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# Introduction to Basic Electrochemistry for Fuel Cells and Electrolysis

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- ***Introduction***
  - Thermodynamics and theoretical energy efficiency
  - Reaction mechanisms and kinetics limitations
- ***The Polymer Electrolyte Fuel Cell***
  - Principle of a Polymer Electrolyte Fuel Cell
  - Cell components (membrane, catalysts, etc.)
  - Survey of various applications of PEFC
- ***The Direct Methanol Fuel Cell***
  - Reaction mechanisms and kinetics limitations
  - The fuel crossover problem
- ***Conclusions***

# The Hydrogen/Oxygen Fuel Cell

$H_2 + ½ O_2 \rightarrow H_2O$ + electricity (+ heat)

with $\Delta G°_r$ = - 237 kJ/mole ; $\Delta H°_r$ = - 286 kJ/mole

It looks like the reverse of water electrolysis :

$H_2O$ + electricity $\rightarrow H_2 + ½ O_2$

## Electrical Energy :

**$W_e = - \Delta G° \approx$ 118 MJ/kg $\approx$ 33 kWh/kg**

**Standard e.m.f. : $E° = - \Delta G/nF$ = 1.229 V**

**Theoretical efficiency : $\varepsilon = \Delta G/\Delta H$ = 83% (25°C)**

**C.F. Schönbein, W.R. Grove, Philosophical Magazine, (1839)**

1801 : Discovery of the Volta Cell
1839 : Birth of Georges Leclanché
1859 : Gaston Planté discovered the $Pb/PbO_2$ battery
1867 : Invention of the Leclanché cell

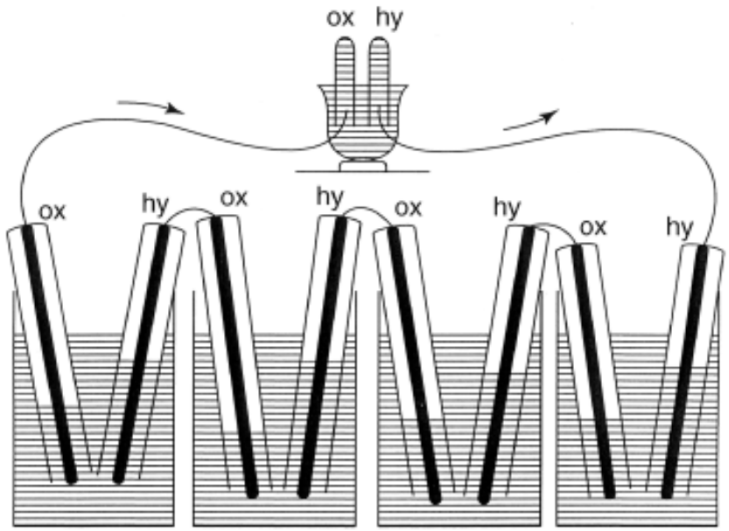
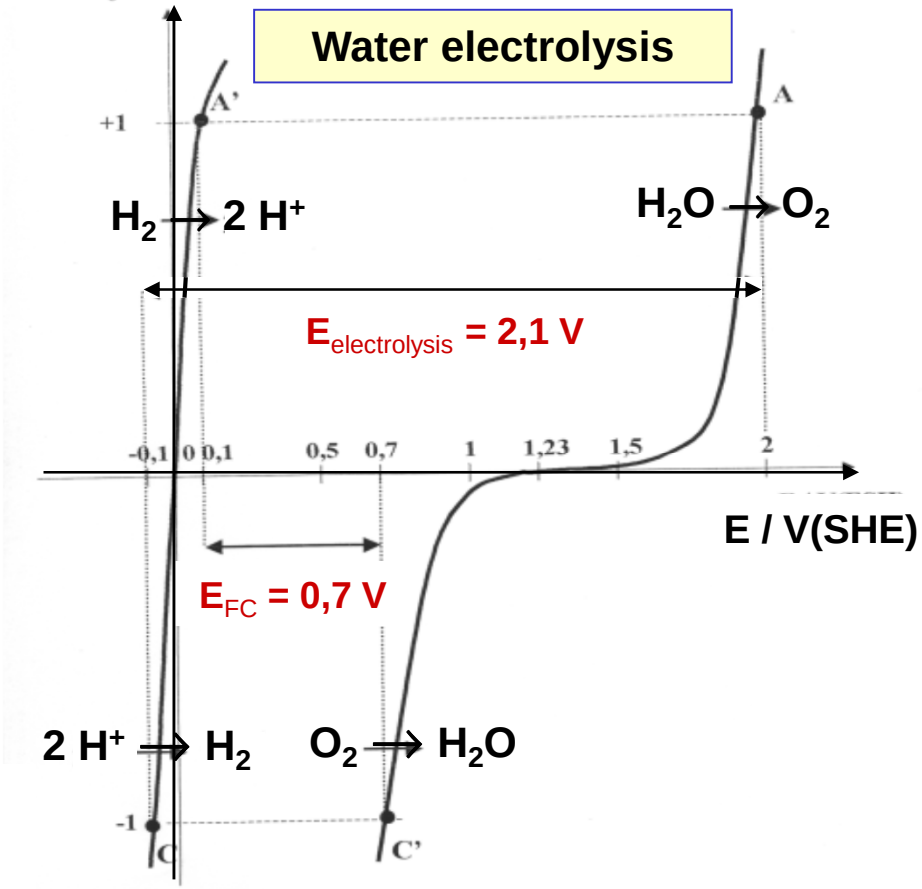



**Figure 15.** Grove's gaseous voltaic battery (1842). (Reproduced from Liebhafsky and Cairns (1968).[8])

# Practical energy efficiency of water electrolysis and fuel cells

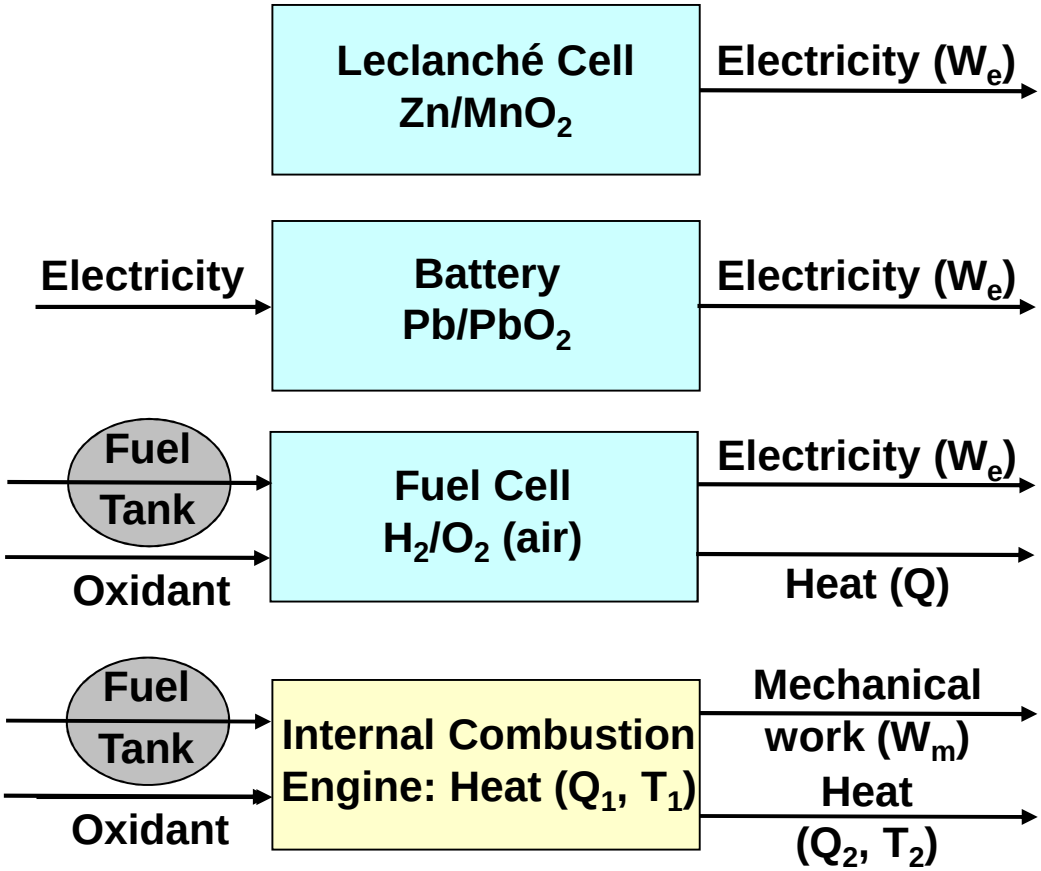
$j = I/S = n\,F\,v_i$ (A/cm²)




Electrolysis efficiency
1.23/2.1 ≈ 59%
Fuel Cell efficiency
0.7/1.23 ≈ 57%

Overall efficiency
(1.23/2.1)x(0.7/1.23 )
= 0.7/2.1 ≈ 33%

- **How does work a fuel cell : it is an electrochemical device which transforms directly the combustion energy of a fuel (- ΔG) into electricity (and heat)**
- **Comparison with other electric source and Internal Combustion Engine (ICE)**




## Energetic Efficiency

**Electrochemical Source**

$\varepsilon = W_e/(-\Delta H) = \Delta G/\Delta H$

$\approx$ 80 to 97 %

Practical efficiency $\approx$ 40 to 60 %

**Thermal Engine (Carnot)**

$\varepsilon_r = W_m/(-\Delta H) = (Q_1-Q_2)/Q_1$

$= 1 - Q_2/Q_1 = 1 - T_2/T_1$

e.g. $\varepsilon = 1 - T_2/T_1 \approx$ 30 to 45 %

Practical efficiency $\approx$ 18 to 30 %

# Thermodynamic Relations

## A key variable in Electrochemistry: the Electrochemical Potential

- ***Definition***
- ***Thermodynamic relations***
  - Equilibrium between 2 charged phases $\alpha$ and $\beta$
  - Nernst potential
  - The Standard Hydrogen Electrode (SHE)
- ***Theoretical energy efficiency***
  - Under standard conditions ($j = 0$)
  - As a function of temperature

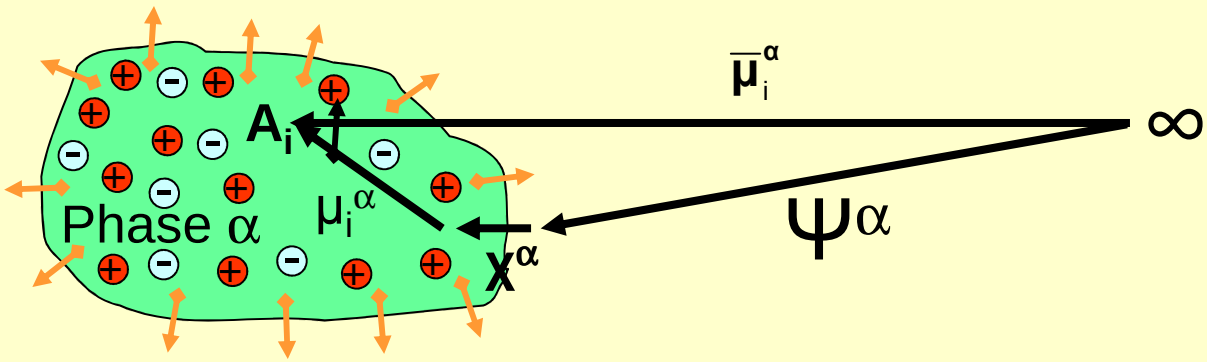
# *Definition of the Electrochemical potential*

Consider a charged phase α containing different species (i) : solvent molecules ($H_2O$), chemical species $A_i$ of charge $z_i$ ($z_i = 0$ for a neutral species, $z_i > 0$ for a cation, $< 0$ for an anion).

The **Electrochemical Potential** $\bar{\mu}_i$ of one mole of species (i) in phase α is the total work to bring species (i) from a standard reference point (with no interaction), usually Infinity (∞), to the bulk phase α :

$$\Psi = \sum_i \frac{q_i}{4\pi\,\varepsilon_o \varepsilon_r\, r_i}$$

$$X = \sum_i \frac{N_i\, \vec{p}_i . \vec{r}_i}{4\pi\,\varepsilon_o \varepsilon_r\, r_i^3}$$

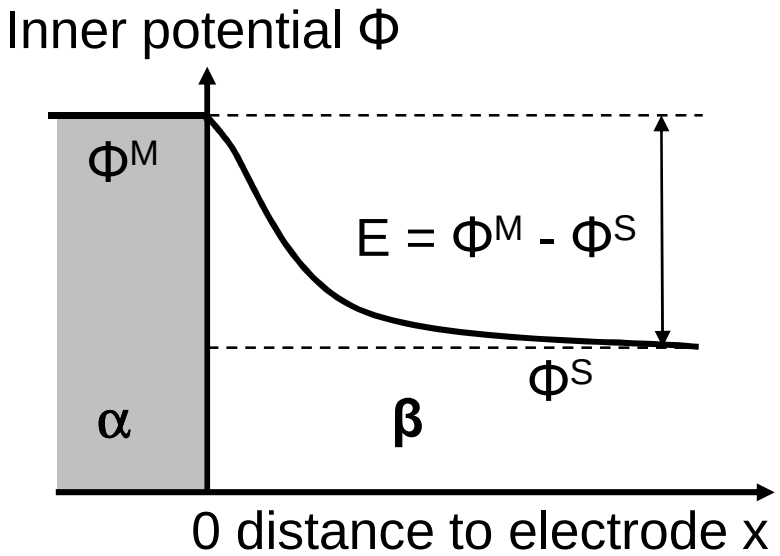



$$\bar{\mu}_i^\alpha = (\partial \Delta \bar{G}^\alpha / \partial N_i)_{T,P,N_j} = \mu_i^\alpha + z_i\, F\, \Phi^\alpha \quad \textbf{with} \quad \Phi^\alpha = \Psi^\alpha + \chi^\alpha$$

$\mu_i^\alpha$ = chemical potential; F = Faraday = $\mathcal{N} e_o$ = 96485 C

Φ = inner potential; Ψ = outer potential; X = surface potential

# Equilibrium at the electrode-electrolyte Interface




$$\bar{\mu}_i^{\alpha} = \bar{\mu}_i^{\beta} \quad \text{i.e.} \quad \Delta\bar{\mu}_i = \bar{\mu}_i^{\alpha} - \bar{\mu}_i^{\beta} = 0$$

$$\bar{\mu}_i^{M} = \mu_i^{M} + z_i F \Phi^{M} = \bar{\mu}_i^{S} = \mu_i^{S} + z_i F \Phi^{S}$$

$$E = \Phi^{M} - \Phi^{S} = (\mu_i^{S} - \mu_i^{M}) / z_i F$$

**E: electrode potential; $[A_i]$: activity**

$$A_i^{z_A} + n_i e^- \longleftrightarrow B_i^{z_B} \text{ with } \mu_i = \mu_i^o + RT\,Ln[A_i] \text{ and } n_i = z_i^A - z_i^B$$

$$\bar{\mu}_A^S + n_i \bar{\mu}_e^M = \bar{\mu}_B^S \longrightarrow E = \Phi^M - \Phi^S = (\mu_A^S - \mu_B^S + \mu_e^M)/nF$$

$$E = (\mu_A^o - \mu_B^o)/nF + RT/nF\,Ln([A]/[B]) + \mu_e^M/F$$

$$E = E^o_{A/B} + RT/nF\,Ln([A]/[B]) + \mu_e^M/F$$

**which looks like a Nernst law, but E is not directly measurable**

Only the potential difference between 2 electrodes, the potential of each is defined by 2 electrochemical systems in equilibrium, is measurable :

$$A_1^{zA1} + n_1\, e^- \longleftrightarrow B_1^{zB1} \quad \text{and} \quad A_2^{zA2} + n_2\, e^- \longleftrightarrow B_2^{zB2}$$

$$E_{eq} = E_2 - E_1 = E^o_{A2/B2} - E^o_{A1/B1} + RT/nF\ Ln([A_2]\,[B_1]/[B_2]\,[A_1])$$

since the electron chemical potential ($\mu_e^M/F$) cancels out with the same metal (Cu) as connecting leads at the extremity of the measuring device.

This corresponds to the overall chemical reaction :

$$a_2\, A_2^{zA2} + b_1\, B_1^{zB1} \longleftrightarrow a_1\, A_1^{zA1} + b_2\, B_2^{zB2}$$

with equilibrium constant $K_e = ([A_1]^{a1}[B_2]^{b2}/\ [A_2]^{a2}[B_1]^{b1}) = \exp(-\Delta G_r/RT)$
where the reaction free energy is related to the chemical potentials:

$$\Delta G_r = \sum_j \Delta N_j\, \mu_j - \sum_i \Delta N_i\, \mu_i \qquad (j = \text{products},\ i = \text{reactants})$$

so that: $E_{eq} = E_2 - E_1 = -\Delta G_r / nF$ or $\Delta G_r + nF\,E_{eq} = \Delta \overline{G}_r = 0$

## Important remarks : Activity and Fugacity

- For an electrolytic solution the activity $[A_i]$ of species (i) is related to its concentration $C_i = N_i/V$ ($N_i$ moles in solution of volume V) by:

  $[A_i] = \gamma_i C_i$ where $\gamma_i$ is the activity coefficient
  ($\gamma_i \rightarrow 0$ if $C_i \rightarrow 0$ ~ ideal solution)

- For a gaseous phase the fugacity of a gaseous species (i) is related to its partial pressure through its chemical potential $\mu_i = \mu_i^o + RT \, Ln \, (f_i / P_o)$ where
$P_o$ is the pressure of a reference state ($P_o$ = 1 bar usually) and $f_i$ is proportional to the partial pressure $p_i$, i.e. $f_i = \gamma_i \, p_i$ with an activity coefficient $\gamma_i \rightarrow 0$ if $p_i \rightarrow 0$ ~ ideal gas)

- In the following, activity and fugacity will be assimilated to concentration and partial pressure, respectively.

# Thermodynamic Relations

$\Delta G < 0$ for spontaneous reaction ; $E_{cell} = E_c - E_a$

$\Delta G = - S\Delta T + V\Delta P + \Sigma\, \mu_i\, \Delta N_i$ with $\mu_i = \mu_i^o + RT\, Ln[A_i]$

Then : $W_e = - nF\, E_{cell} = \Delta F_T + P\, \Delta V = \Delta G_{T,P} = \Delta H - T\, \Delta S$

For an half cell whose electrode potential is controlled by an electrochemical reaction :

$$A_i + n_i\, e^- \longleftrightarrow B_i \quad \text{with} \quad \mu_i = \mu_i^o + RT\, Ln[A_i]$$

$$E_{eq} = E^o_{A/B} + (RT/nF)\, Ln\, ([A_i] / [B_i]) \text{ with}$$

$$E^o_{A/B} = (\mu_A^o - \mu_B^o) / nF = - \Delta G^o/nF \text{ (standard state)}$$

one may define a standard Redox potential $E^o_{A/B}$ in the potential scale of the Standard Hydrogen Electrode (SHE).

The Redox potential of all electrochemical systems can thus be classified in the SHE scale (electrochemical series).

# Reference electrode: the Standard Hydrogen Electrode (SHE)

$2\,H^+ + 2\,e^- \longleftrightarrow H_2$ $\quad$ $Pt/H_2$ (p=1 bar) / ([$H^+$]=1), 25°C

$A_i + n_i\,e^- \longleftrightarrow B_i$

$A_i + n_i/2\,H_2 \longleftrightarrow B_i + n_i\,H^+$ $\quad$ with $\Delta G_r < 0$ or $> 0$

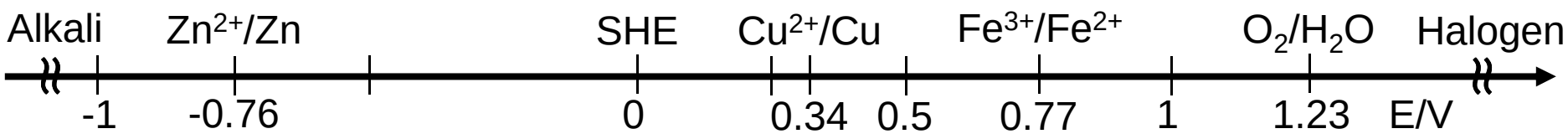
$$\Delta G_r = \sum_i \Delta N_i\,\mu_i - \sum_j \Delta N_j\,\mu_j = \mu_{B_i} + n_i\,\mu^o_{H^+} - (\mu_{A_i} + n_i/2\,\mu^o_{H_2}) = -n_i F\,E_{eq}$$

**which gives:**

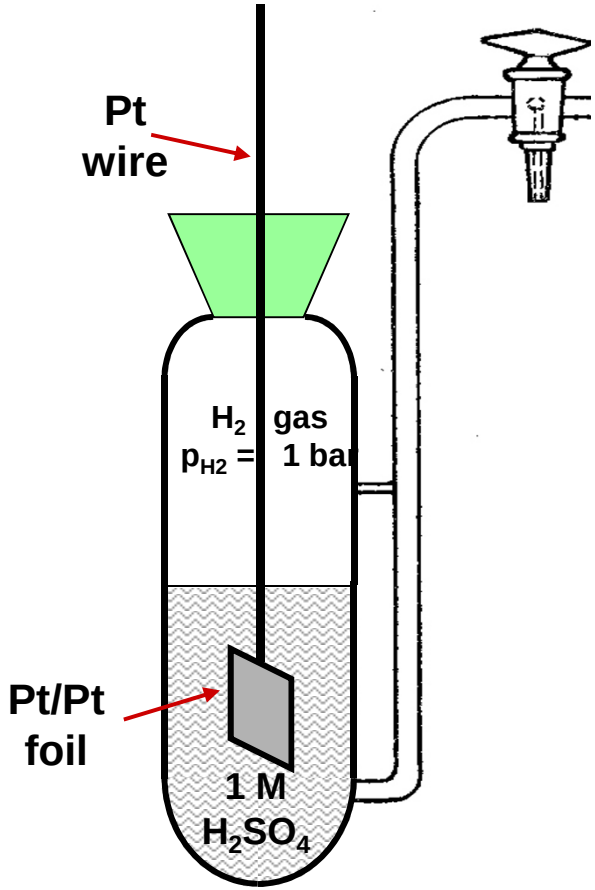
$$E_{eq} = E_{A/B} - E_{SHE} = (\mu_A - \mu_B)/nF - (\mu^o_{H^+} - 1/2\,\mu^o_{H_2})/F = (\mu_A - \mu_B)/nF$$

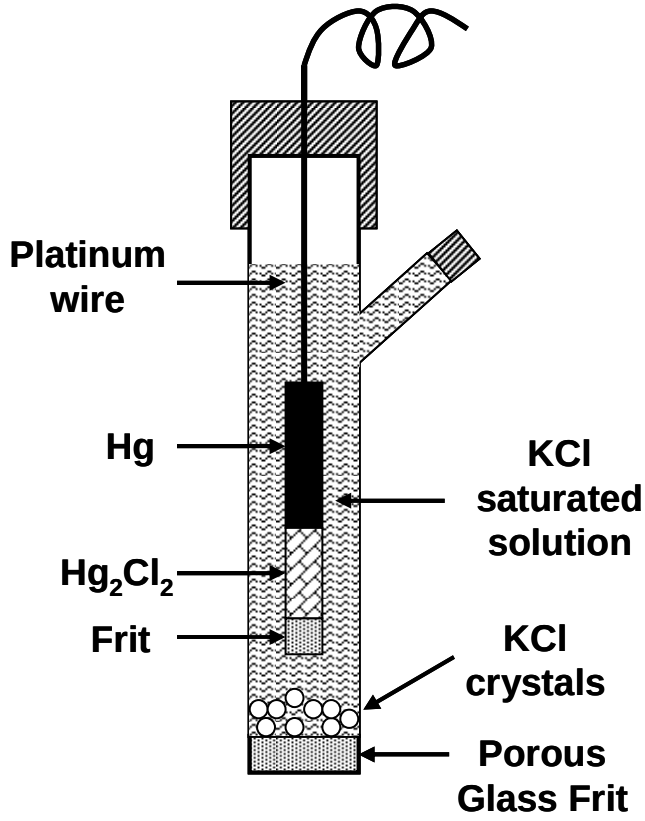
since $E_{SHE} = (\mu^o_{H^+} - 1/2\,\mu^o_{H_2})/F = 0 \quad \forall\, T$ by definition

**Thus** $E_{eq} = E^o_{A/B} + (RT/nF)\,\mathrm{Ln}\,([A_i]/[B_i])$ ≈ **Nernst law**



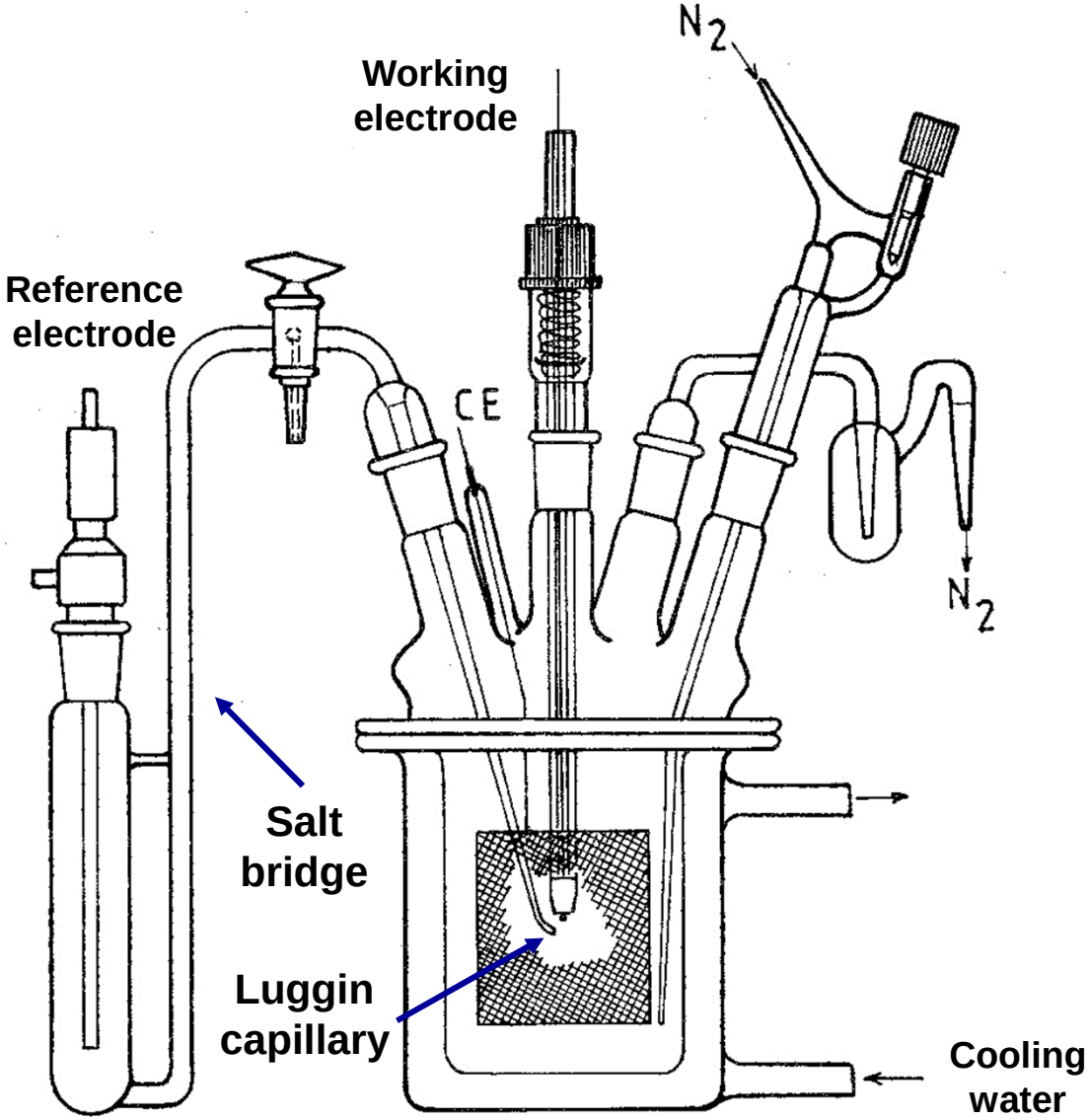
# Reference electrodes:




**Standard Hydrogen Electrode (SHE)** **Saturated Calomel Electrode (SCE)**

**Scheme of a 3-electrode cell for electrochemical measurements with the potential control of the working electrode by a potentiostat**



# Nernst equation for the $H_2/O_2$ system

## Electrochemical half-cell reactions:

$$\begin{cases} H_2 \longrightarrow 2\,H^+ + 2\,e^- \\ 1/2\,O_2 + 2\,H^+ + 2\,e^- \longrightarrow H_2O \end{cases}$$

Overall reaction : $H_2 + ½\,O_2 \longrightarrow H_2O$ Then :

$$E_{eq} = -\,\Delta G_r/nF = -\Delta G^o/2F + (RT/2F)\,Ln[(p_{H_2})\,(p_{O_2})^{½}\,/\,p_{H_2O}]$$

$$E_{eq} = E^o + (RT/2F)\,Ln[(p_{H_2})\,(p_{O_2})^{½}\,/\,p_{H_2O}]$$

with $E^o = -\Delta G^o/2F$ is the standard cell voltage, i.e. $E^o = 1.229$ V at 25°C, where $p_{H_2}$, $p_{O_2}$, and $p_{H_2O}$ are the partial pressure of hydrogen, oxygen and water, respectively.

Therefore by increasing the pressure of reactants ($H_2$ and $O_2$) and decreasing the pressure of the product (water) one can increase the cell voltage. The variation of $E_{eq}$ with T is contained mainly in the entropic term, i.e.$\Delta S_r^o = nF\,(dE^o/dT)$ : temperature coefficient.

# Thermodynamics of Hydrogen Oxidation

Anode

$H_2 \longrightarrow 2\,H^+ + 2\,e^-$ acid medium

$H_2 + 2\,OH^- \longrightarrow 2\,H_2O + 2\,e^-$ alkaline medium

Cathode

$1/2\,O_2 + 2\,H^+ + 2\,e^- \longrightarrow H_2O$ acid medium

$1/2\,O_2 + H_2O + 2\,e^- \longrightarrow 2\,OH^-$ alkaline medium

---

$H_2 + 1/2\,O_2 \longrightarrow H_2O$ overall reaction

with $\Delta G° = -237$ kJ and $\Delta H° = -286$ kJ/mole $H_2$ (standard state)

Energy efficiency under standard conditions: $\varepsilon_r^{cell} = \Delta G° / \Delta H° = 0.829$

$$E^{\circ}_{eq} = E^{+}_{c} - E^{-}_{a} = -\frac{\Delta G^{\circ}}{nF} = \frac{237 \times 10^{3}}{2 \times 96500} = 1{,}23 \text{ Volt}$$

$$W_e = -\frac{\Delta G^{\circ}}{3600 \times M} = \frac{237 \times 10^{3}}{3600 \times 2} = 32.9 \approx 33 \text{ kWhr/kg}$$

# Reversible energy efficiency (I = 0)

For a Fuel Cell working under standard conditions (25℃, 1 bar) :

$$\varepsilon_r^{cell} = \frac{W_e}{(-\Delta H)} = \frac{n\,F\,E_{eq}}{(-\Delta H)} = \frac{\Delta G}{\Delta H} = 1 - \frac{T\,\Delta S}{\Delta H} = \frac{237}{286} = 83\%$$

For a Thermal Engine, such as an ICE, working between an hot source $Q_1$ at 350℃ and a cold source $Q_2$ at 80℃ :

$$\varepsilon_r^{thermal} = \frac{W_r}{(-\Delta H)} = 1 - \frac{Q_2}{Q_1} = 1 - \frac{T_2}{T_1} = 1 - \frac{353\,(80°C)}{623\,(350°C)} = 43\%$$

# Thermodynamic data for the $H_2/O_2$ combustion reaction (kJ/mol) as a function of temperature

| Physical state of water | T/K | ΔH | ΔG | $E_{eq}$ | Efficiency (ε=ΔG/ΔH) |
|---|---|---|---|---|---|
| Standard state | 298 | -285.83 | -237.17 | 1.229 | 0.830 |
| Liquid | 328 | -284.88 | -232.32 | 1.203 | 0.816 |
| Liquid | 348 | -284.25 | -229.14 | 1.187 | 0.806 |
| Liquid | 368 | -283.61 | -225.99 | 1.171 | 0.797 |
| | | | | | |
| Gaseous | 298 | -241.82 | -228.58 | 1.185 | 0.945 |
| Gaseous | 400 | -242.84 | -223.90 | 1.160 | 0.922 |
| Gaseous | 500 | -243.82 | -219.05 | 1.135 | 0.898 |
| Gaseous | 600 | -244.75 | -214.01 | 1.109 | 0.874 |
| Gaseous | 700 | -245.62 | -208.81 | 1.082 | 0.850 |
| Gaseous | 800 | -246.42 | -203.50 | 1.055 | 0.826 |
| Gaseous | 900 | -247.16 | -198.09 | 1.027 | 0.801 |
| Gaseous | 1000 | -247.82 | -192.60 | 0.998 | 0.777 |

# Thermodynamic data for the $H_2/O_2$ combustion reaction (kJ/mol): $H_2 + 1/2\ O_2 \longrightarrow H_2O$

**In the liquid state of water (273 K < T < 373 K) :**

$$\Delta H = \Delta G + T\,\Delta S = \Delta H_{HHV} = \Delta H_{LHV} + \Delta Q_{Cond}$$

so that in the standard state (T = 298.15 K, p =1 bar) :

$$\Delta Q_{Cond} = \Delta H_{HHV} - \Delta H_{LHV} = -\ 285.8 + 241.8 = -\ 44\ \text{kJ/mol}$$

$$\boldsymbol{\varepsilon_r^{HHV} = \Delta G^\circ / \Delta H^\circ_{HHV} = 237/286 = 0.83}$$

**In the gaseous state of water (T > 373 K) :**

$$\Delta H = \Delta G + T\,\Delta S = \Delta H_{LHV}$$

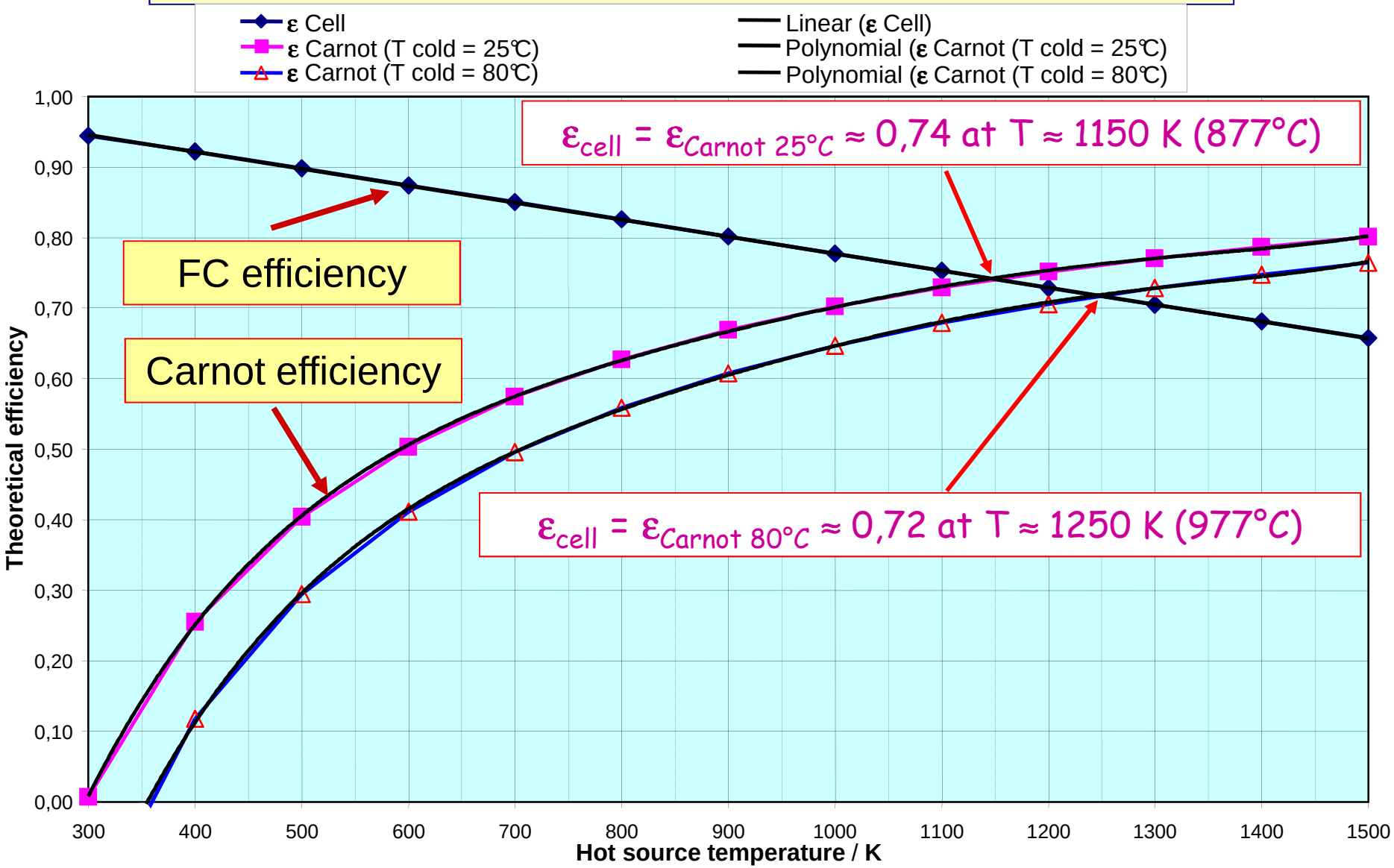
so that at e.g. T = 400 K (≈ 127℃, p =1 bar) :

$$\Delta H = \Delta H_{LHV} = -\ 242.84\ \text{kJ/mol}$$

$$\boldsymbol{\varepsilon_r^{LHV} = \Delta G^\circ / \Delta H^\circ_{LHV} = 224/243 = 0.92}$$

**HHV = High Heating Value ; LHV = Low Heating Value ; $\Delta Q_{Cond}$ = Heat of Condensation**

# Theoretical energy efficiency (FC vs. Carnot)



# Kinetics Relations

## A typical kinetics law in Electrochemistry: the Butler-Volmer equation

- ***Kinetics of a simple electrochemical reaction***

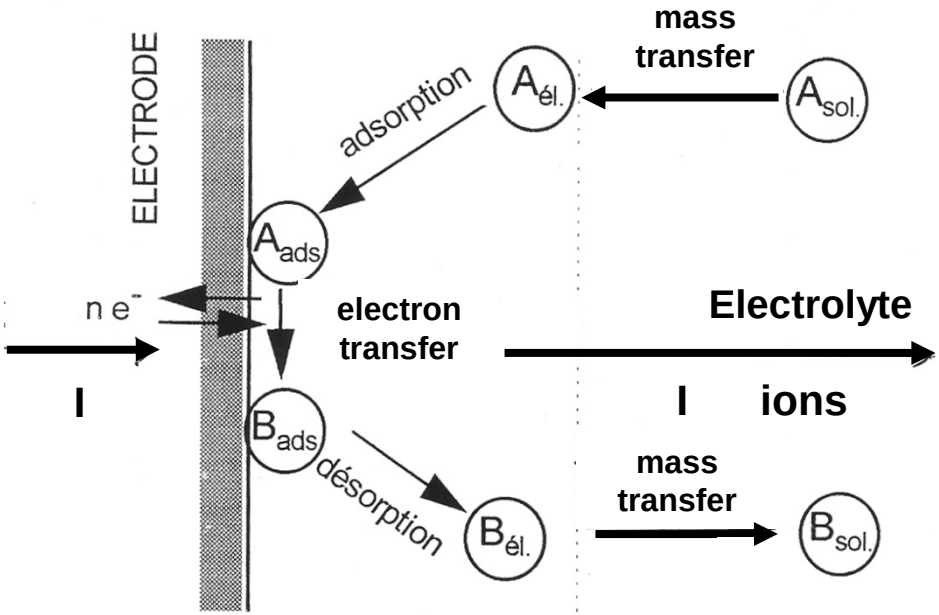
- ***The Butler-Volmer law***
  - Establishment of the Butler-Volmer law
  - Mass transfer limitations
  - Cell voltage vs. current density curves
  - Energy efficiency under working conditions ($j \neq 0$)

# Kinetic relations for a simple electrochemical reaction : $A_i + n_i\, e^- \longleftrightarrow B_i$

$$I = dQ/dt = nF\,(|dN_A|/dt) = nF\,(|dN_B|/dt)$$

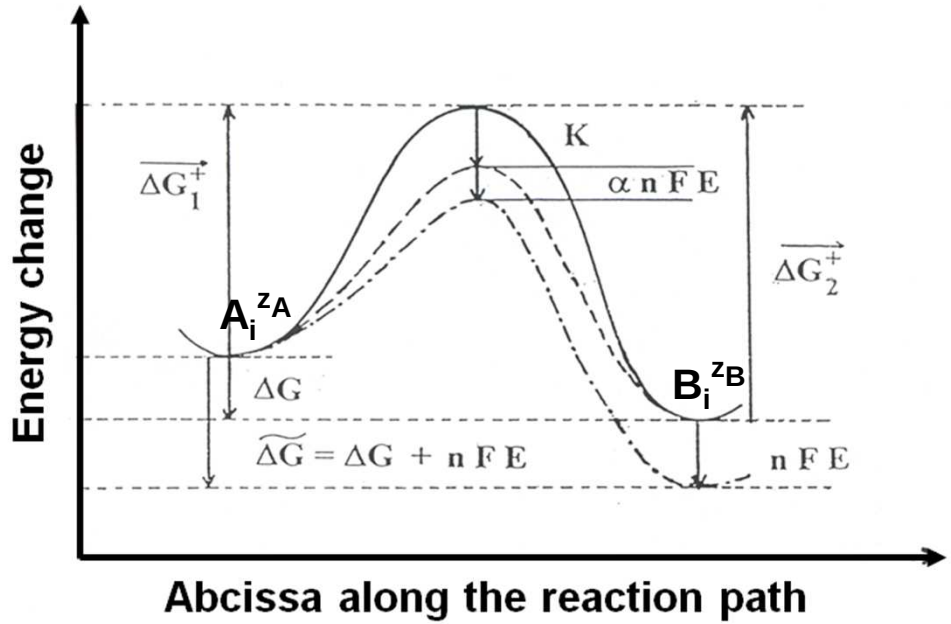
$$I = nF\,v \text{ with the reaction rate } v = (|dN_A|/dt)$$

**I < 0 for a reduction reaction ;  I > 0 for an oxidation reaction**




**Reaction mechanism**

# Kinetics of a charge transfer reaction (heterogeneous reaction) : $A_i^{z_A} + n_i\, e^- \longleftrightarrow B_i^{z_B}$




## Activation barrier for an electrochemical reaction (K is the decrease in activation energy due to the electrode catalyst)

$$\Delta\overline{G} = \Delta G + nFE \neq 0 \quad \Rightarrow I \neq 0 \quad \begin{cases} \Delta\overline{G} \leq 0 \;\Rightarrow\; I \leq 0 : \text{reduction reaction (cathodic)} \; I_c = -\, nF\, v_c \\ \Delta\overline{G} \geq 0 \;\Rightarrow\; I \geq 0 : \text{oxidation reaction (anodic)} \; I_a = nF\, v_a \end{cases}$$

## Expression of the reaction rates with the Arrhenius law

$$v_c = k_c(E,T)\, S\, C_A^{elec} = k_c^o\, S\, C_A^{elec} \exp(-\Delta\overline{G}_c^+ / RT) \text{ with } \Delta\overline{G}_c^+ = \Delta G_c^+ + \alpha\, nF\, E$$

$$v_a = k_a(E,T)\, S\, C_B^{elec} = k_a^o\, S\, C_B^{elec} \exp(-\Delta\overline{G}_a^+ / RT) \text{ with } \Delta\overline{G}_a^+ = \Delta G_a^+ - (1-\alpha)\, nF\, E$$

**where $\alpha$ is the charge transfer coefficient ($0 < \alpha < 1$), i.e. the fraction of electrical energy which activates the reduction reaction ($A \rightarrow B$), and $(1-\alpha)$ nFE activating the oxidation reaction ($B \rightarrow A$). Thus:**

$$j = I/S = nF\left[k_a^o\, C_B^{elec} \exp(-\Delta G_a^+ / RT) \exp[(1-\alpha)nFE/RT] - k_c^o\, C_A^{elec} \exp(-\Delta G_c^+ / RT) \exp[-\alpha nFE/RT]\right]$$

- At equilibrium $v_a = v_c$ and $j = 0$, so that $j_a = -j_c$, $E = E_{eq}$ and $C_i^{elec} = C_i^o$ :

$$j_a = -j_c = j_o = nFk_a^o C_B^o \exp(-\Delta G_a^{+o} RT) \exp[(1-\alpha)nFE_{eq}/RT] = nFk_c^o C_A^o \exp(-\Delta G_c^{+o}/RT) \exp(-\alpha nFE_{eq}/RT)$$

Then $E_{eq} = E^o_{A/B} + RT/nF\, Ln(C_A^o/C_B^o)$ with $E^o_{A/B} = \exp(-\Delta G^o/RT) \approx$ **Nernst law**

and $\mathbf{j_o = nF\,(k_c^o)^{1-\alpha}\,(k_a^o)^{\alpha}\,(C_A^o)^{1-\alpha}\,(C_B^o)^{\alpha} = nF\,k_s^o\,(C_A^o)^{1-\alpha}\,(C_B^o)^{\alpha}}$

- Out of equilibrium $j = j_a - j_c \neq 0$. Dividing j by $j_o$ one obtains:

$j(\eta) = j_o\,[(C_B^{elec}/C_B^o) \exp\{(1-\alpha)(nF/RT)\eta\} - (C_A^{elec}/C_A^o) \exp\{-\alpha(nF/RT)\eta\}]$ or

$\mathbf{j(\eta) = j_o\,[\exp\{(1-\alpha)(nF/RT)\eta\} - \exp\{-\alpha(nF/RT)\eta\}]}$ (no mass transfer limitation)

**Butler-Volmer law with $\eta = E - E_{eq}$ the overvoltage and $j_o$ the exchange current density**

# Expression of the Butler-Volmer law in some limiting cases

- Very often $\alpha = ½$ so that $j(\eta) = 2\, j_o\, sh[(nF/2RT)\, \eta]$ ~ **hyperbolic sinus curve**
If $\alpha = 0$ or 1 then $j(\eta) = j_o\, [\exp(nF/RT\, \eta) - 1]$ or $j(\eta) = j_o\, [1 - \exp(nF/RT)\, \eta]$

- For $|\eta| << RT/nF$ ($\approx$ 25/n mV at 25°C) then $j(\eta) = j_o\, (nF/RT)\, \eta = \eta/R_t$ or $\eta = R_t\, j$ with $R_t = RT/nFj_o$ the charge transfer resistance (~ **Ohm's law**)

- For $\eta >> RT/nF$ then $j(\eta) = j_o\, \exp[(1-\alpha)nF/RT\, \eta]$ or $\eta = RT/(1-\alpha)nF\, Ln(j/j_o)$
and for $\eta << -RT/nF$ then $j(\eta) = -j_o\, \exp[-\alpha\, nF/RT\, \eta]$ or $\eta = -RT/\alpha nF\, Ln(-j/j_o)$
i.e. $\eta = a \pm b \log |j|$ ~ **Tafel law** with the Tafel slopes $b_i = 2.3\, RT/\alpha_i nF$ in V $dec^{-1}$

- For the Hydrogen Oxidation Reaction (HOR) the exchange current density is very high ($j_o \approx 1$ mA $cm^{-2}$) so that the reaction is reversible and the Ohm's law does apply (linear relationship between overvoltage and current density)

- For the Oxygen Reduction Reaction (ORR) the exchange current density is small ($j_o \approx 1$ µA $cm^{-2}$ ) so that the reaction is irreversible (one may neglect the reverse reaction, i.e. water oxidation) and one may write:
$j(\eta) = -j_o\, \exp(-\alpha\, nF/RT\, \eta)$ or $\boldsymbol{\eta_c^{act} = -RT/\alpha_c nF\, Ln(|j|/j_o)}$ ~ activation overvoltage

# Mass transfer limitations : concentration overvoltage

The reaction kinetics can be controlled by the mass transfer (diffusion, migration, convection) of the reacting species inside the electrolytic phase, so that the current density is proportional to the mass flux density $J_i$ of species (i): $j_i = |z_i|F\ J_i$ with $J_i = 1/S\ \Delta N_i/\Delta t = C_i\ v_i$ ($v_i$ is the velocity).

$J_i$ can be expressed by the **Nernst-Planck equation**:

$$\vec{J}_i = -\frac{C_i D_i}{RT}\vec{\nabla}\overline{\mu}_i + C_i\vec{v}_i^{ext} = -D_i\vec{\nabla}C_i - \frac{z_i F}{RT}D_i C_i\vec{\nabla}\Phi + C_i\vec{v}_i^{ext}$$

In the following we will neglect the contribution of the **migration current** $j_i^m = |z_i|\ Fu_i\ C_i\ \mathcal{E} = |z_i|\ \lambda_i\ C_i\ \mathcal{E} = \kappa_i\ \mathcal{E}$ and the **convection current** $j_i^{cv} = |z_i|F\ C_i\ v_i^{ext}$ so that we will only consider the diffusion process (**Fick's laws**) of species (i):

$$\vec{J}_i^d = -D_i\ \vec{\nabla}C_i \quad \text{(Fick's 1st law)} \qquad \text{and } \vec{j}_i^d = |z_i|F\ \vec{J}_i^d$$

$$\frac{\partial C_i}{\partial t} = -\operatorname{div}\vec{J}_i^d = D_i\ \Delta C_i \quad \text{(Fick's 2nd law} \approx \text{mass conservation)}$$

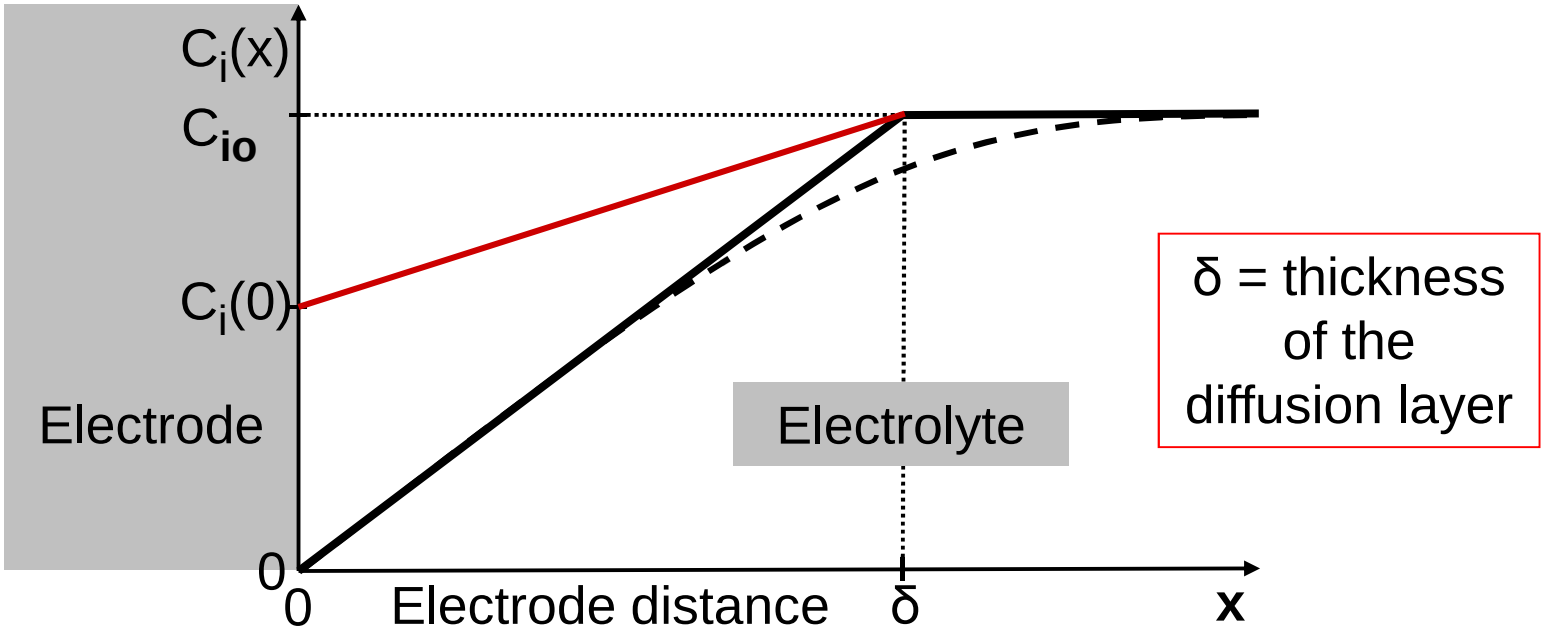
with $D_i$ = diffusion coefficient; $u_i = z_i F D_i/RT$ = electric mobility;
$\lambda_i = Fu_i$ = molar conductivity; $K_i = |z_i|\ \lambda_i\ C_i$ = ionic conductivity;
$\mathcal{E} = -\nabla\Phi$ = electrical field

# Resolution of Fick's equations (in the approximation of a semi-infinite linear diffusion, under steady state conditions):

$$J_i^d = -D_i\,\partial C_i/\partial x, \quad \partial C_i/\partial t = 0 \quad \text{and } j_i^d = \pm|z_i|F\,D_i\,|\partial C_i/\partial x|_{x=0}$$

$$\partial C_i(x,t)/\partial t = D_i\,\partial^2 C_i(x,t)/\partial x^2 = 0 \text{ leading to } (\partial C_i/\partial x) = \frac{C_{io} - C_i(0)}{\delta}$$

$$\text{and } C_i(x) = (\partial C_i/\partial x)_{x=0}\,x + C_i(0) = \frac{C_{io} - C_i(0)}{\delta}x + C_i(0) \quad (0 \le x \le \delta)$$



# Mass transfer limitations : concentration overvoltage

For the electrochemical reaction, $\mathbf{A_i + n_i\, e^- \longleftrightarrow B_i}$, the rate of which is controlled only by diffusion, the current density can be written as:

$$|j| = |j_i^d| = nF\, D_i\, |c_{io} - c_i(0)| / \delta, \text{ with } n = z^A - z^B$$

with $c_i(0)$ the concentration at the electrode surface.

For high rate, i.e. high current densities, all the reacting species arriving at the electrode surface are immediately consumed and their activity (concentration) becomes 0. Thus the concentration gradient reaches a maximum value, leading to a limiting current density:

$$j_{li} = nF\, D_i\, c_{io} / \delta$$

with $D_i$ (in $m^2/s$ or $cm^2/s$) the diffusion coefficient of species (i), $c_{io}$ its concentration in the bulk of electrolyte and $\delta$ the thickness of the diffusion layer (in the approximation of a semi-infinite linear diffusion).

# Mass transfer limitations : concentration overvoltage

By doing the ratio of j with $j_{li}$ one may obtain:

$$|j|/j_{li} = [c_{io} - c_i(0)] / c_{io} = 1 - c_i(0)/c_{io} = 1 - p_i(0)/p_{io}$$

The superficial concentration (or partial pressure for gaseous species) is :

$$c_i(0)/c_{io} = p_i(0)/p_{io} = 1 - |j| / j_{li}$$

For a very fast transfer reaction, only limited by mass transfer, the Nernst equation does apply at the surface, leading to concentration overvoltages:

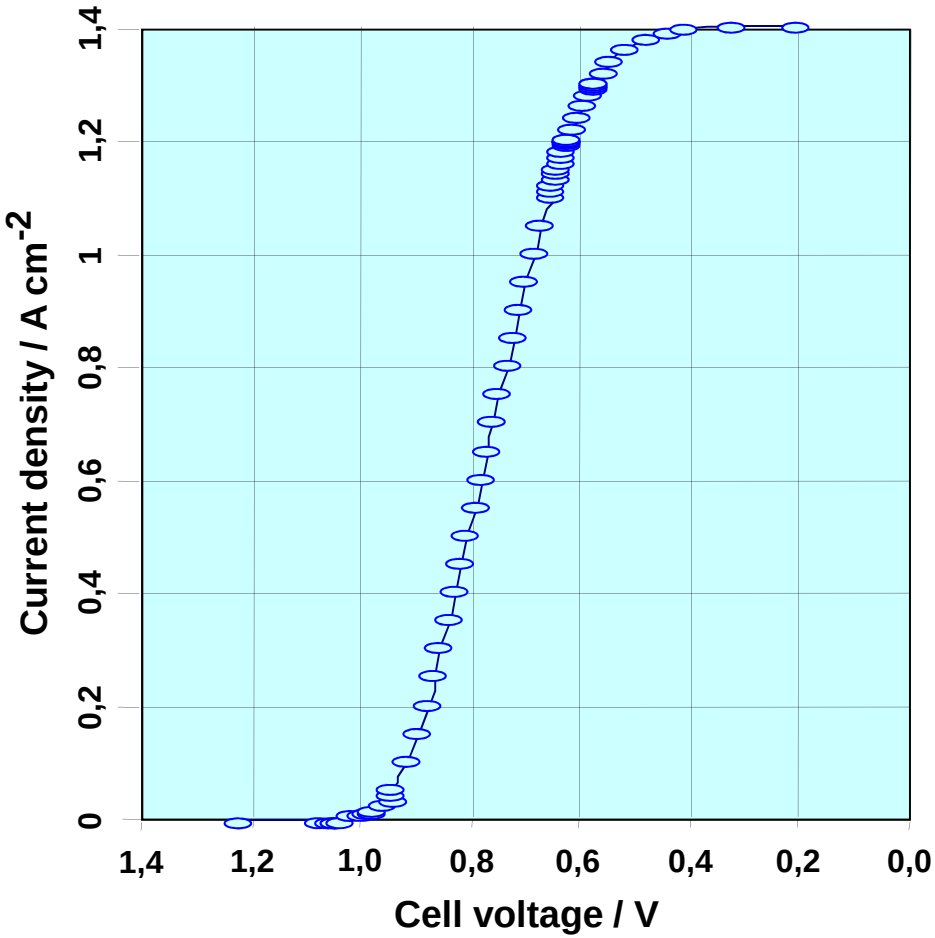
$$E_{eq} = E^o_{A/B} + (RT/nF)\ Ln\ (c_A(0)/c_{Ao} / c_B(0)/c_{Bo}) = E_{1/2} + (RT/nF)\ Ln[(j-j_{lc})/(j_{la}-j)]$$

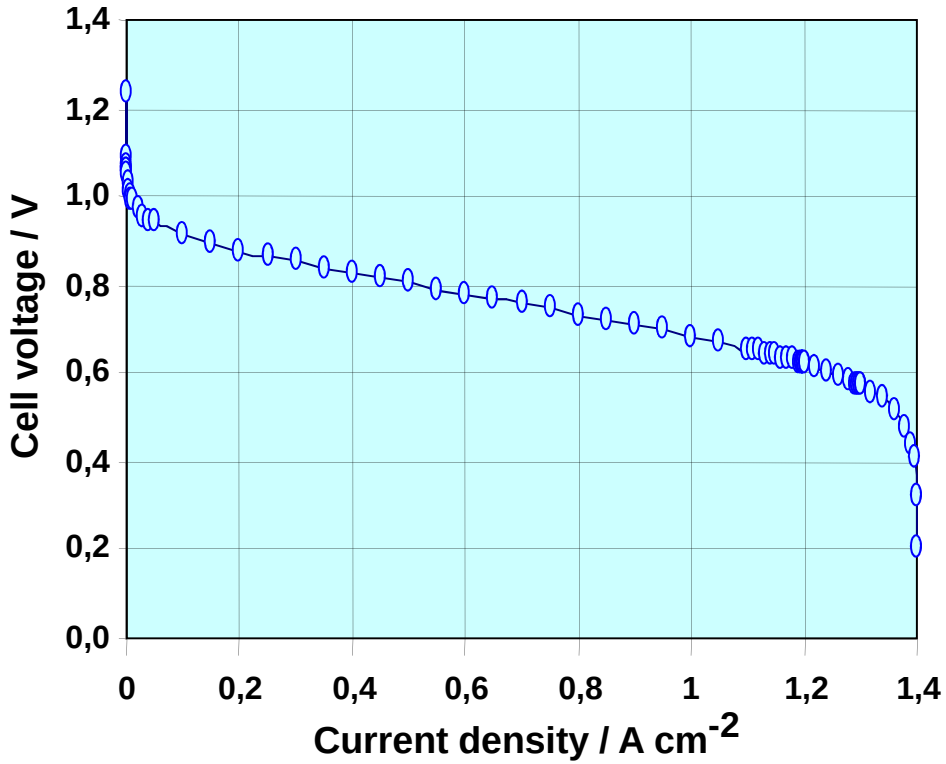
(equation of a **Polarographic Wave** assuming the same diffusion coefficients)

$$\left|\eta_a^{conc}\right| = \frac{RT}{n_a F}\left|\ln\left(1-\frac{|j|}{j_{l_a}}\right)\right| \text{ at the anode}$$

$$\left|\eta_c^{conc}\right| = \frac{RT}{n_c F}\left|\ln\left(1-\frac{|j|}{j_{l_c}}\right)\right| \text{ at the cathode}$$

# E(j) curves limited by mass transfer (diffusion)




Tafel slope $b_c$ = 60 mV/dec.

Limiting current $j_{lc}$ = 1.4 A/cm$^2$

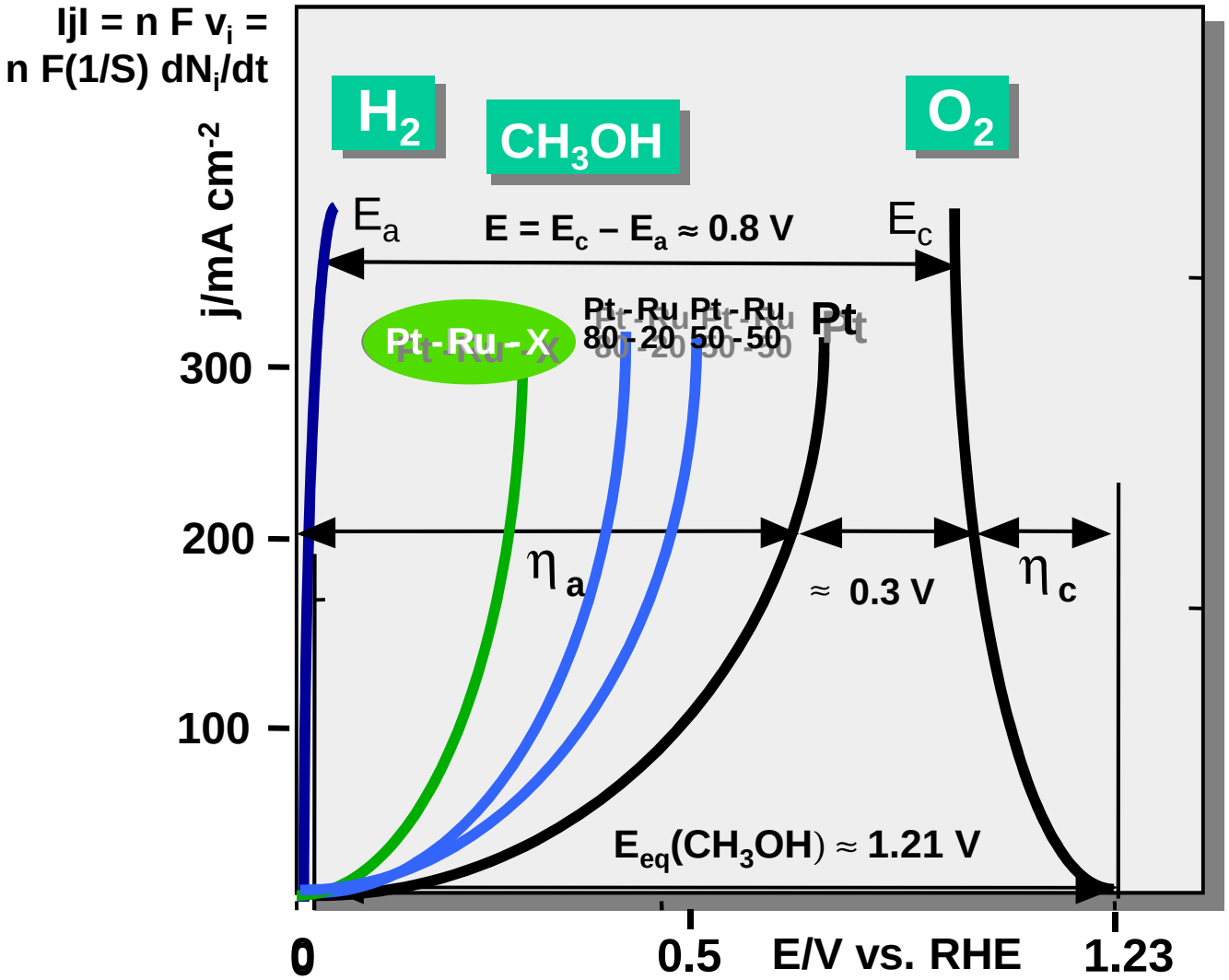
# Cell voltage vs. current density E(j) curves

The cell voltage vs. current density characteristics for the $H_2/O_2$ fuel cell, taking into account charge transfer overvoltages, concentration overvoltages and ohmic drop can thus be written as:

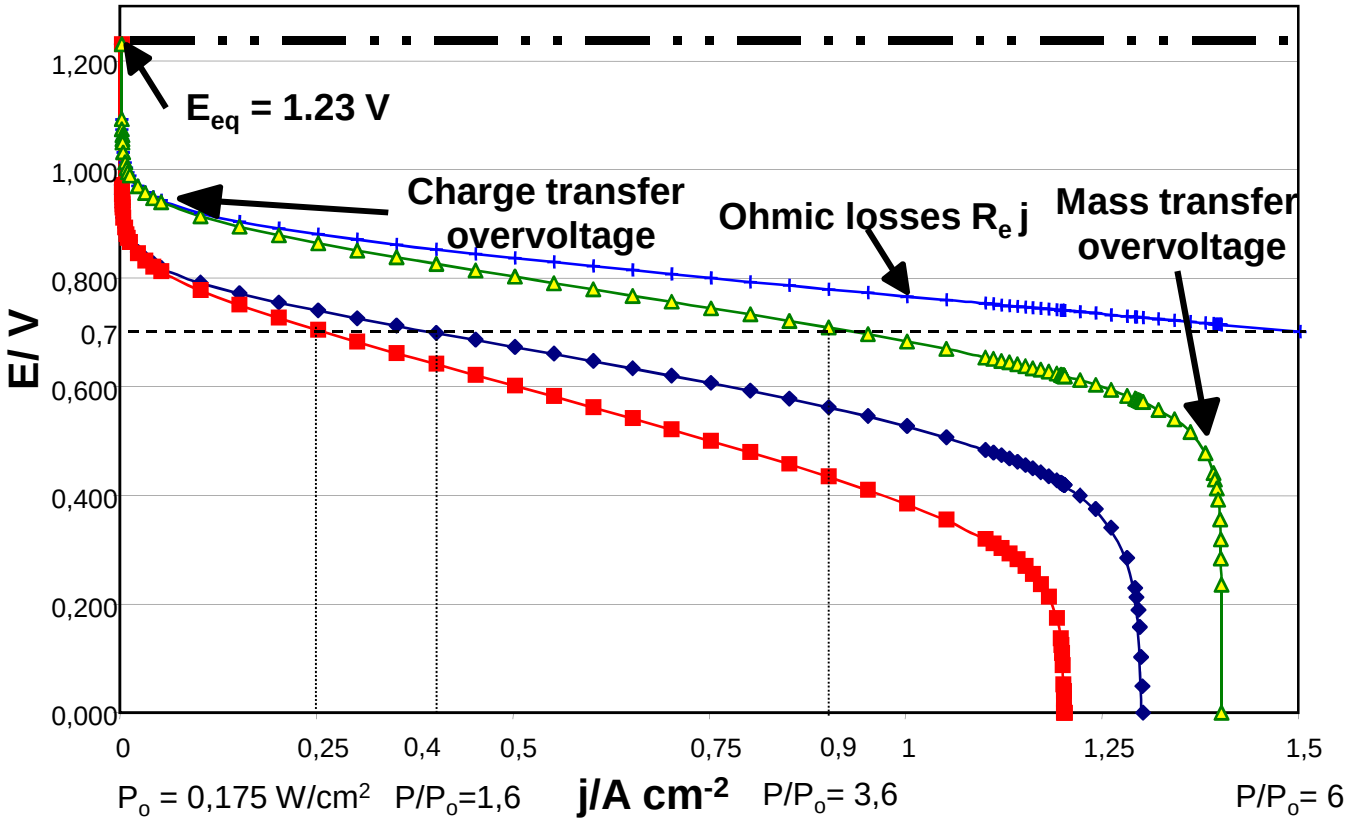
$$E(j) = E_c(j) - E_a(j) - R_e|j| = E_{eq} - (|\eta_a^{act}(j)| + |\eta_a^{conc}(j)| + |\eta_c^{act}(j)| + |\eta_C^{conc}(j)|) - R_e|j|$$

$$E(j) = E_{eq} + \frac{RT}{\alpha nF}\ln\frac{j_{o_a} \times |j_{o_c}|}{j^2} + \frac{RT}{nF}\ln\left[\left(1 - \frac{|j|}{j_{l_a}}\right) \times \left(1 - \frac{|j|}{j_{l_c}}\right)\right] - R_e|j|$$

# Current density vs. electrode potential for electrochemical reactions involved in fuel cells



## Cell voltage vs. current density E(j) curves




$$E(j) = E_c(j) - E_a(j) - R_e\, j = E_{eq} - (|\eta_c(j)| + |\eta_a(j)| + R_e\, |j|)$$

# Energy efficiency under working conditions ($j \neq 0$)

$$E(j) = E_c^+(j) - E_a^-(j) - R_e|j| = E_{eq} - (|\eta_a(j)| + |\eta_c(j)| + R_e|j|) \quad \langle \quad E_{eq} = E_{eq}^+ - E_{eq}^-$$

$$\begin{cases} \eta_a = E^-(j) - E^-_{eq} & \text{with } \eta_a > 0 \text{ (fuel oxidation)} \\ \eta_c = E^+(j) - E^+_{eq} & \text{with } \eta_c < 0 \text{ (oxygen reduction)} \end{cases}$$

$R_e$ = electrolyte and interface resistance

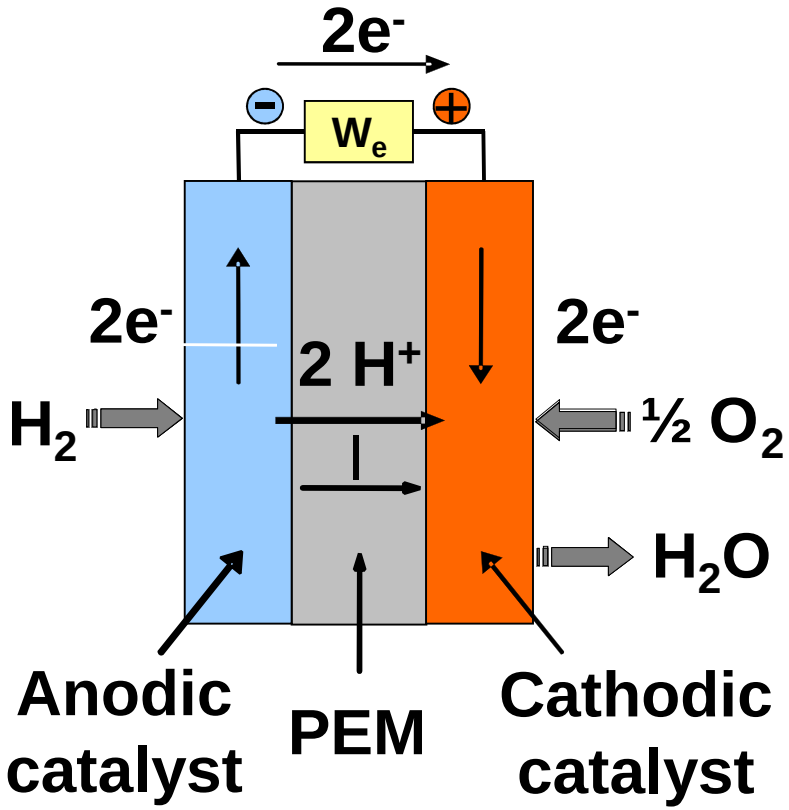
$$\varepsilon_E = \frac{E(j)}{E_{eq}} = 1 - \frac{(|\eta_a(j)| + |\eta_c(j)| + R_e|j|)}{E_{eq}} = \frac{0.7}{1.23} \approx 57\% \text{ and } \varepsilon_F = \frac{j}{j_m} = \frac{n_{exp}}{n}$$

$$\boldsymbol{\varepsilon_{cell} = \frac{n_{exp}\, F\, E(j)}{(-\Delta H)} = \frac{n\, F\, E_{eq}}{(-\Delta H)} \times \frac{E(j)}{E_{eq}} \times \frac{n_{exp}}{n} = \varepsilon_r^{cell} \times \varepsilon_E \times \varepsilon_F}$$

**$\varepsilon_{cell}$ = 0.83 x 0.57 x 0.99 ≈ 47% and $\varepsilon_{CHP}$ ≈ 85 to 95%**

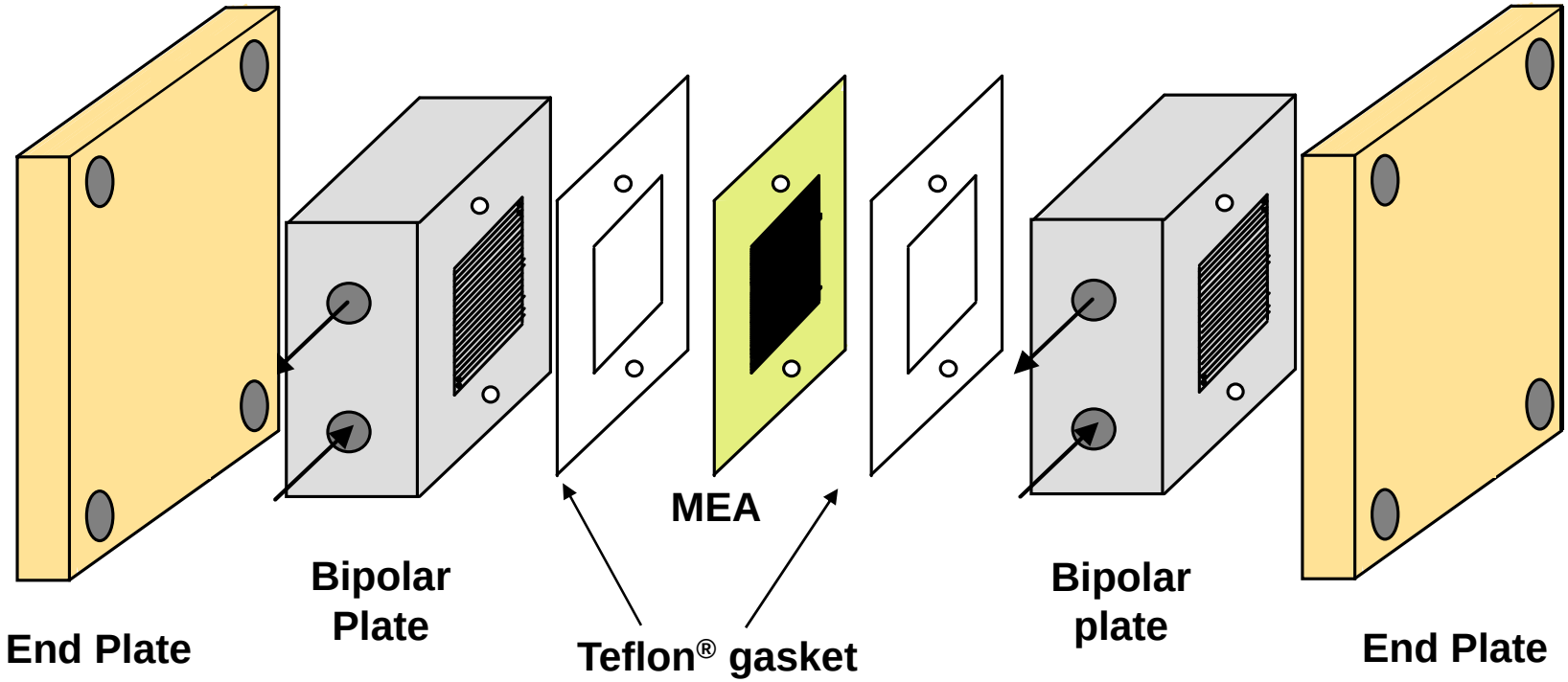
- **The Polymer Electrolyte Fuel Cell (PEFC)**
  - Principle of a Polymer Electrolyte Fuel Cell
  - Cell components (membrane, catalysts, etc.)

# *Schematic representation of a PEFC elementary cell*



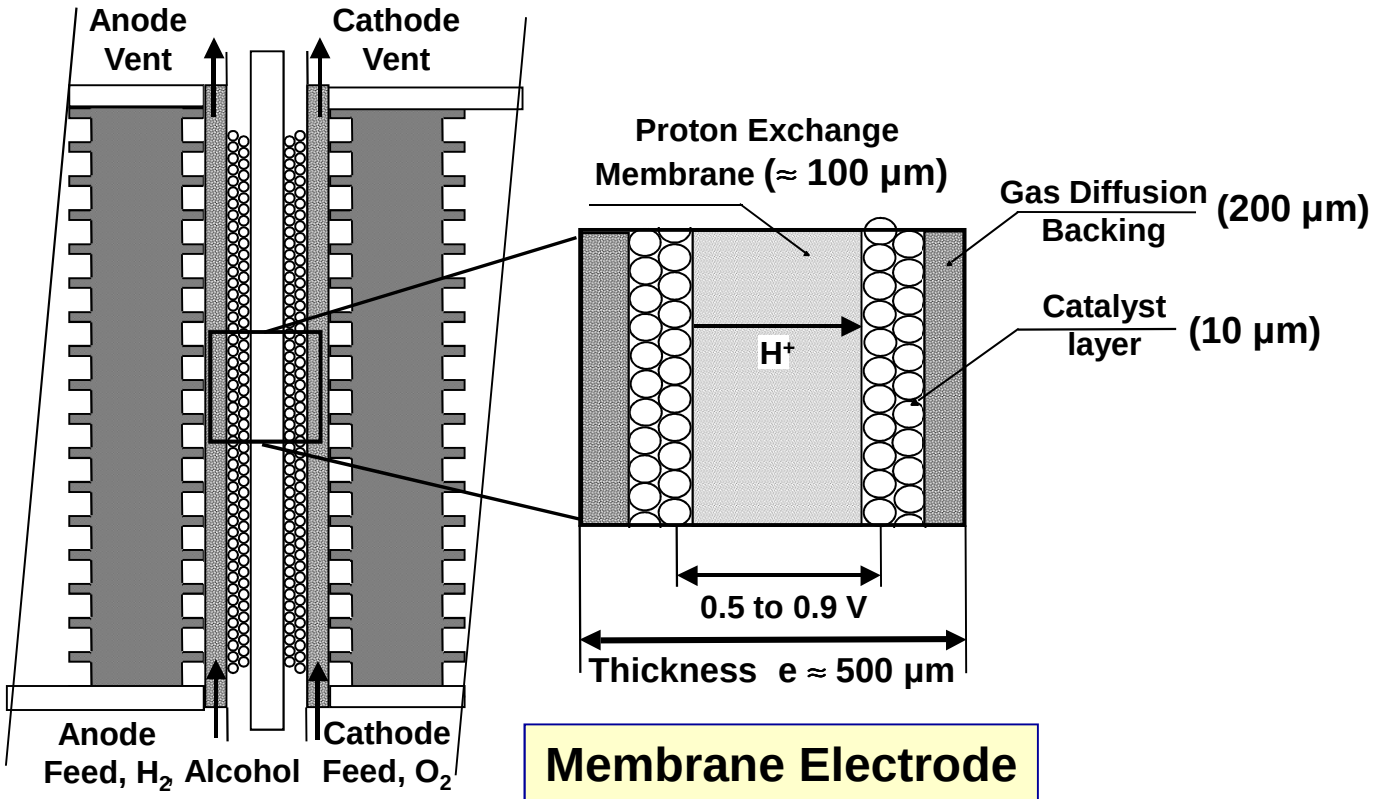

**Overall reaction: $H_2 + ½\ O_2 \rightarrow H_2O$ with $\Delta G < 0$**

# Polymer Electrolyte Fuel Cell (PEFC)



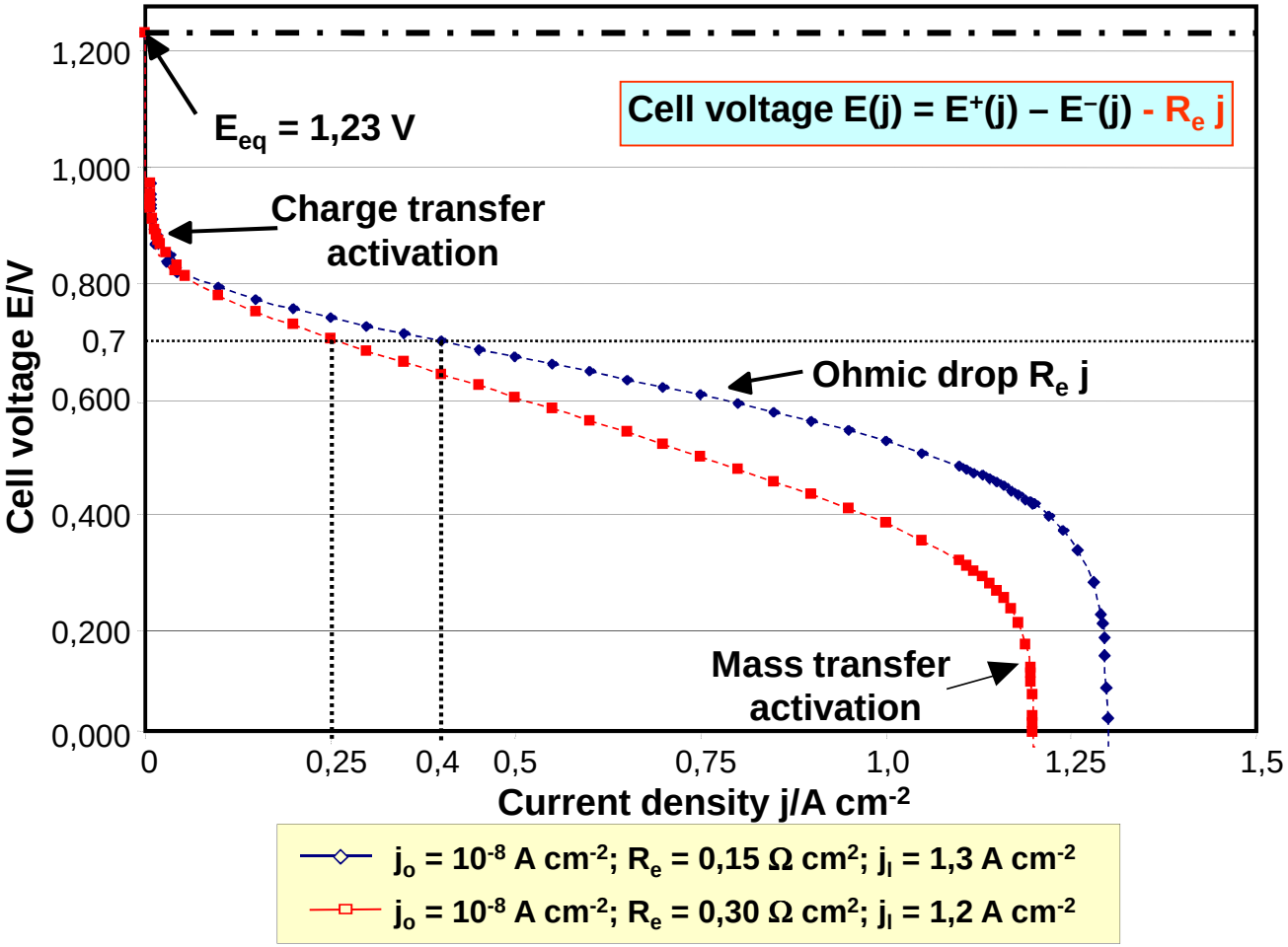

## Schematic representation of a PEFC elementary cell

# Schematic representation of the Membrane Electrode Assembly (MEA)



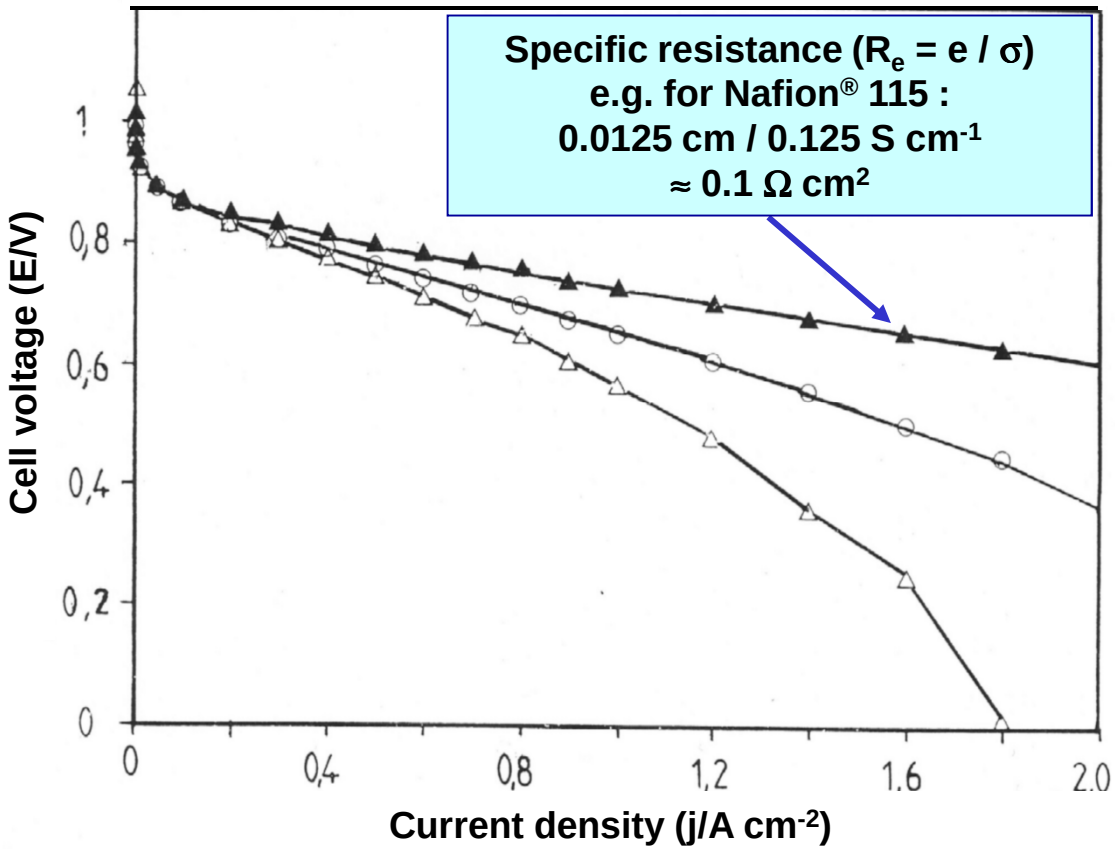

**Membrane Electrode Assembly (MEA)**

# Influence of the membrane specific resistance ($R_e = e/\sigma$) on the cell voltage-current density characteristics E(j)

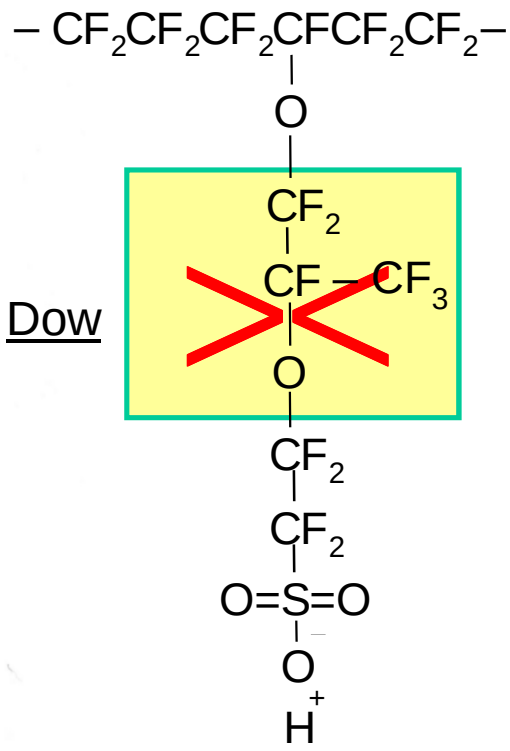


# E(j) characteristics of a PEFC elementary cell with different membranes :

▲ Dow (e = 125 µm) ; o Nafion® 115 (e = 125 µm) ; Δ Nafion® 117 (e = 175 µm)

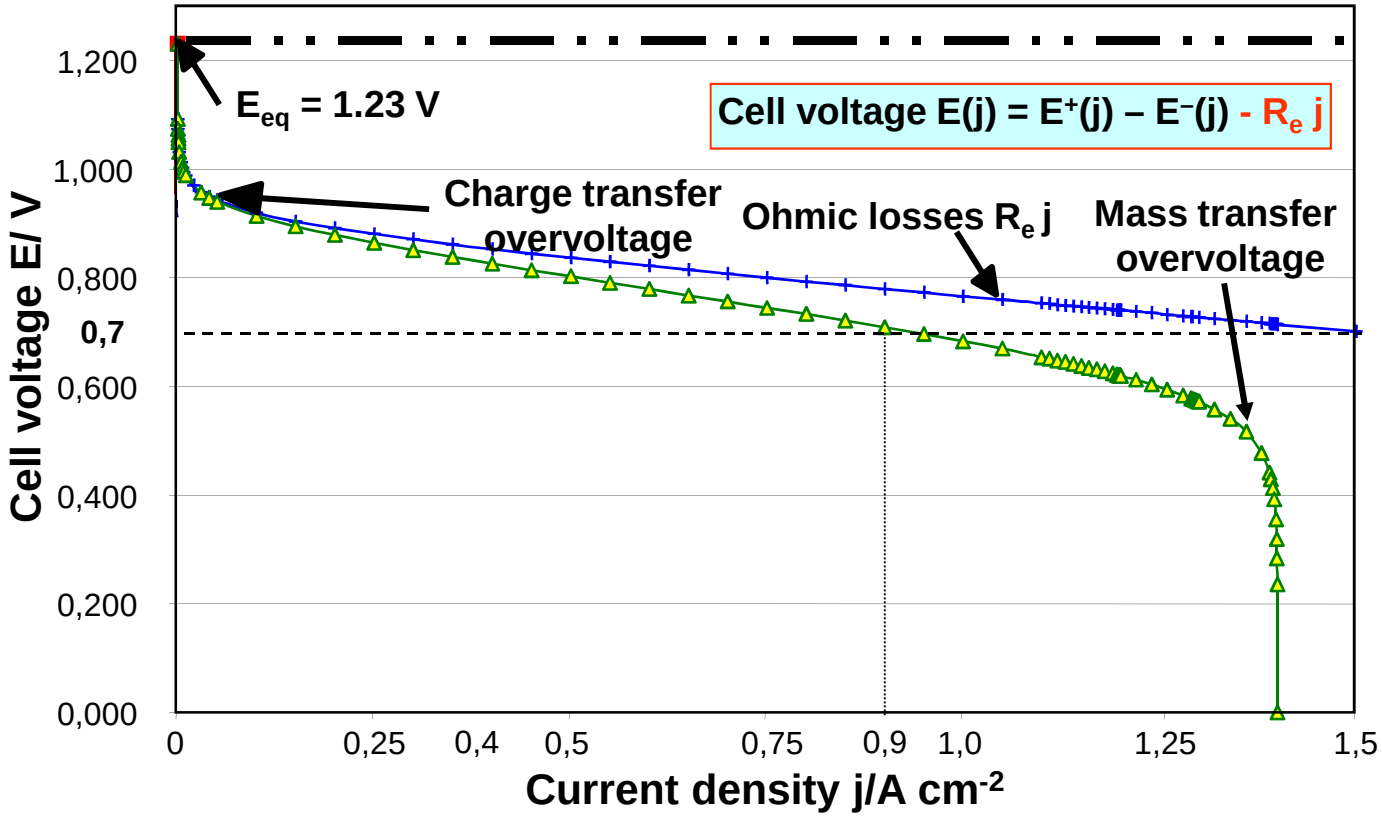



DUPONT NAFION®




After K. Prater (Ballard), J. Power Sources, 29 (1990) 239

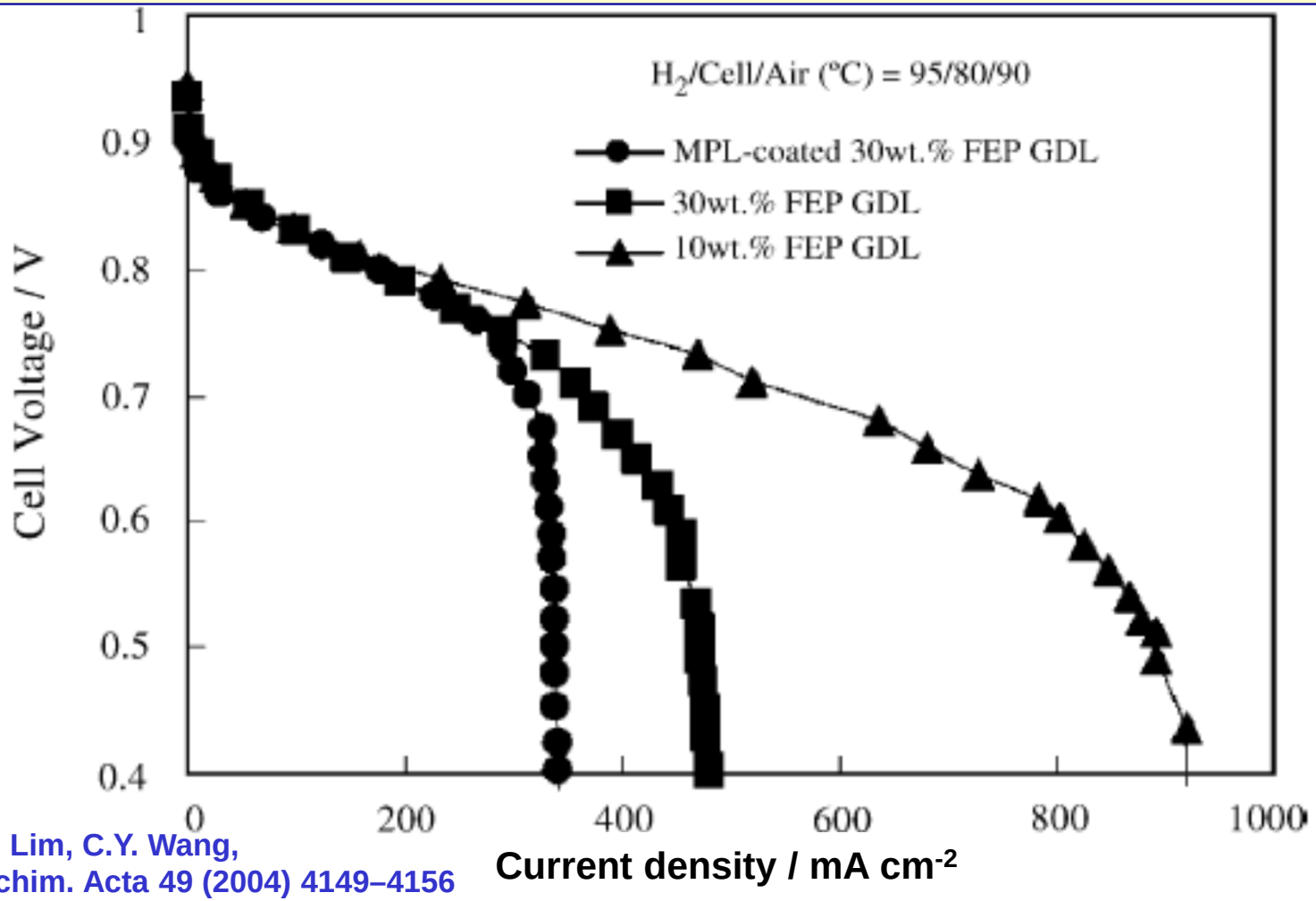
# Influence of the mass transfer limitations (limiting current density $j_l$) on the cell voltage-current density characteristics E(j)




$j_0 = 10^{-6}$ A cm$^{-2}$ ; $R_e = 0{,}10\ \Omega$ cm$^2$ ; $j_l = 2{,}2$ A cm$^{-2}$

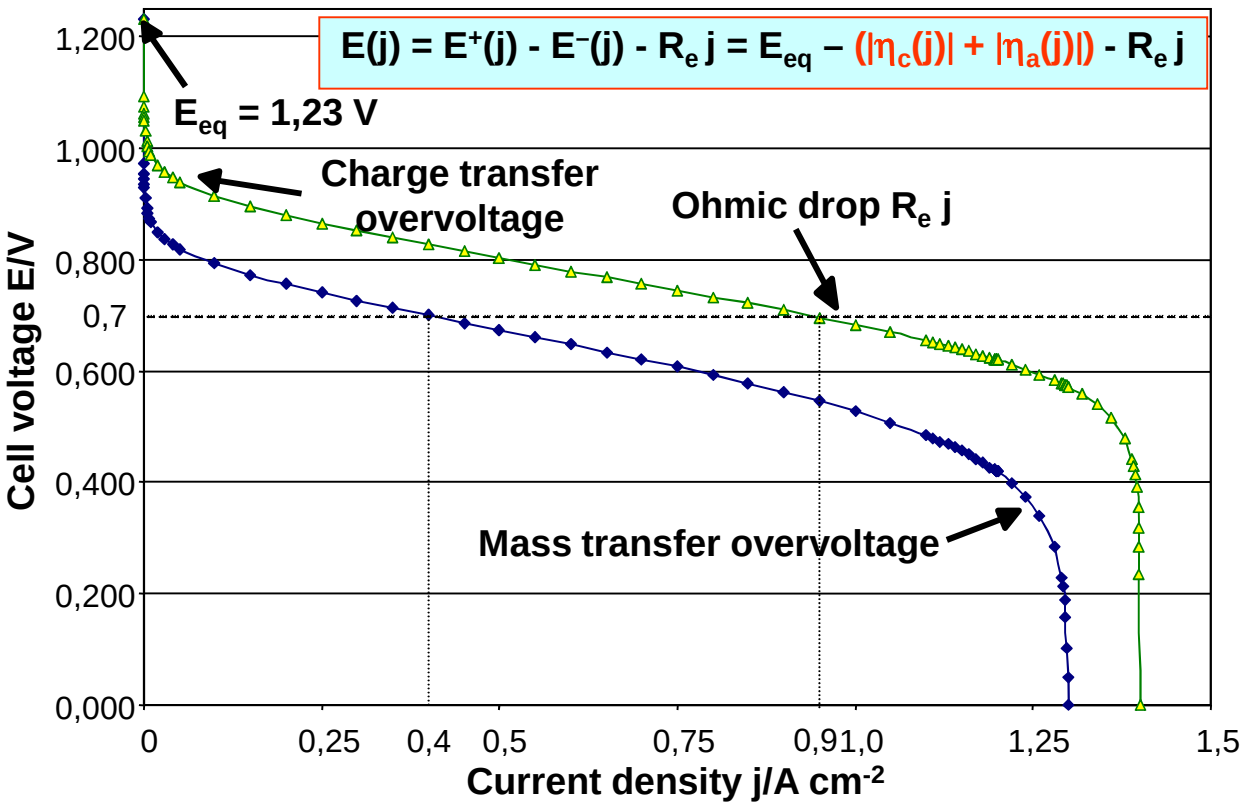
$j_0 = 10^{-6}$ A cm$^{-2}$ ; $R_e = 0{,}15\ \Omega$ cm$^2$ ; $j_l = 1{,}4$ A cm$^{-2}$

**Cell voltage vs. current density curves for an $H_2$/air FC with MEAs using three different types of carbon cathode GDL (80℃, 0.22 mg cm $^{-2}$ Pt loading) :**
**(●) microporous layer-coated and 30 wt.% FEP-impregnated;**
**(■) 30 wt.% FEP-impregnated; (▲) 10 wt.% FEP-impregnated.**




After C. Lim, C.Y. Wang,
Electrochim. Acta 49 (2004) 4149–4156

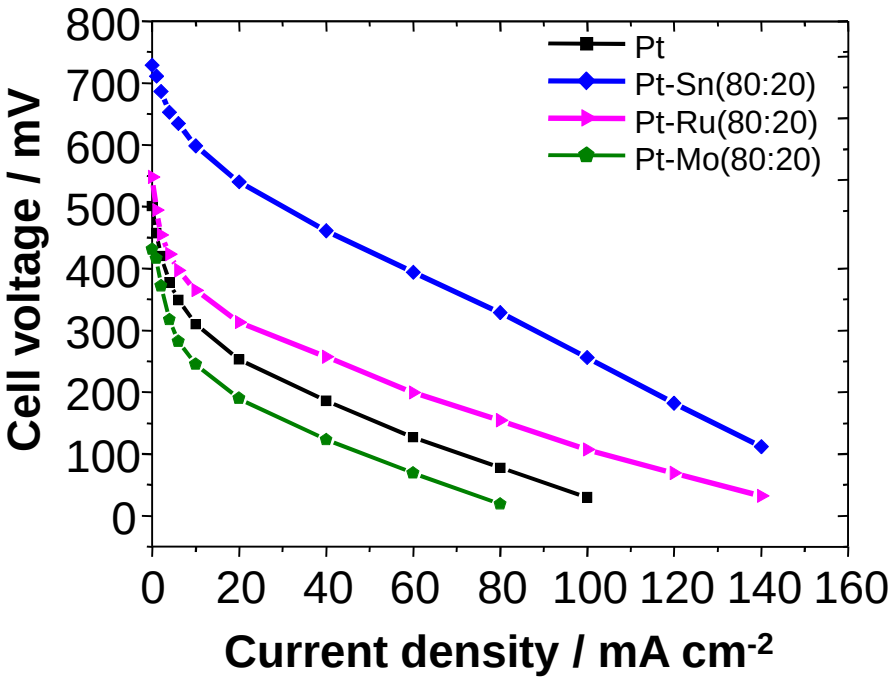
# Influence of the catalytic properties of electrodes (exchange current density $j_o$) on the cell voltage E(j)



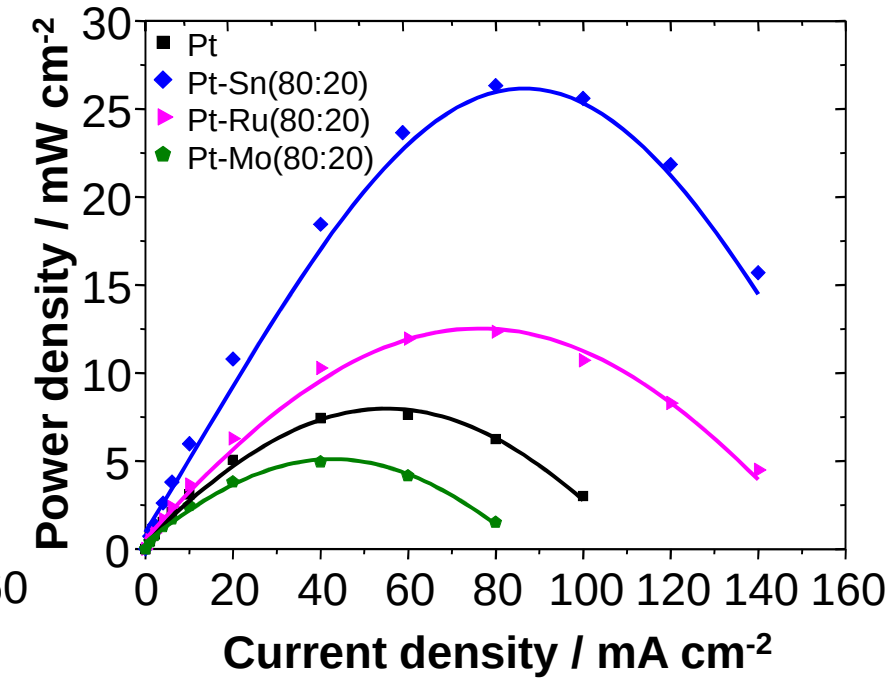

$j_o = 10^{-6}$ A cm$^{-2}$; $R_e = 0,15\ \Omega$ cm$^2$; $j_l = 1,4$ A cm$^{-2}$

$j_o = 10^{-8}$ A cm$^{-2}$; $R_e = 0,15\ \Omega$ cm$^2$; $j_l = 1,3$ A cm$^{-2}$

# Fuel cell characteristics of a DEFC recorded at 110°C.
## Influence of the nature of the bimetallic catalyst (30% loading).




**Polarization curves**




**Power density curves**

**Anode catalyst : 1.5 mg.cm$^{-2}$ ; Cathode catalyst : 2 mg.cm$^{-2}$ (40% Pt/XC72 E-TEK)**
**Membrane : Nafion® 117; Ethanol concentration : 1 M**

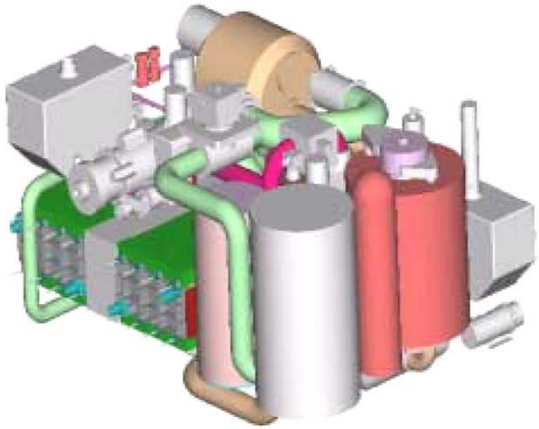
**After C. Lamy et al.,** in "Catalysis for Sustainable Energy Production", edited by P. Barbaro and C. Bianchini, Wiley-VCH, Weinheim, 2009, Chap.1, pp. 3-46.

# Survey of various applications of PEM Fuel Cells

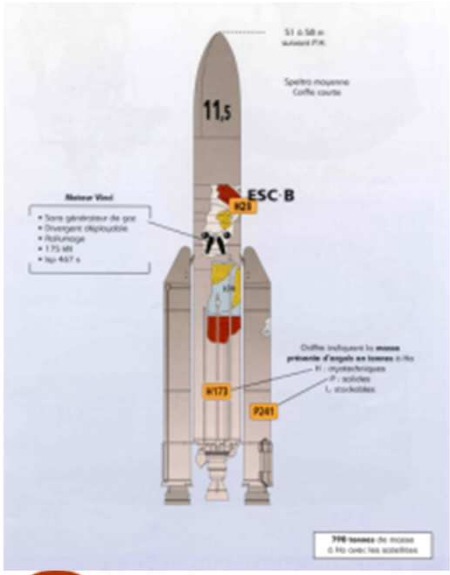
- **What are their uses ??** Production of **electric energy** (and eventually heat in CHP systems) in **a wide range** of power (1 W to about 10 MW) with **a similar energy efficiency**:
  - Electric Power Plant (1 to 10 MW)
  - Electric Vehicle (10 to 200 kW)
  - Auxiliary Power Unit (APU from 1 to 100 kW)
  - Aerospace power supply (1 to 50 kW)
  - Household Application (1 to 10 kW)
  - Power supply for portable electronics (1 to 100 W)

# City Bus equipped with a 200 kW FC for the 2008 Olympic Games in Beijing

# APU for aircrafts and spacecrafts

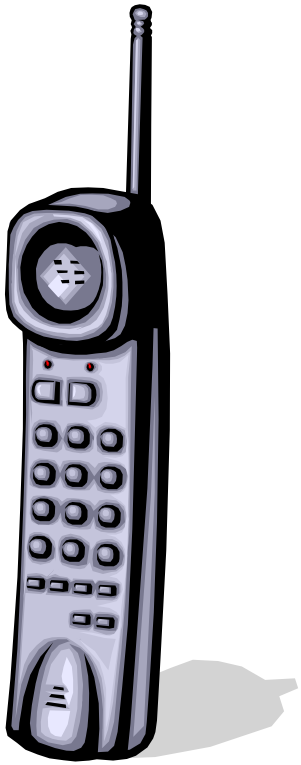
Fuel Cell System




Snecma Moteurs *(SAFRAN Group)*

# Airbus 320 equipped with a PEFC APU as demonstrated by DLR (Germany)

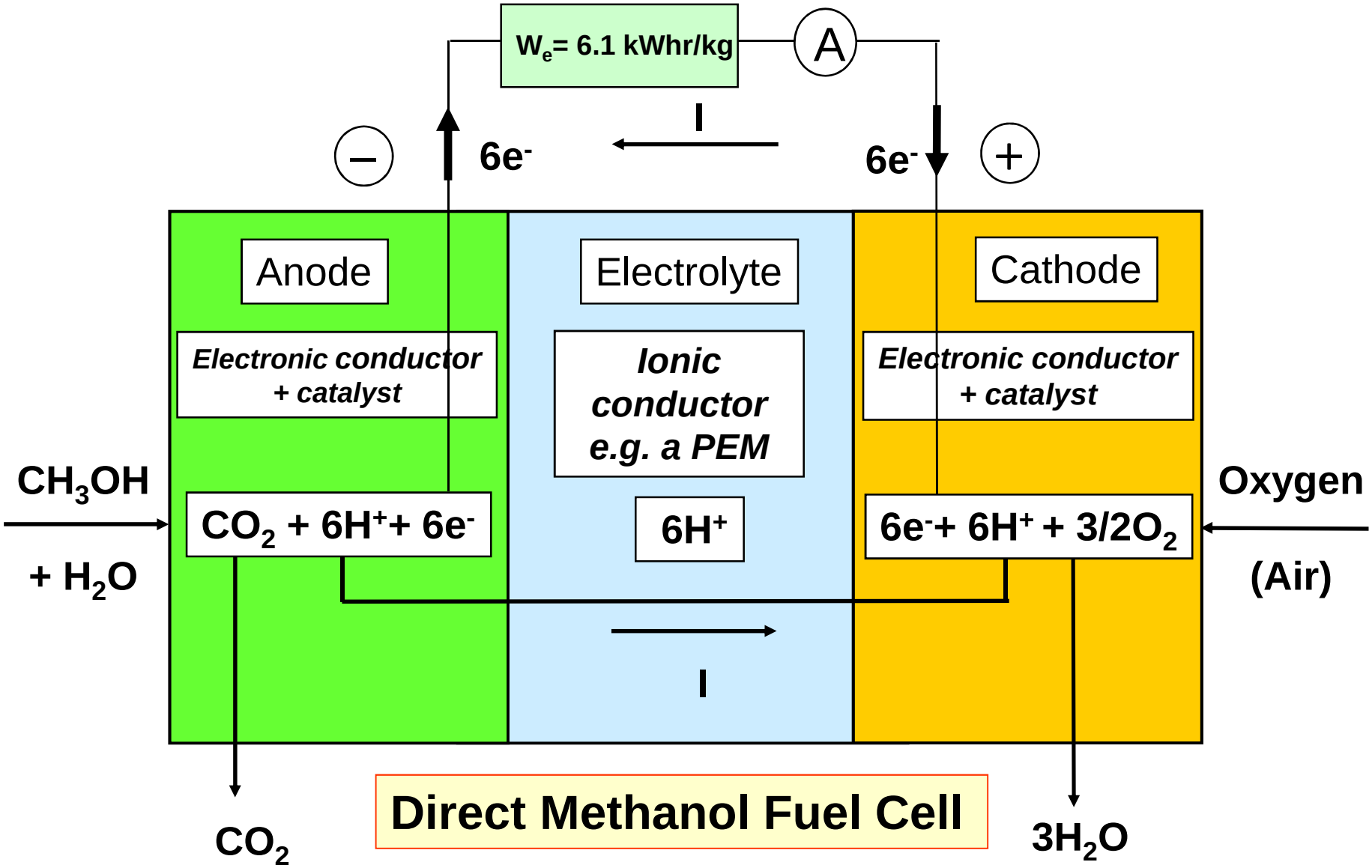
# Application to portable electronics (1 to 100 W)



| | |
|---|---|
| Laptop Computer ~ **10-100 W** | Cell Phone ~ **1-10 W** |

## The Direct Methanol Fuel Cell (DMFC)

- Principle of a Direct Methanol Fuel Cell
- Reaction mechanisms and kinetics problems




**Direct Methanol Fuel Cell**

# Reaction mechanism of the electrocatalytic oxidation of methanol at platinum-based electrodes

$$Pt + CH_3OH \rightarrow Pt - CH_3OH_{ads}$$

$$Pt - CH_3OH_{ads} \rightarrow Pt - CHO_{ads} + 3\,H^+ + 3\,e^-$$

$$Pt - CHO_{ads} \rightarrow Pt - CO_{ads} + H^+ + e^-$$

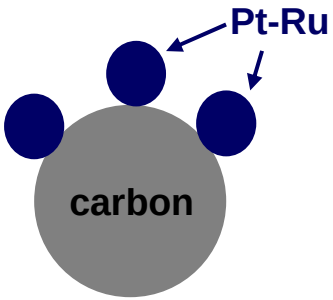
$$Ru + H_2O \rightarrow Ru - OH_{ads} + H^+ + e^-$$

$$Pt - CO_{ads} + Ru - OH_{ads} \rightarrow Pt + Ru + CO_2 + H^+ + e^-$$

---

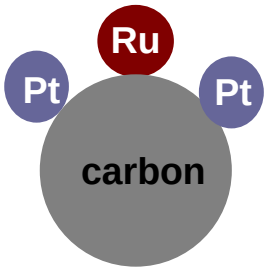
**Overall reaction** $\mathbf{CH_3OH + H_2O \rightarrow CO_2 + 6\,H^+ + 6\,e^-}$

**This a complex 6-electron reaction mechanism, which needs the preparation of bimetallic and plurimetallic electrocatalysts for methanol oxidation catalysts**



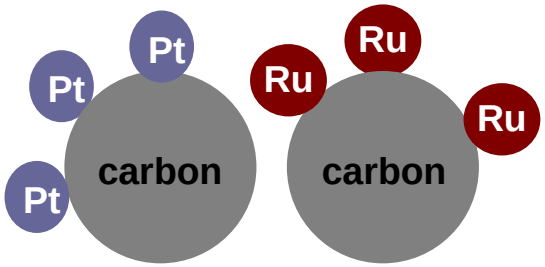

**Pt-Ru alloy**

**Pt-Ru/XC72**




**Pt and Ru on the same support**

**Pt+Ru/XC72**

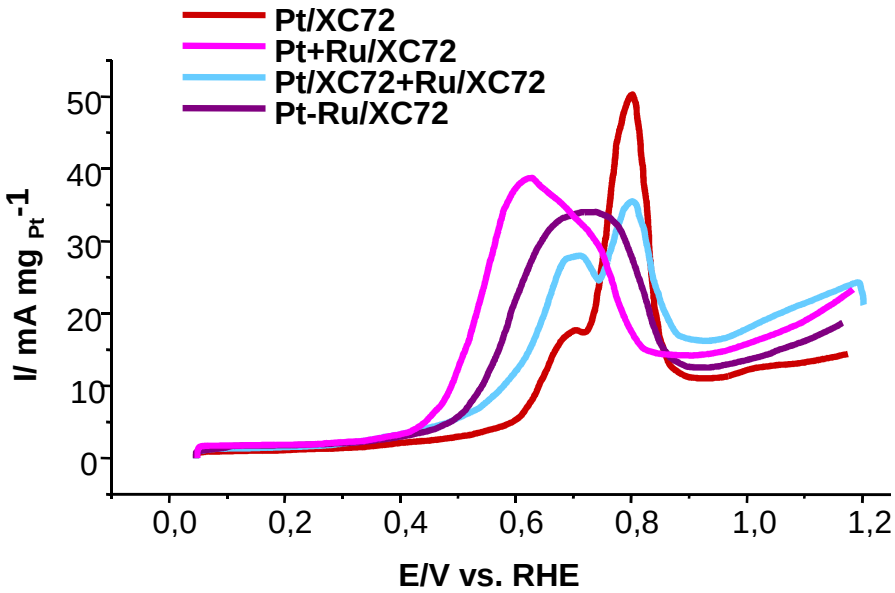


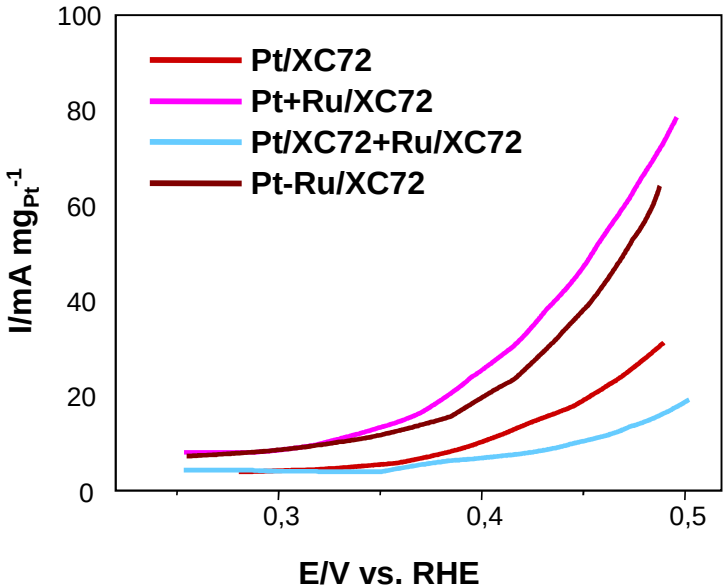

**Pt and Ru on different supports**

**Pt/XC72+Ru/XC72**

**Modification of platinum by Ruthenium using the colloidal method (after Bönnemann et al.)**

# Evaluation of the electrocatalytic activity of PtRu / C electrodes by cyclic voltammetry (room temperature)



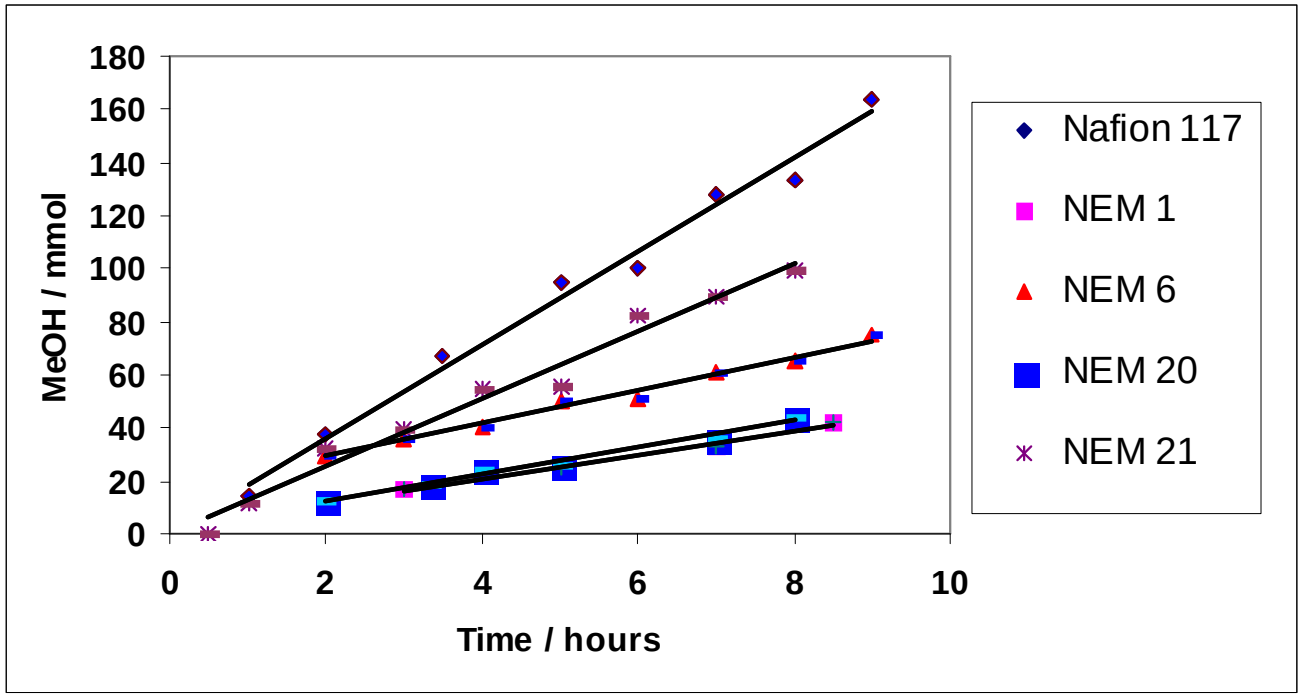

**Oxidation of preadsorbed CO (v=50mV $s^{-1}$)**

On same C particles > Alloy > On different C particles > Platinum

**Oxidation of 0.1M methanol (v=5mV $s^{-1}$)**

On same C particles > Alloy > Platinum > On different C particles

# Effect of the crossover of the fuel through the polymer membrane




**Permeability to methanol of different Solvay membranes in comparison with Nafion®117 at room temperature.**

As a result of the crossover of the fuel to the cathode, the electrode potential $E_m$ will be determined by a mixed reaction resulting from the reduction of oxygen and the oxidation of methanol at the same potential $E_m$. As both reactions are quite irreversible, a Tafel behavior is practically always observed. Under these conditions, the current density ($j_m$) and mixed potential ($E_m$) are given by the equations :

$$j_m = j_{oa}\, 10^{\frac{(E_m - E_a^o)}{b_a}} = j_{oc}\, 10^{-\frac{(E_m - E_c^o)}{b_c}}$$

and :

$$E_m = \frac{b_c E_a^o + b_a E_c^o}{b_a + b_c} + \frac{b_a b_c}{b_a + b_c} \log \frac{j_{oc}}{j_{oa}}$$

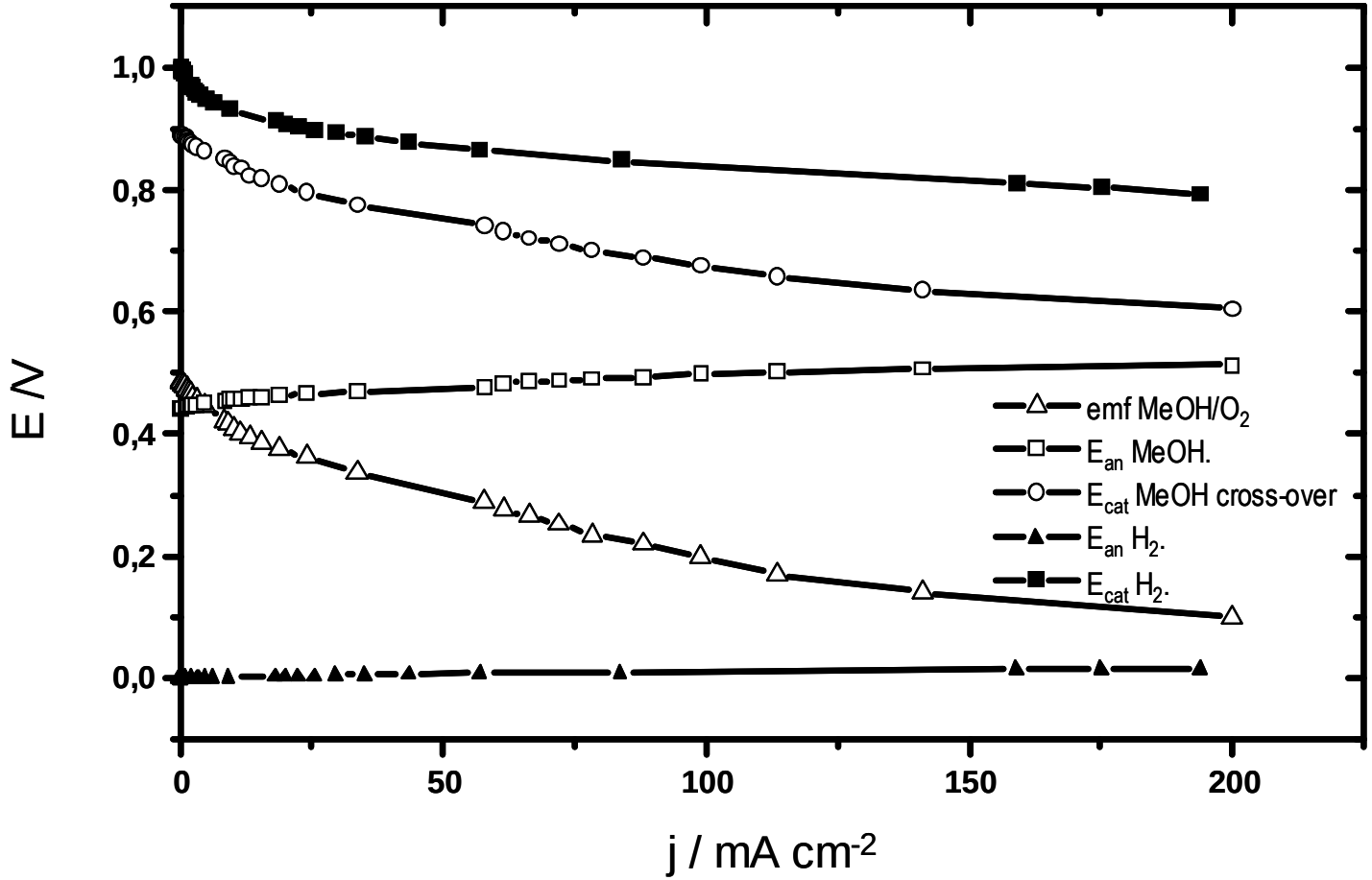
where $j_{oi}$ and $b_i$ are the exchange current density and the Tafel slopes, respectively, for both half-cell reactions.

This will result in a negative shift, $\Delta E_m$, of the mixed potential at the oxygen cathode, as given by the following equation :

$$\Delta E_m = \frac{b_a b_c}{b_a + b_c} \log \frac{j_{oa}}{j_{o'a}} \approx \frac{120}{2} \log 10^{-3} \approx -180 \text{ mV}$$

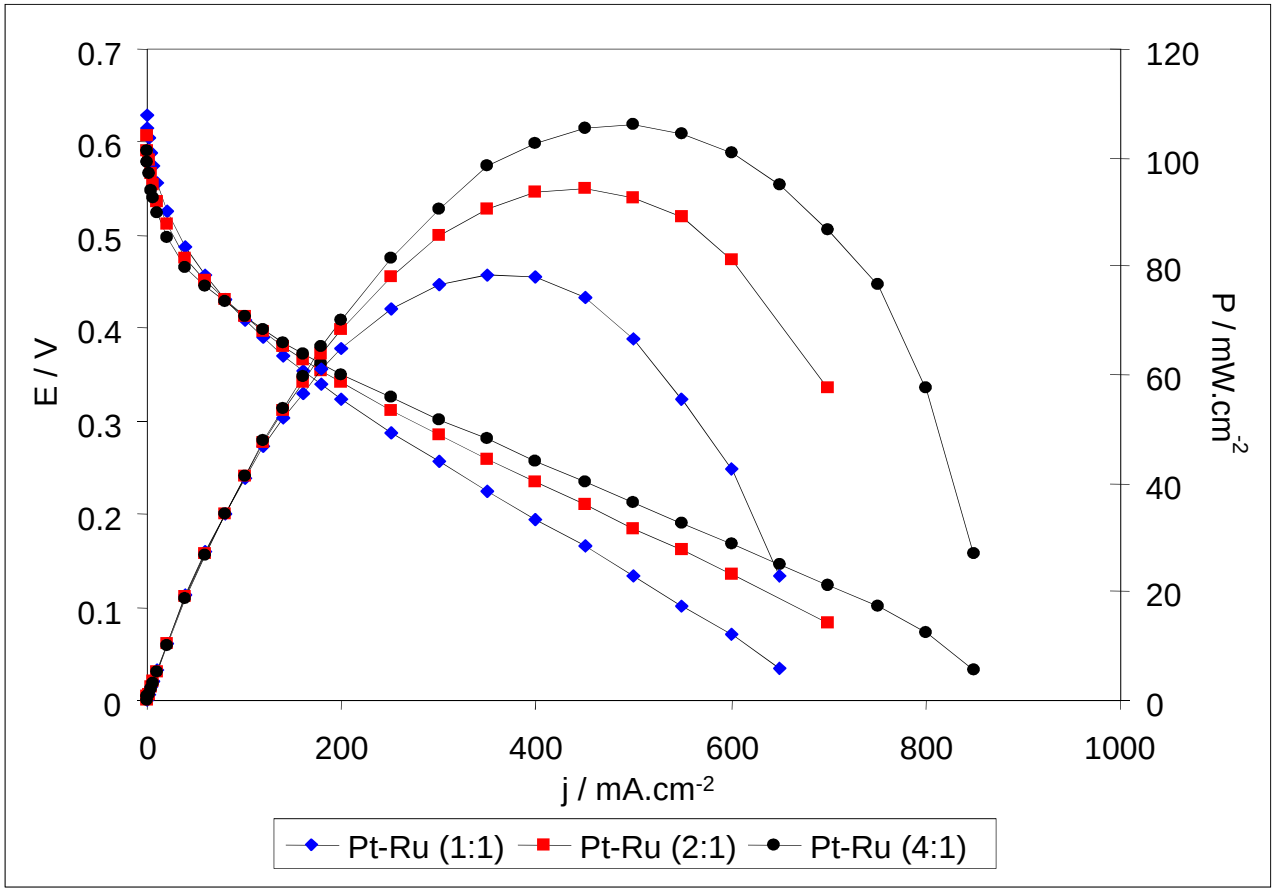
with $j_{o'a} = 10^3\, j_{oa}$ and $b_a \approx b_c \approx 120$ mV/decade for both the oxygen reduction (at high current densities) and the methanol oxidation reactions.

# Effect of methanol crossover through the membrane




**Polarization curves of an $H_2/O_2$ PEFC and a DMFC in the presence of methanol at the cathodic compartment : (■) potential of the PEFC cathode; (O) potential of the DMFC cathode ; (△) DMFC cell voltage**

# E(j) and P(j) curves of a single DMFC with Pt-Ru/C electrodes of different Pt-Ru atomic ratios




**Anode 2 mg.cm$^{-2}$ Pt-Ru / C, Nafion 117, Cathode 2 mg.cm$^{-2}$ Pt / C, [MeOH] = 2 M, 2 mL/min., $P_{MeOH}$ = 2 bar ; $T_{cell}$ = 110°C, $O_2$ = 120 mL/min., $P_{O_2}$ = 2.5 bar ; $T_{MeOH}$ = $T_{O_2}$ = 95°C.**

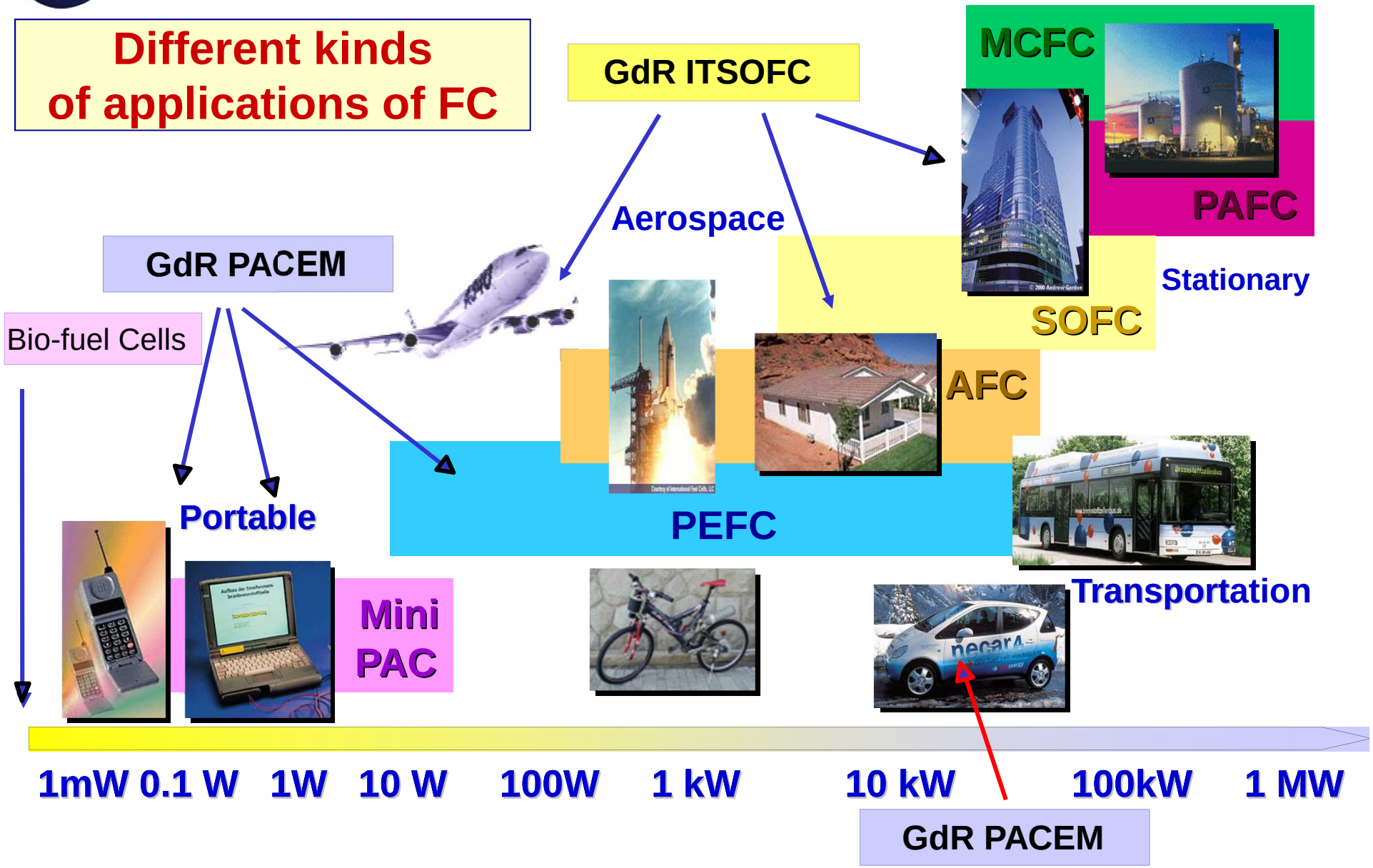
# Applications of DMFC to portable electronics: cell phone, laptop computer, cam recorder, etc.



## TOSHIBA DMFC for portable applications

GDR n°3339
Piles A Combustible, Systèmes

# Different kinds of applications of FC



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# *Thank you for your kind attention*