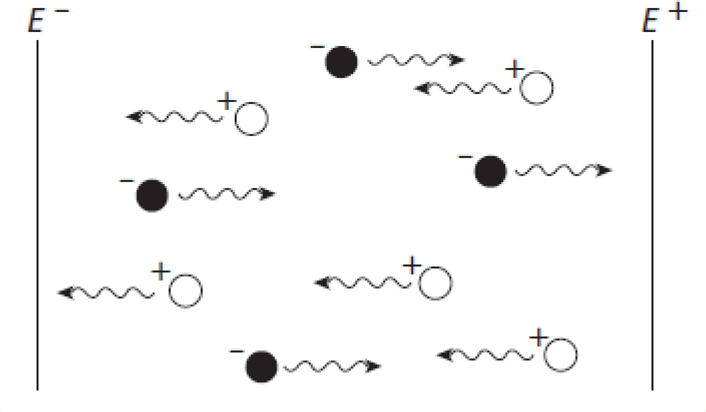


ION TRANSPORT IN AN ELECTROLYTE

Migration. It is driven by an externally applied potential difference: charged species are here driven by a gradient in the electrical potential across the material

$$\dot{n}_{j,x} = -\frac{z_j F}{RT}\, D_{j,x}\, C_{j,x}\, \frac{\partial \phi}{\partial x}$$

Where v_x is the velocity field along the x direction.



ION TRANSPORT IN AN ELECTROLYTE

Summarising, the three contributions can be summed composing the Nernst-Plank equation, governing ion transport:

$$\dot{n}_{j,x} = -D_{j,x}\frac{\partial C_j}{\partial x} + C_{j,x}v_x - \frac{z_j F}{RT}\, D_{j,x}\, C_{j,x}\, \frac{\partial \phi}{\partial x}$$

Which can be related to the current density:

$$i = \left(-D_{j,x}\frac{\partial C_j}{\partial x} + C_{j,x}v_x - \frac{z_j F}{RT}\, D_{j,x}\, C_{j,x}\, \frac{\partial \phi}{\partial x}\right) z_j F$$

And be thus used to model the current flow and the ion transport along the cartesian plane.

ION TRANSPORT IN AN ELECTROLYTE

Finally, by defining as u_j the mobility of the j-ion in the electrolyte as a function of the ionic charge, concentration and size, as well as in function of the operating temperature and pressure:

$$u_j = \left| \frac{z_j F^2 D_j}{RT} \right|$$

The current density can be expressed as:

$$i = -z_j F D_{j,x} \frac{\partial C_j}{\partial x} + z_j F C_{j,x} v_x - u_j C_{j,x} \frac{\partial \phi}{\partial x}$$

In static electrolyte systems the convective term is null, and, in open circuit conditions (where the produced current is zero), diffusion and migration counterbalance each others.

ION TRANSPORT IN AN ELECTROLYTE

In this framework ion mobility can be related to ionic conductivity as:

$$\sigma_j = F\left|z_j\right|F u_j C_j$$

It can be noticed that the overall ion conductivity is directly proportional to the charge number characterizing the ion, to its mobility and to the concentration of the charge carriers.

Finally, we can see as:

$$\sigma_j = \frac{F^2}{RT} z_j^2 D_j C_j$$

The conductivity of the electrolyte is strongly related to ion diffusivity as well. Although the relation suggests that ion conductivity for ionic solutions could increase by increasing ion concentration in solution, the gain of performances is limited by ion-ion interaction.

ION TRANSPORT IN AN ELECTROLYTE

In comparison to electronic conduction, ion conductivity relies on ion mobility, which allows much lower relative charge carrier concentration, compared with electron conductors.

Moreover, not all of the molecules in an electrolyte are charge carriers, while all molecules in a metal are closely packed and are all participating to electron conduction, and valence electrons are characterized by high mobility.

Consequently, ion conductivity losses are predominant with respect electron conductivity ones.

ELECTRON TRANSPORT

It is usually not investigated, as the fast charge transfer characterizing electrons, make electron transport not an issue to be faced. In fact, electron conductivity it usually is in the range $10^4 – 10^6$ s/cm when ionic conductivity ranges from 0.1 to 1 s/cm.

For 1 mm thick metal slab, voltage losses related to electron transport phenomena, with a current density of 1 A/cm^2 and $\sigma = \langle\sigma\rangle = 10^5\ s/cm$, can be quantified in the order of:

$$\Delta V = iAR = iA\frac{L}{A\sigma} = 1\frac{0.1}{10^5} = 1\ \mu V$$

Usually electron transport problems become evident only if the cell (or stack) are wrongly assembled or if aged current collectors oxidised.

HEAT (GENERATION AND) TRANSPORT

During fuel cell operation, heat flux (q) is formed due to current and to the departure of the operational potential to the thermal voltage:

$$q = i(V_{TN} - V) = q_r + q_i$$

The reversible heat flux is generated by the entropy variation,

$$q_r = i(V_{TN} - V^0) = i\left(-\frac{\Delta H}{nF} - \frac{\Delta G}{nF}\right) = -i\frac{T\Delta S}{nF}$$

While the irreversible heat flux is generated by the losses within the fuel cell:

$$q_r = i(V^0 - V) = i(\eta_A + \eta_\Omega + \eta_{MT}) = -i\frac{T\Delta S}{nF}$$

HEAT (GENERATION AND) TRANSPORT

Heat transfer does not affect particularly single cells or small stacks (about 5 cells). For assemblies composed by a larger cell number it is crucial designing correctly the flow rate of the coolant to be flown across the stack plates in order to ensure safe and continuous operation of fuel cell stacks.

The heat transferred from the bipolar plates to the coolant can be calculated being equal to:

$$\dot{Q} = \dot{m}_c c_c (T_{out} - T_{in})$$

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