

Fuel cell system fundamentals and Pinch analysis

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Part 1 - Fuel Cell introduction

Agenda

- Basic introduction to different fuel cell technologies
- Describe main components of a Galvani and Electrolytic cell
- Basic fuel cell thermodynamics and performance
- Describe main voltage losses affecting the fuel cell
- Understand how main fuel cell parameters affect cell voltage using a Matlab model.

Good references:

- Fuel cell handbook <https://www.netl.doe.gov/sites/default/files/netl-file/FCHandbook7.pdf>
- Fuel cell fundamentals by Ryan O'Hayre, Suk-Won Cha, Whitney Colella, and Fritz B. Prinz <https://ebookcentral.proquest.com/lib/agder/detail.action?docID=4505263>



Chemical reaction vs electrochemical reaction

- A chemical reaction is a process in which reactants rearrange in the products
- Electrochemical reaction is characterized by a transfer of electrons, in other words, some substances will gain electrons and some will lose them. This class of reactions it is also called redox.

- **Oxidation**

It is called Oxidation because the reactant loses electrons



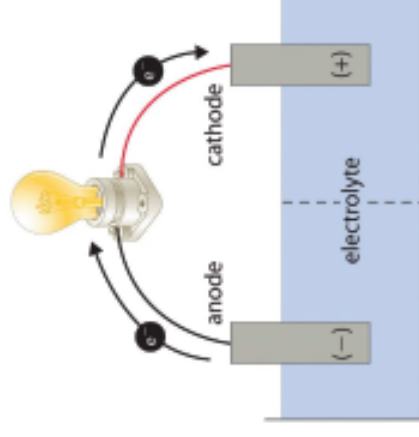
- **Reduction**

In a reduction process the reactants acquire an electron



Galvanic Cells: A simple fuel cell

- A **galvanic cell** (or voltaic cell) transforms the energy in the reactants generating an electrical current or *electromotive force*
- The **electrolytic cell** convert the electrical current into chemical energy (i.e. gasses)
- In both cases there is a redox reaction involved, however it operates in the opposite direction.
- A cell consists of:
 - 2 electrodes: they collect the electrons
 - Electrolyte: it transport charges (protons; anions)



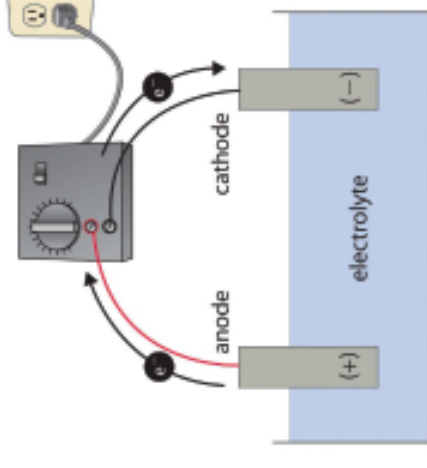
GALVANIC CELL

Energy released by spontaneous redox reaction is converted to electrical energy.

Oxidation half-reaction:
 $Y \rightarrow Y^+ + e^-$

Reduction half-reaction:
 $Z + e^- \rightarrow Z^-$

Overall cell reaction:
 $Y + Z \rightarrow Y^+ + Z^-$ ($G < 0$)



ELECTROLYTIC CELL

Electrical energy is used to drive nonspontaneous redox reaction.

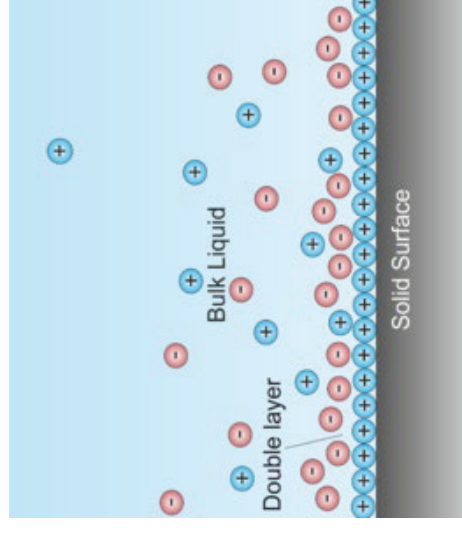
Oxidation half-reaction:
 $Z^- \rightarrow Z + e^-$

Reduction half-reaction:
 $Y^+ + e^- \rightarrow Y$

Overall cell reaction:
 $Y^+ + Z^- \rightarrow Y + Z$ ($G > 0$)

Electric double layer

- A phenomena that happen at the **electrode/electrolyte interface**
- Transition region between 2 phases in which there is an **imbalance of charges which strongly interact.**
- It is the area of the electrode where electrochemical reaction occurs like for instance a metal immersed in a solution. It will be a thin layer between the metal and the solution.
- We should remind that in nature a **bulk is characterized by neutral charged unless electrically perturbed**



SOURCE: Wikipedia Larrysgood



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Fuel cell types

Fuel cells are divided according to electrolyte material

Note the different ions crossing the electrolyte, different temperature of operations and material.

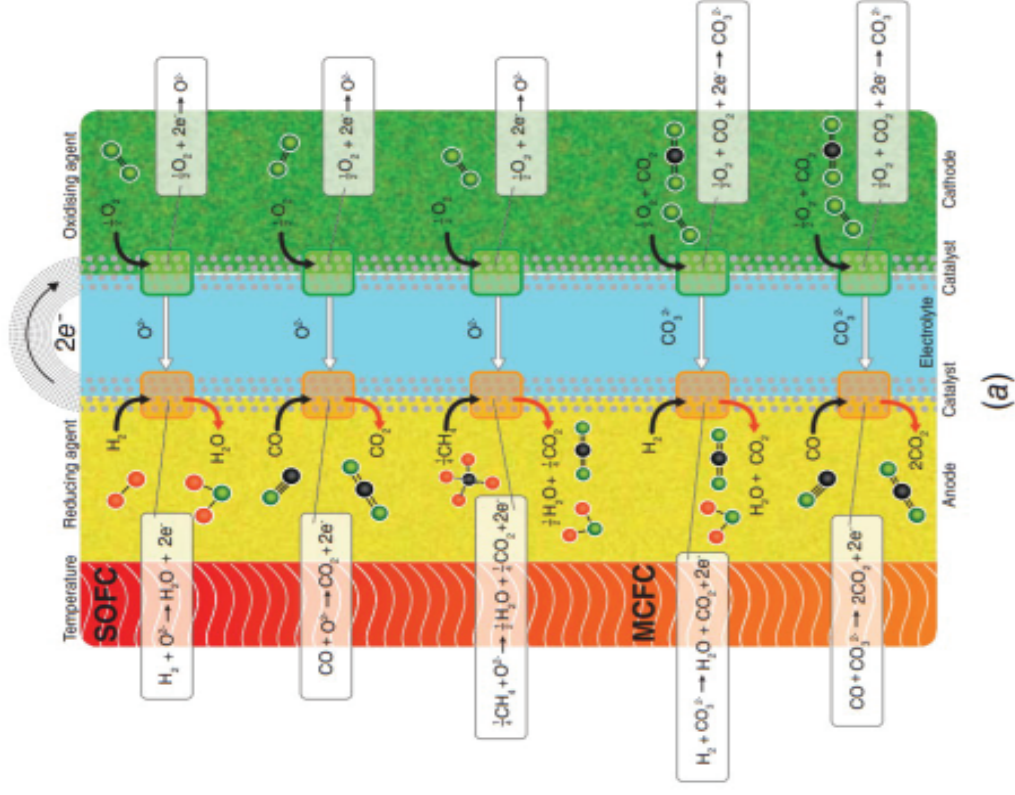
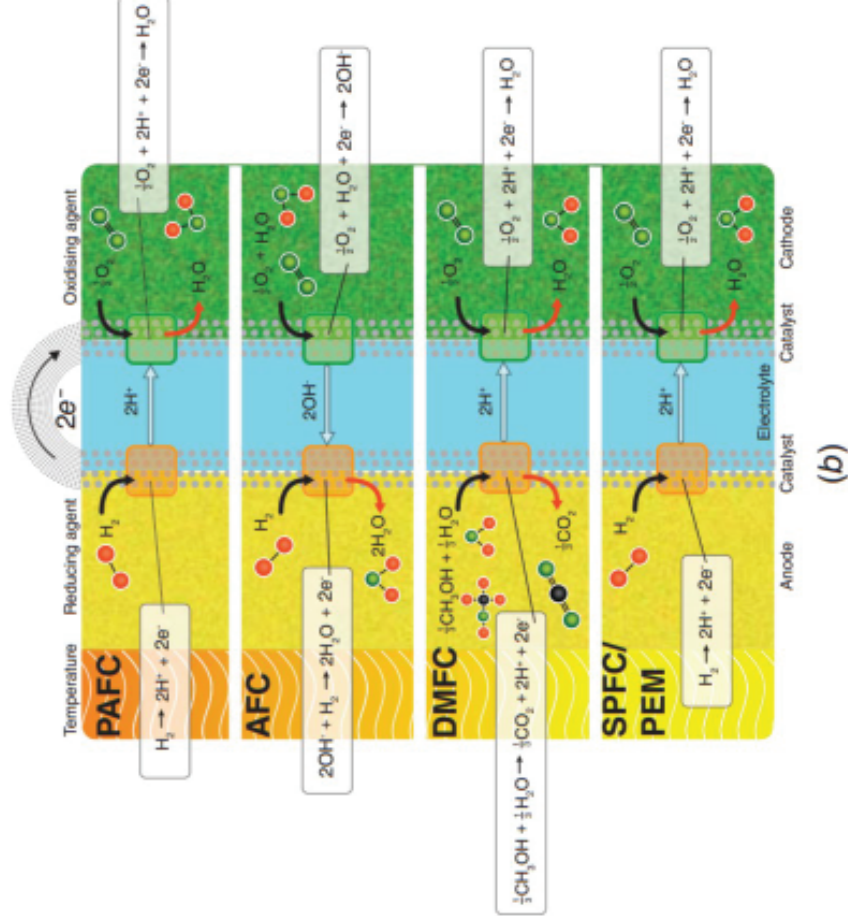
There are 5 main fuel cell types.

1. Phosphoric acid fuel cell (PAFC)
2. Polymer electrolyte membrane fuel cell (PEMFC)
3. Alkaline fuel cell (AFC)
4. Molten carbonate fuel cell (MCFC)
5. Solid-oxide fuel cell (SOFC)

PS the classification of FC is provided in Chapter 8 of Fuel cell fundamentals



Classification of Fuel cells



Summary of electrochemical reaction if different type of Fuel cell

- The table from the US department of Energy provide a comparison between different type of fuel cells

U.S. DEPARTMENT OF **ENERGY** | Energy Efficiency & Renewable Energy

FUEL CELL TECHNOLOGIES PROGRAM

Comparison of Fuel Cell Technologies

Fuel Cell Type	Common Electrolyte	Operating Temperature	Typical Stack Size	Efficiency	Applications	Advantages	Disadvantages
Polymer Electrolyte Membrane (PEM)	Perfluoro sulfonic acid	50-100°C 122-212°F typically 80°C	< 1kW-100kW	60% transportation 30% stationary	<ul style="list-style-type: none"> Backup power Portable power Distributed generation Transportation Specialty vehicles 	<ul style="list-style-type: none"> Solid electrolyte reduces corrosion & electrolyte management problems Low temperature Quick start-up 	<ul style="list-style-type: none"> Expensive catalysts Sensitive to fuel impurities Low temperature waste heat
Alkaline (AFC)	Aqueous solution of potassium hydroxide soaked in a matrix	90-100°C 194-212°F	10-100 kW	60%	<ul style="list-style-type: none"> Military Space 	<ul style="list-style-type: none"> Cathode reaction factor in alkaline electrolyte leads to high performance Low cost components 	<ul style="list-style-type: none"> Sensitive to CO₂ in fuel and air Electrolyte management
Phosphoric Acid (PAFC)	Phosphoric acid soaked in a matrix	150-200°C 300-392°F	400 kW 100 kW module	40%	<ul style="list-style-type: none"> Distributed generation 	<ul style="list-style-type: none"> Higher temperature enables CHP Increased tolerance to fuel impurities 	<ul style="list-style-type: none"> Pt catalyst Long start up time Low current and power
Molten Carbonate (MCFC)	Solution of lithium, sodium, and/or potassium carbonates, soaked in a matrix	600-700°C 1112-1292°F	300 kW-3 MW 300 kW module	45-50%	<ul style="list-style-type: none"> Electric utility Distributed generation 	<ul style="list-style-type: none"> High efficiency Fuel flexibility Can use a variety of catalysts Suitable for CHP 	<ul style="list-style-type: none"> High temperature corrosion and breakdown of cell components Long start up time Low power density
Solid Oxide (SOFC)	Yttria stabilized zirconia	700-1000°C 1292-1832°F	1 kW-2 MW	60%	<ul style="list-style-type: none"> Auxiliary power Electric utility Distributed generation 	<ul style="list-style-type: none"> High efficiency Fuel flexibility Can use a variety of catalysts Solid electrolyte Suitable for CHP & CHHP Hybrid/GT cycle 	<ul style="list-style-type: none"> High temperature corrosion and breakdown of cell components High temperature operation requires long start up time and limits

For More Information
More information on the Fuel Cell Technologies Program is available at <http://www.hydrogenandfuelcells.energy.gov>.

U.S. DEPARTMENT OF **ENERGY** | Energy Efficiency & Renewable Energy

EERE Information Center
1-877-EERE-INFO (1-877-337-3463)
www.eere.energy.gov/informationcenter
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From

https://web.archive.org/web/20130301120203/http://www1.eere.energy.gov/hydrogenandfuelcells/fuelcells/pdfs/fc_comparison_chart.pdf

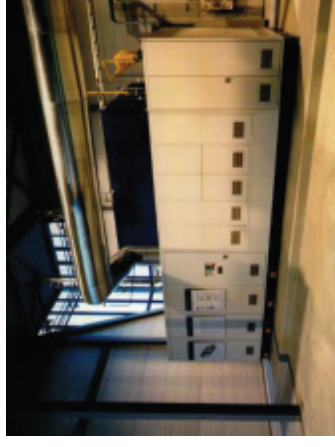
Stationary Fuel Cell Power Systems



**Fuel Cell Energy
2 MW MCFC**



**Plug Power 7kW
Residential PEFC**



**Siemens-Westinghouse
100kW SOFC**



**UTC Fuel Cells
200kW PAFC**



**Ballard 250kW
PEFC**



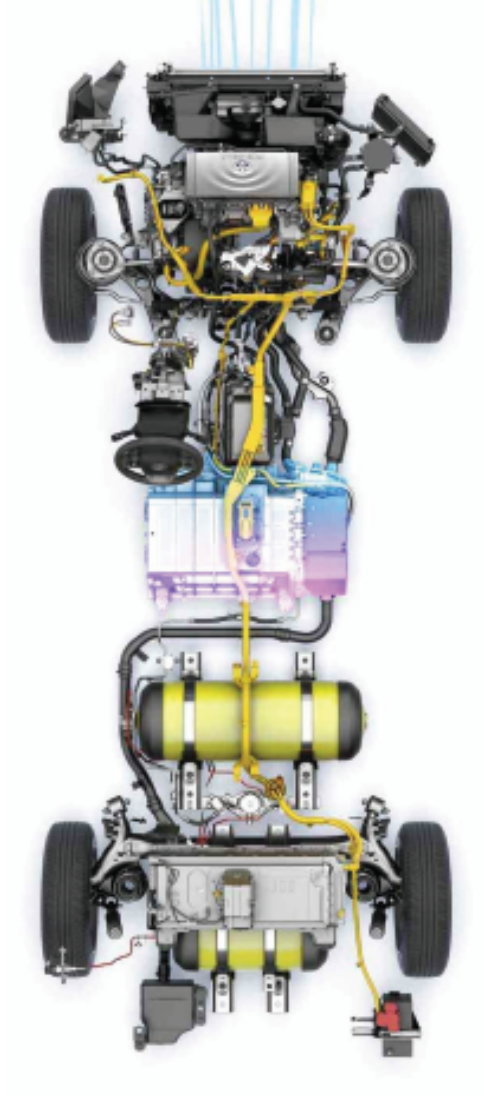
**Plug Power 10 kW
Residential unit**



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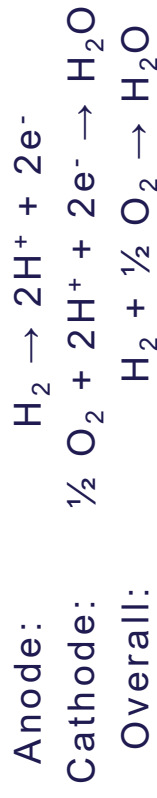
Breakthrough Technologies Institute: www.fuelcells.org

Fuel cell system In the car



Gibbs free energy and voltage

The FC reactions are:



The standard free energy of an electrochemical reaction

$$\Delta G = -nFE$$

E : Reversible potential at equilibrium or ideal potential 1.23V

F : Faraday constant(i.e. magnitude of the electric charge for moles of electrons)

n : nr of electrons exchanged in the electrochemical reaction $\text{H}_2 + \frac{1}{2} \text{O}_2 \rightarrow \text{H}_2\text{O}$



Relationship between Gibbs Free energy and equilibrium

- For a general reaction $aA + bB \rightarrow cC + dD$ the equilibrium constant is defined:

$$K = \frac{[C]^c [D]^d}{[A]^a [B]^b}$$

- Where A;B;C;D are the concentrations and a;b;c;d are the stoichiometric coefficient of the reaction
- The relationship between the eq constant and the Gibbs free energy of reaction is given below:

$$\Delta G = -RT \ln(K)$$



Nernst Equation

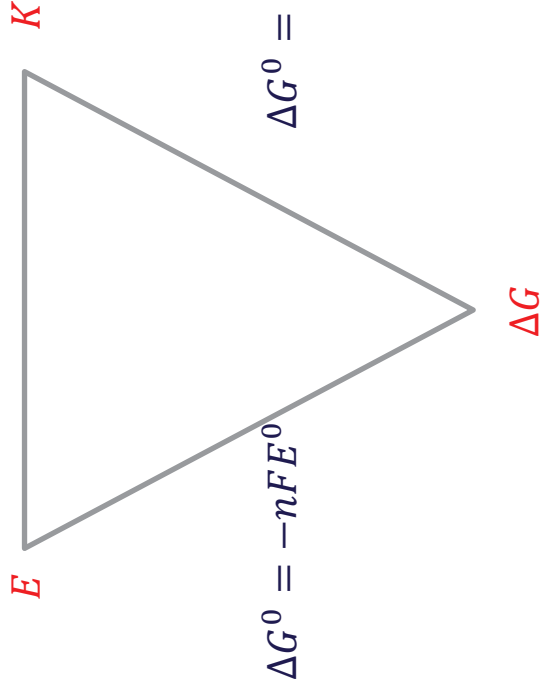
- The relationship accounts for the effect of pressure and temperature when calculating the cell electrical potential E
- E° represents the ideal standard potential at standard condition
- If pressure and temperature of the reactants H_2 and O_2 is increased the equilibrium potential E will also increase.
- For a cell reaction $H_2 + O_2 \rightarrow H_2O$ the Nernst eq is:

$$E = E^\circ + \frac{RT}{nF} \ln \left(\frac{P_{H_2} \cdot P_{O_2}^{1/2}}{P_{H_2O}} \right)$$



Relationship among Gibbs Free Energy, Eq Const, and Potential

$$E^{\circ} = \frac{RT}{nF} \ln \left(\frac{P_{H_2} \cdot P_{O_2}^{1/2}}{P_{H_2O}} \right)$$



Inspired by: <https://www.albert.io/blog/gibbs-free-energy-ap-chemistry-crash-course/> it is also available on other sources



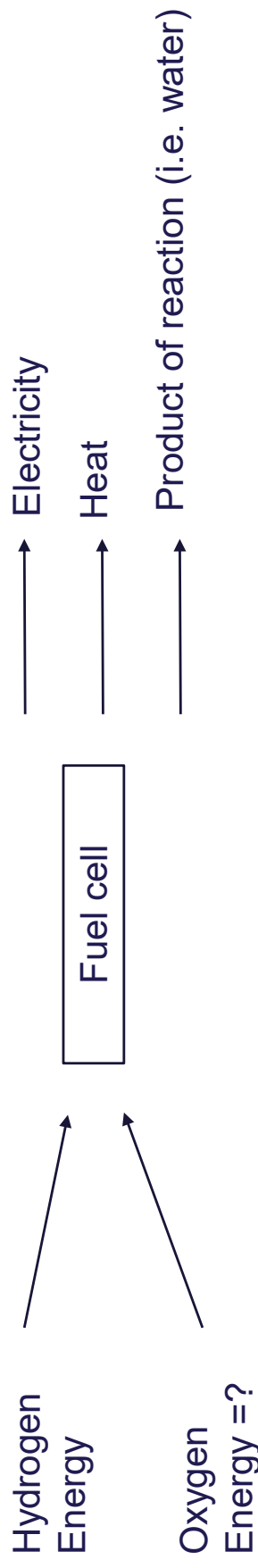
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Fuel cell efficiency

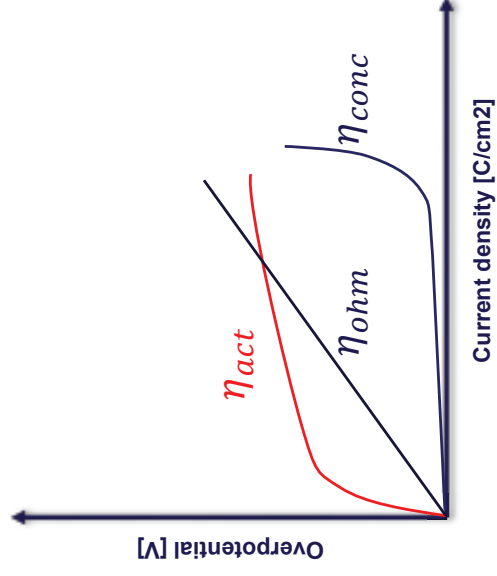
The maximum efficiency obtained by a cell can be obtained using

$$\Delta G^{\circ}_{rxn,T} = \Delta H^{\circ}_{rxn,T} - T \cdot \Delta S^{\circ}_{rxn,T}$$

$$\eta_{max} = \frac{\Delta G^{\circ}_{rxn,298}}{\Delta H^{\circ}_{rxn,298}}$$

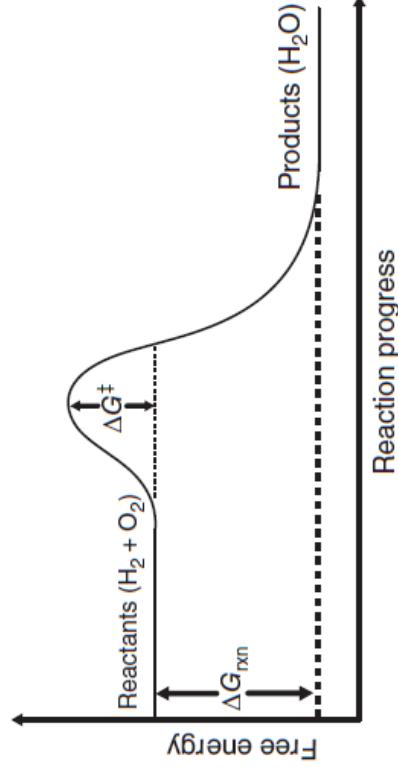


Activation overvoltage



Rate of the electrochemical reaction

- Reactions happen spontaneously when the reactants free energy is larger than products free energy
- The activation energy is represented by the energy “barrier” that the reaction has to overcome to convert reactants into products.
- The activation energy limits the rate of reaction



Source: Fuel cell fundamentals Chapter 3



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Net rate of reaction

- In the **forward reaction**, hydrogen releases one electron the metal catalyst (i.e. platinum)
- In the **backward reaction**, the hydrogen ion gain an electron from the metal.
- At equilibrium both this reactions must balance; although both reactions are taking place the net rate is 0

$$J = C_R f_1 e^{-\Delta G_1/RT} - C_P f_2 e^{-\Delta G_2/RT}$$

Forward reaction

Backward reaction

J: net reaction rate

C_R/C_P: reactant/product surface concentration

f₁/f₂: decay rate to product/reactant (i.e. likelihood that the reaction will convert to product/reactant)

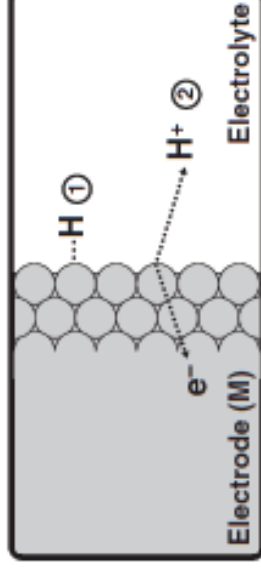


Figure 3.4. Schematic of chemisorbed hydrogen charge transfer reaction. The reactant state, a chemisorbed hydrogen atom ($M \cdots H$), is shown at 1. Completion of the charge transfer reaction, as shown at 2, liberates a free electron into the metal and a free proton into the electrolyte ($(M + e^-) + H^+$).



Chemisorbed
Hydrogen

Source: Fuel cell fundamentals Chapter 3



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Net rate of reaction

- We can restate the rate of reaction as a function of ΔG of reaction

$$J = C_R^* f_1 e^{-\Delta G_1/RT} - C_P^* f_2 e^{-\Delta G_2/RT}$$

Forward reaction Backward reaction

- The activation barrier for the overall reaction can be calculated as the difference between the activation barrier for forward and backward reaction.

$$\Delta G_{react} = \Delta G_1 - \Delta G_2$$

- Therefore ΔG_2 can be expressed as a function of ΔG_{react} and ΔG_1

$$J = C_R^* f_1 e^{-\Delta G_1/RT} - C_P^* f_2 e^{-(\Delta G_{react} - \Delta G_1)/RT}$$

- At equilibrium the reaction rate of reaction is 0

$$J = 0$$

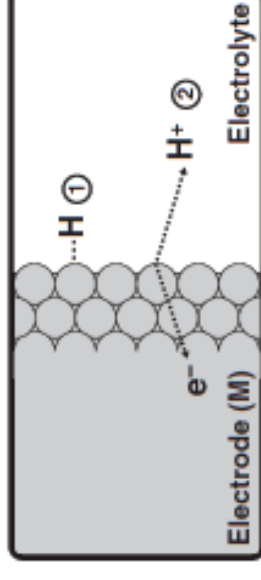


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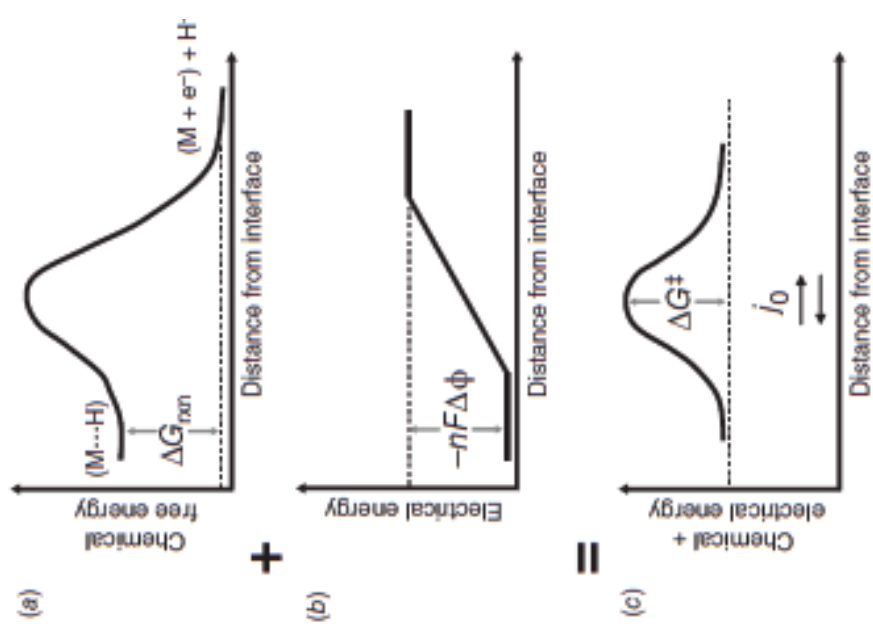
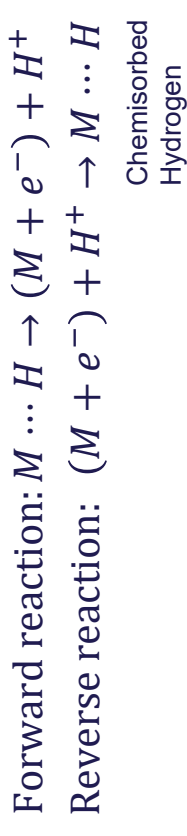
Chemisorbed
Hydrogen

Source: Fuel cell fundamentals Chapter 3



Potential of reaction at equilibrium

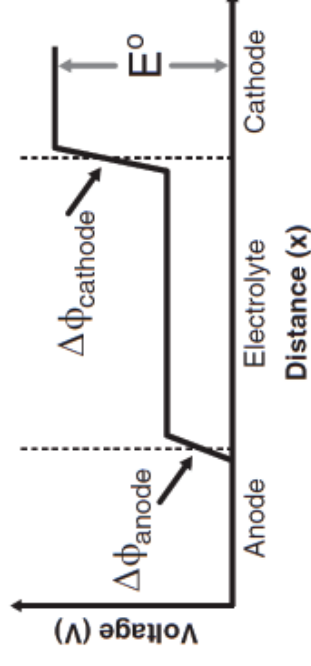
- When the forward reaction has a faster rate than the backward reaction, the reaction products are favored. This is evident from the chemical potential
- The charge accumulation continues until potential difference across the interface counterbalance the chemical potential
- The combined effect of chemical and electrical potential will be 0 at thermochemical equilibrium



Potential of reaction at equilibrium in a fuel cell

- In a fuel cell we have 2 electrodes, electrochemical reactions occurs both at anode and cathode, hence generating 2 electrical potentials.
- The overall cell voltage, E^0 , will be the sum of the 2 electrode potentials.

$$E^0 = \Delta\phi_{Anode} + \Delta\phi_{Cathode}$$



Butler Volmer equation

- Current density and reaction rate are related by the relationship:

$$j = nFJ$$

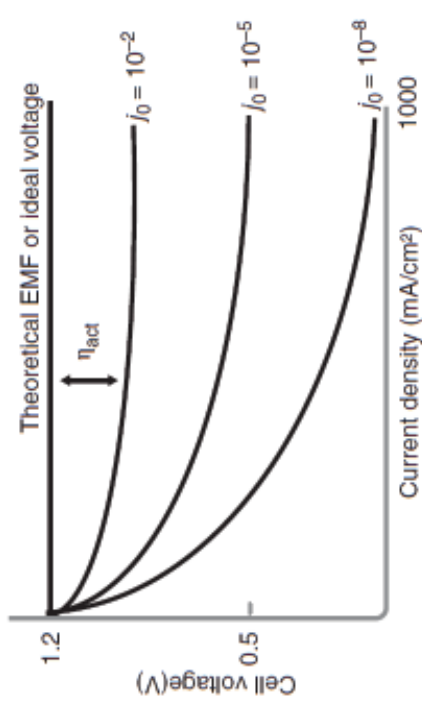
Lower case j → Capital case J

- The current density is defined as (Butler Volmer eq.):

$$j = j_0 \left(\frac{C_R^*}{C_R^{0*}} e^{\alpha n F \eta / (RT)} - \frac{C_P^*}{C_P^{0*}} e^{-(1-\alpha) n F \eta / (RT)} \right)$$

- η : activation voltage loss
- n : number of electron transferred by the electrochemical reaction
- α : charge transfer coefficient (proportional to the energy "barrier")
- C_R^* , C_P^* : actual reactant and product concentration
- C_R^{0*} , C_P^{0*} : reference reactant and product concentration
- j_0 : reference current density

- Current density increases exponentially with activation overvoltage



Source: Fuel cell fundamentals Chapter 3

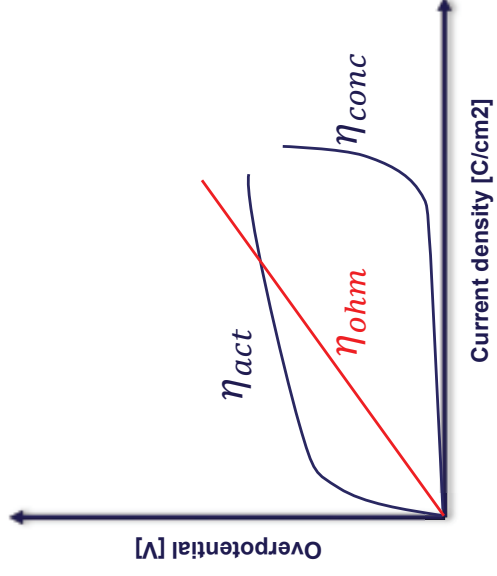


Butler Volmer equation

- Based on this equation we can say that there are different ways increase cell performance.
- Increase reactant concentration (e.g. increase reactant flow rate and pressure)
- Reduce the activation barrier (e.g. better catalyst material)
- Increase temperature (i.e. higher temperature will cause a larger moments in the gas and a higher probability to engage in reactions)
- Increase the reaction sites (i.e. more sites available for electrochemical reactions)

$$j = j_0 \left(\frac{C_R^*}{C_R^{0*}} e^{\alpha n F \eta / (RT)} - \frac{C_P^*}{C_P^{0*}} e^{-(1-\alpha) n F \eta / (RT)} \right)$$

Ohmic overvoltage



Fuel cell charge transport

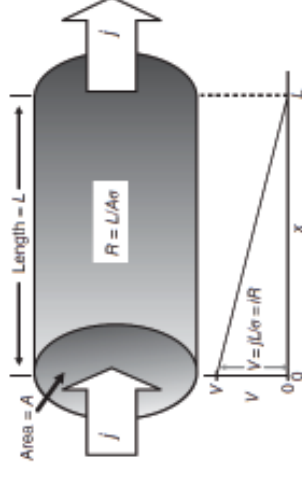
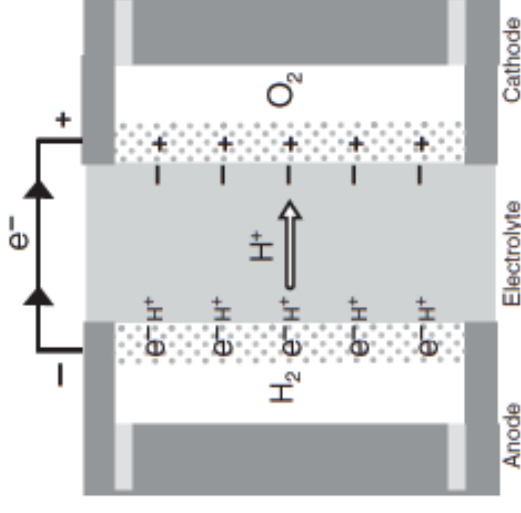
- The current density can be related to charge transport via a relationship with voltage and conductivity, σ

$$j = \sigma \frac{dV}{dx}$$

- We can deduce the voltage as a function of current and resistance:

$$j = \sigma \frac{V}{L} \qquad V = j \frac{L}{\sigma} = i \left(\frac{L}{A\sigma} \right) = iR$$

$i = jA$ R : resistance



Source: Fuel cell fundamentals Chapter 4

Charge transport

- Charge transport is linear and is evident in the electrolyte where there is a reduction of voltage from anode to cathode due to resistance of the electrolyte to the hydrogen ion

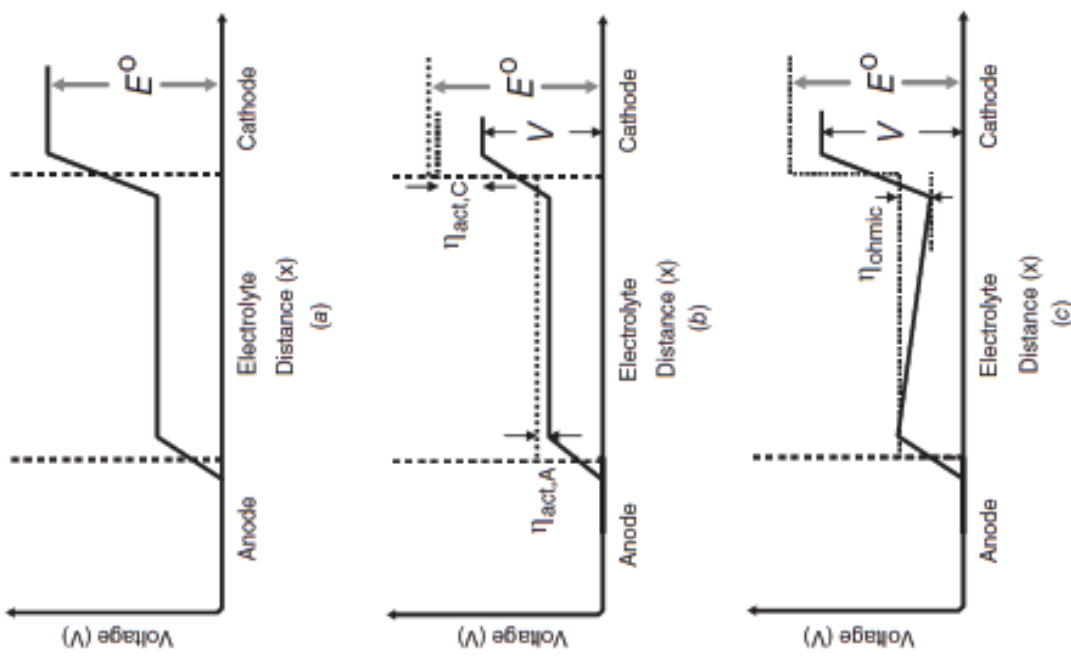
$$\eta_{Ohm} = i \cdot R_{Ohm} = i(R_{Elec} + R_{Ionic})$$

$$R_{Ionic} \gg R_{Elec}$$

$$\eta_{Ohm} = j \cdot ASR$$

ASR: Area specific resistance [$\Omega \cdot cm^2$]

$$ASR = A_{FC} R_{Ohmic} = \frac{L}{\sigma}$$

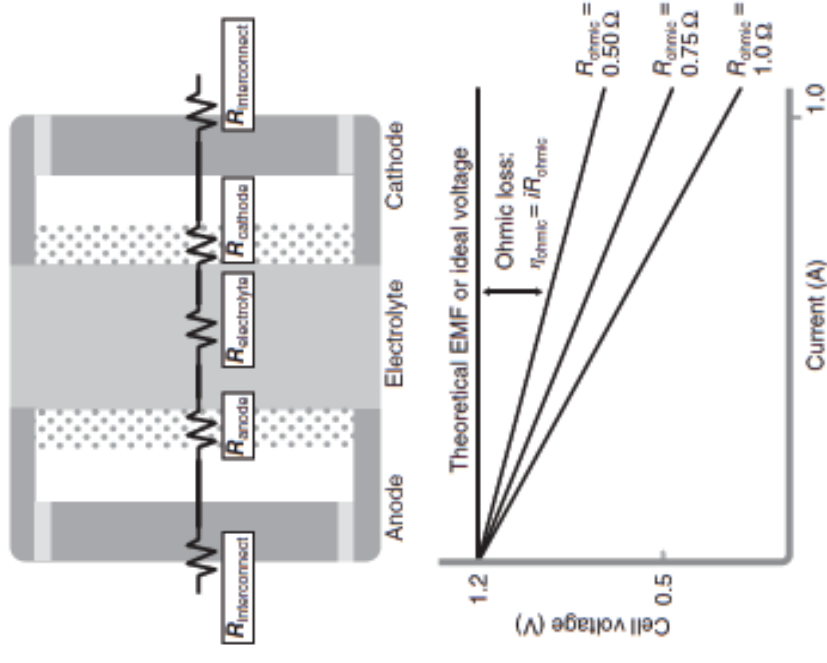


Source: Fuel cell fundamentals Chapter 3



Charge transfer

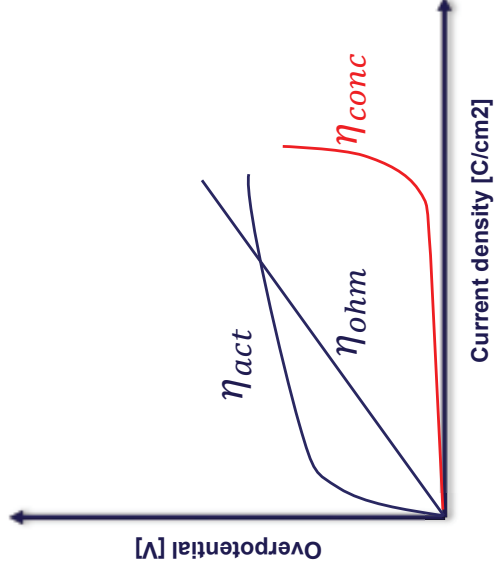
- Resistances in different stacked components can be summed
- The electrolyte accounts for most of the resistance
- Charge transfer reduces cell voltage



Source: Fuel cell fundamentals Chapter 4



Concentration overvoltage



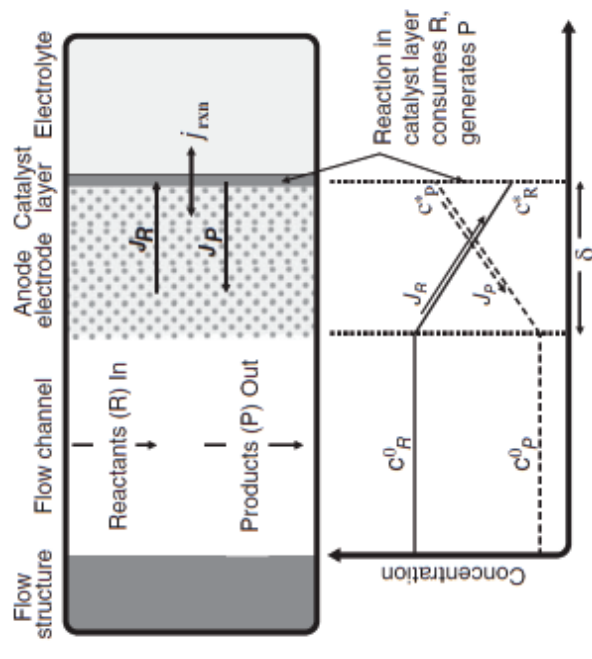
Mass transport in FC

Combination of:

(1) Nernstian losses: Due to depletion of reactants (and their activity) in the channel

$$E = E^0 - \frac{RT}{2F} \ln \frac{a_{H_2O}}{a_{H_2} a_{O_2}^{1/2}}$$

(2) Reaction losses: Activation losses increases due depletion of reactants (J_R reduces along the gas diffusion layer)



Source: Fuel cell fundamentals



Gas depletion along the channel

- Reactants are consumed along the channel
- In the right figure we consider mass transport by diffusion along the GDL and convection along the channel

- The oxygen mass flux is depending on current density produced at the fuel cell electrolyte (Faraday Law):

$$J_{O_2}^{RXN} = M_{O_2} \frac{j(x)}{4F}$$

$$\frac{1}{2} H_2 \Leftrightarrow H^+ + e^-$$

$$H^+ + e^- + \frac{1}{4} O_2 \Leftrightarrow H_2O$$

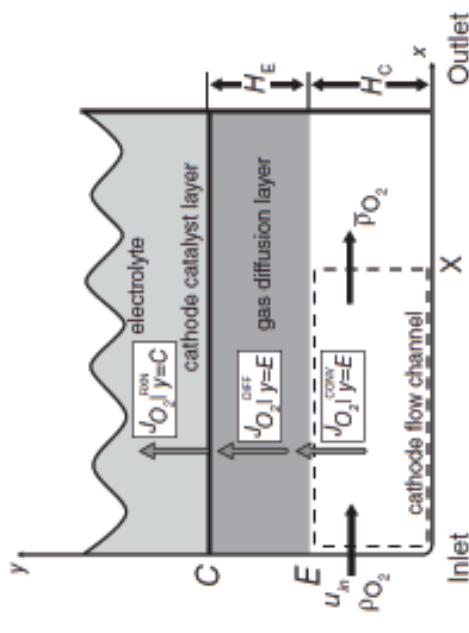
- Oxygen gas consumed by the electrochemical reaction has to be provided by diffusion across the gdl (Fick law):

$$J_{O_2}^{Diff} = -D_{O_2}^{Eff} \frac{\rho_{O_2}^E - \rho_{O_2}^C}{H_E}$$

- Convective mass transport across the channel

$$J_{O_2}^{Conv} = -h_m(\rho_{O_2}^E - \hat{\rho}_{O_2}^{Channel})$$

$$\text{Steady state } J_{O_2}^{RXN} = J_{O_2}^{DIFF} = J_{O_2}^{CONV}$$



Source: Fuel cell fundamentals



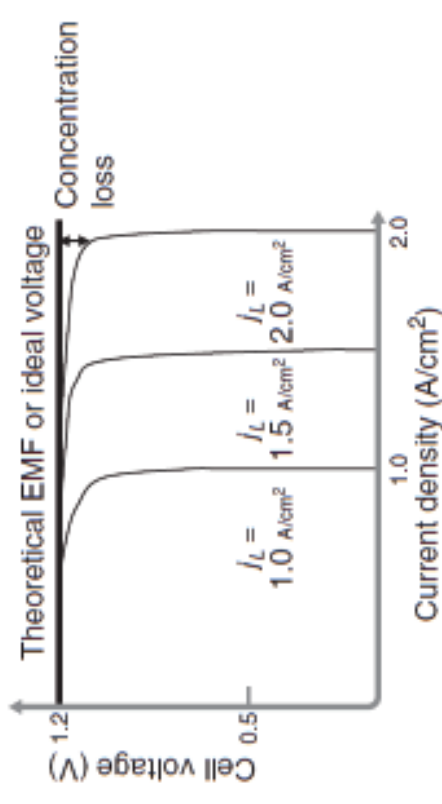
Limiting current density

- When reactants concentration drops to is very low, current cannot be produced. We call this instance “Limit current density”:

$$j_L = nFD^{eff} \frac{C_R^0}{\delta} \leftarrow \text{Gas diffusion layer thickness}$$

- In a fuel cell where hydrogen and oxygen are the reactants

The conversion rate is 0



Source: Fuel cell fundamentals



Cell performance

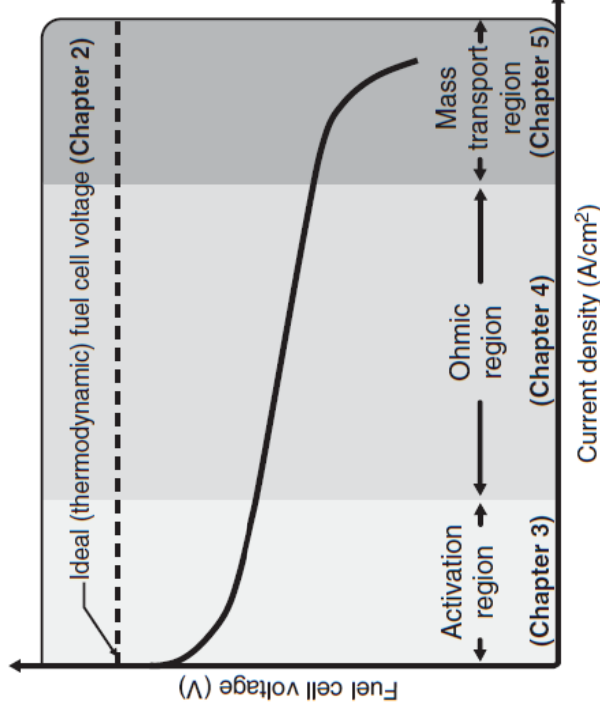
Under load a decrease of cell voltage is experienced

$$V = E - \eta_{act} - \eta_{ohm} - \eta_{conc}$$

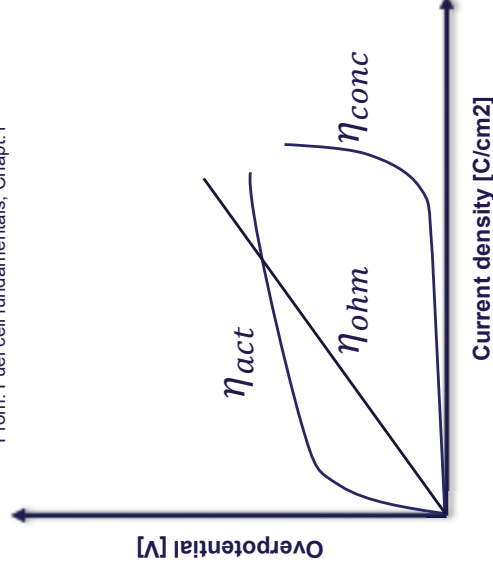
η_{act} : **Activation overvoltage** due to kinetics of reaction. It occurs at all current densities but is dominant at low current density and is associated with sluggish electrode reaction kinetics

η_{ohm} : **Ohmic resistance** due to Ohmic resistance. Resistances to charge conduction through the various cell components demonstrate a linear dependence with current.

η_{conc} : due to mass transport. The cell is essentially “starved” of reactants as they cannot be supplied at the rate at which the electrode reactions demand.

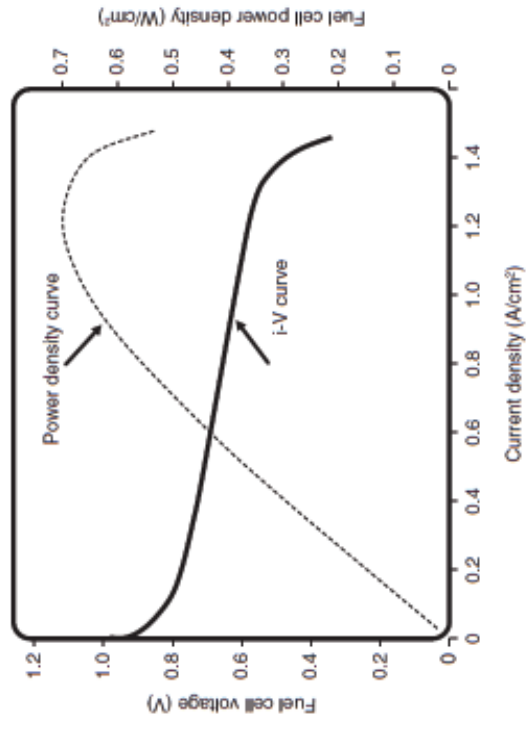


From: Fuel cell fundamentals, Chapt.1



Fuel cell power

$$\text{Power} = I * V$$



From: Fuel cell fundamentals, Chapt.1



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