

# Relation between activation losses and membrane efficiency in the fuel cell operation

F. Maršík, P. Novotný

New Technology Center, University of West Bohemia in Pilsen

Conference

Hydrogen Days 2014

2 – 4 April, 2014, Prague, Czech Republic

# Content

Introduction

Balance of energy - I. Law of Thermodynamics

Balance of entropy - II. Law of Thermodynamics

Efficiency of chemical machines - non-volumetric work

Electro-osmotic coupling

Polarization curve

Reverse flow

Conclusion

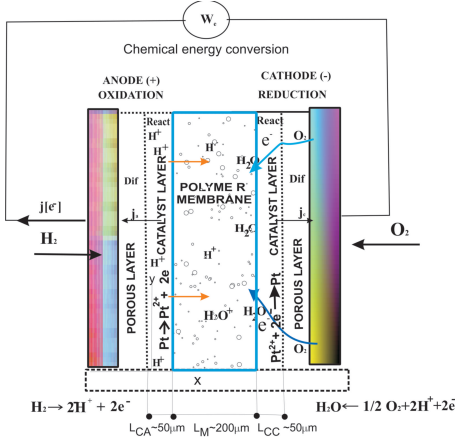
Publications

# Motivation

Thermodynamic analysis of the transport processes in the hydrogen fuel cells (HFC) is oriented to the following items:

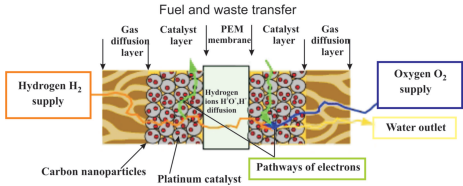
- ▶ to formulate adequate global theory of the transformation of chemical energy into electricity and analyze **the possible maximum efficiency**
- ▶ include all relevant internal processes like **electro-osmotic coupling**, chemical degradation, etc.,
- ▶ to derive the entropy production for the HFC and to define all **relevant thermodynamic forces and fluxes** for the HFC performance,
- ▶ to find the **maximum coupling between diffusion flux and electric flux** and consequently to estimate the maximum efficiency of the transformation of the chemical energy into electricity,
- ▶ to formulate the relation of the **reactants and products transport** to the global HFC efficiency.

HFC structure and corresponding relevant processes.



Chemical energy transformation

Fuel and waste transfer



# Balance of enthalpy-alternative form of the balance of energy, **non-volumetric work application**

Deformation tensor

$$\mathbf{e} = \mathbf{e}_{el} + \mathbf{e}_{dis} \quad \text{and} \quad \nabla \mathbf{v} = \mathbf{d}_{el} + \mathbf{d}_{dis}$$

the enthalpy for solids and fluids

$$h = u - \frac{\mathbf{t}}{\rho} \mathbf{e}_{el} \quad \text{for solids,} \quad h = u + \frac{p}{\rho} \quad \text{for fluids}$$

**I. Law of thermodynamics** has with respect to the above decomposition the alternative form

$$\rho \dot{h} = -\rho \mathbf{e}_{el} \left( \frac{\dot{\mathbf{t}}}{\rho} \right) + \mathbf{t} \dot{\mathbf{e}}_{dis} - \operatorname{div} \mathbf{q} + \mathbf{j}_e \mathcal{E} + \rho \mathcal{E} \left( \frac{\dot{\mathbf{P}}}{\rho} \right) + \rho \mathbf{B} \left( \frac{\dot{\mathcal{M}}}{\rho} \right) + Q^{EX}$$

$$\dot{H} - \dot{Q} = \int_V \left[ -\rho \mathbf{e}_{el} \left( \frac{\dot{\mathbf{t}}}{\rho} \right) + \mathbf{t} \dot{\mathbf{e}}_{dis} + \mathbf{j}_e \mathcal{E} + \rho \mathcal{E} \left( \frac{\dot{\mathbf{P}}}{\rho} \right) + \rho \mathbf{B} \left( \frac{\dot{\mathcal{M}}}{\rho} \right) \right] dV + Q^{EX}$$

$$dH - dQ = V dp + \sum_{\alpha} \mu_{\alpha} dN_{\alpha} \quad \text{classical form}$$

## Entropy balance-general concept

For all real cyclic processes  $\mathcal{C}$  running in the system  $\mathcal{V}$  during which is possible measured in each moment the temperature  $T$ , has to fulfill the inequality

$$\oint \frac{dQ}{T} = \int_{t_1}^{t_2} \frac{\dot{Q}}{T} dt \leq 0 \quad \text{Clausius inequality}$$

i.e., some amount of heat has to be removed from the system

Entropy is defined by the inequality

$$TdS = TdS_{\text{ir}} + TdS_{\text{eq}} \geq dQ \quad \text{for} \quad TdS_{\text{eq}} = dQ$$

$$T\dot{S} = T\dot{S}_{\text{ir}} + T\dot{S}_{\text{eq}} \geq \dot{Q} \quad \text{for} \quad T\dot{S}_{\text{eq}} = \dot{Q}$$

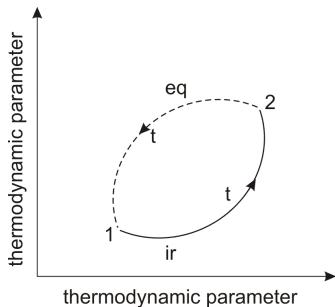
$$\dot{S} - \mathcal{J}(S) = \mathcal{P}(S) \geq 0 \quad \text{II. Law of Thermodynamics}$$

$$\text{for} \quad S = \int_{\mathcal{V}} \rho s d\nu, \quad \mathcal{J}(S) = \int_{\partial\mathcal{V}} -\frac{\mathbf{q}}{T} \mathbf{d}\mathbf{a} + \int_{\mathcal{V}} \frac{\tilde{q}}{T} d\nu,$$

$$\mathcal{P}(S) = \int_{\mathcal{V}} \sigma(S) d\nu \geq 0 \quad \text{entropy production is always positive}$$

## Reversible and irreversible processes

$$\oint \frac{dQ}{T} = \underbrace{\int_1^2 \frac{dQ}{T}}_{\text{ir} \Leftrightarrow dQ=0} + \underbrace{\int_2^1 \frac{dQ}{T}}_{\text{eq} \Leftrightarrow TdS_{\text{eq}}=dQ} = S(1) - S(2) \leq 0 \quad \text{or} \quad S(2) \geq S(1)$$



All periodic processes are composed from the irreversible part "ir" and reversible part "eq". **The entropy of isolated system reach maximum.**

# Stability of the equilibrium (reference) state

The entropy closed the equilibrium state is

$$\begin{aligned} S &= S_{\text{eq}} + dS_{\text{eq}} + \frac{1}{2}d^2S_{\text{eq}} + \dots \\ \text{time derivative } \dot{S} &= \dot{S}_{\text{eq}} + \frac{d}{dt}\dot{S}_{\text{eq}} + \frac{1}{2}\frac{d^2}{dt^2}\dot{S}_{\text{eq}} + \dots \end{aligned}$$

and from entropy balance follows

$$\underbrace{\dot{S}_{\text{eq}} + \frac{d}{dt}\dot{S}_{\text{eq}} - \mathcal{J}(S)}_{\rightarrow 0} = - \underbrace{\frac{1}{2}\frac{d^2}{dt^2}\dot{S}_{\text{eq}} + \mathcal{P}(S)}_{\rightarrow 0}$$

Stability of the equilibrium (reference) state is satisfied by the conditions:

- ▶  $\dot{S}_{\text{eq}} = \mathcal{J}(S)$     $\frac{d}{dt}\dot{S}_{\text{eq}} = 0$  **maximum** (in steady state  $\mathcal{J}(S) = 0$ )
- ▶  $\frac{1}{2}\frac{d^2}{dt^2}\dot{S}_{\text{eq}} = \mathcal{P}(S) \geq 0$  **stability**

## Entropy flux and entropy production.

Entropy flux is induced the heat flux  $\mathbf{j}_q$  and by the diffusion fluxes of fuel and wastes, with the partial chemical potentials  $\mu_\alpha$  and enthalpies  $h_\alpha$

$$\mathbf{j}(s) = \mathbf{j}_{D_\alpha} s_\alpha + \frac{\mathbf{j}_q}{T} = \frac{(\mathbf{j}_q - \sum_\alpha \mathbf{j}_{D_\alpha} \mu_\alpha + \sum \mathbf{j}_{D_\alpha} h_\alpha)}{T} \quad (1)$$

The entropy production (2) is a bilinear form

$$\sigma(s) = \sum_\gamma J_\gamma X_\gamma \geq 0 \quad (2)$$

where  $J_\gamma$  are thermodynamic fluxes and  $X_\gamma$  are thermodynamic. The last inequality is an alternative form of ***II. law of thermodynamics.***

# Entropy production for chemically reacting mixture

Typical form of transport processes  $\mathbf{J}$  and their driving forces  $\mathbf{X}$  in the chemical devices. Corresponding entropy production is

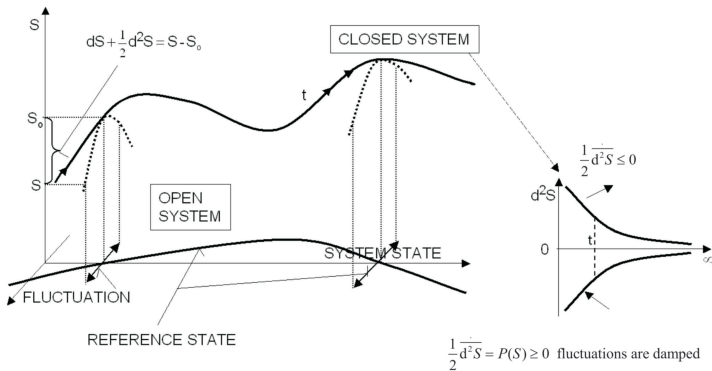
$$\mathcal{P}(S) = \sum_{\gamma} \mathbf{J}_{\gamma} \mathbf{X}_{\gamma} \sim \frac{1}{2} \overline{d^2 S}_{\text{eq}} \geq 0$$

	Flux $\mathbf{J}_{\gamma}$	Force $\mathbf{X}_{\gamma}$
heat flux	$\mathbf{j}_q$	$\nabla \left( \frac{1}{T} \right)$ -heat release
thermodiffusion	$\mathbf{j}_{D_{\alpha}} h_{\alpha}$	$\nabla \left( \frac{1}{T} \right)$ -fuel delivery
concentration diffusion	$\mathbf{j}_{D_{\alpha}}$	$\left( \frac{\nabla \mu_{\alpha}}{T} \right)$ -water dif. in PEM
electric current	$\mathbf{j}_{e, \alpha}$	$\frac{F_{\alpha}}{T} = - \frac{z_{\alpha} F}{M_{\alpha} T} \nabla \phi$ -proton flux
electric field induced	$\rho(\mathbf{E} - \mathbf{E}_{\text{eq}})$	$\frac{1}{T} \left( \frac{\mathbf{P}}{\rho} \right)$ -change of polarization in PEM
magnetic induced	$\rho(\mathbf{B} - \mathbf{B}_{\text{eq}})$	$\frac{1}{T} \left( \frac{\mathbf{M}}{\rho} \right)$ -change of magnetization in PEM
visco-plastic processes for solids	$\mathbf{t}_{dis}(T, \mathbf{d}, \dot{\mathbf{t}}_{dis})$	$\frac{\mathbf{d}}{T}$
viscosity	$\mathbf{t}_{dis} - \sum_{\alpha} \rho_{\alpha} \mathbf{v}_{D_{\alpha}} \otimes \mathbf{v}_{D_{\alpha}}$	$\frac{(\sigma)}{T}$
swelling	$\mathbf{t}_{dis \alpha} \cdot \nabla \left( \frac{1}{T} \right)$	$\mathbf{v}_{D_{\alpha}}$
capillary flux	$\mathbf{j}_{D_c}$	$\frac{\mathbf{f}_s}{T} = + \frac{1}{T} \nabla(\sigma \cdot \mathbf{a})$
chemical reaction and phase transition	$\dot{\zeta}_{\rho}$	$\frac{A_{\rho}}{T}$ - at CL and GDL

# Relation between entropy production and damping of fluctuations

The entropy is convex function of its parameters, which fluctuates around the stable reference state  $S_0$  or around the equilibrium state  $S_{eq}$ .

The probability of fluctuations is  $\text{Pr} \sim \exp \left[ \frac{S - S_{eq}}{k} \right] = \exp \left[ \frac{d^2 S_{eq}}{2k} \right]$



# Global form of the energy balance for chemical devices

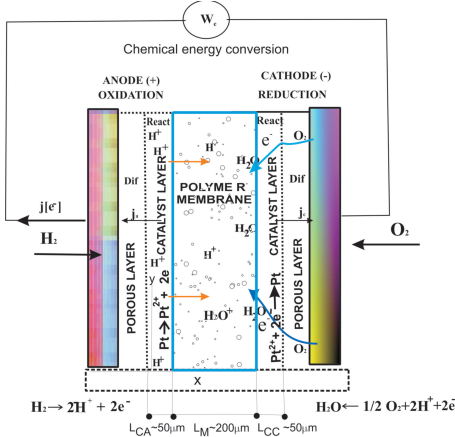
The change of the enthalpy  $\Delta H$  of the whole FC is

$$T\Delta S = T(\Delta S_{eq} + \Delta S_{ir}) \geq \Delta Q = \Delta H + \tilde{W}_e,$$

where  $\Delta Q$  is the heat release during FC operation and it is induced mainly by the chemical reactions.  $\Delta Q < 0$  for the heat outgoing from the system. The alternative formulation of the balance of energy is by the Gibbs free enthalpy  $\Delta G = \Delta H - T\Delta S_{eq} - S_{eq}\Delta T$ , so that the equation has the form

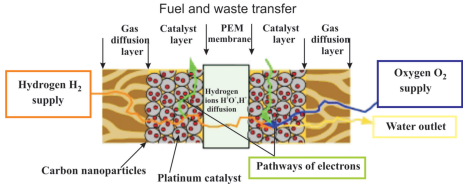
$$\Delta G \leq -S_{eq}\Delta T - \tilde{W}_e + T\Delta S_{ir}.$$

HFC structure and corresponding relevant processes.



Chemical energy transformation

Fuel and waste transfer



# Entropy balance for the fuel cell

The energy balance for non-volumetric work  $\dot{\bar{W}}_e$  is formulated by the enthalpy  $H$

$$\mathcal{J}_q + \mathcal{J}_{Dh} = \dot{H} + \dot{\bar{W}}_e,$$

where  $\mathcal{J}_q$  is the heat flux and  $\mathcal{J}_{Dh}$  is the enthalpy flux. The entropy balance is

$$\dot{S} - \mathcal{J}(S) = \mathcal{P}(S) \geq 0, \quad \text{for} \quad \mathcal{J}(S) = \mathcal{J}_q(S) + \mathcal{J}_{Dh}(S) + \mathcal{J}_{Dg}(S).$$

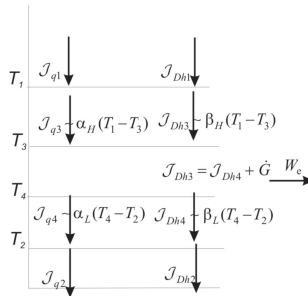
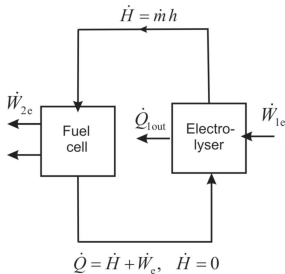
The global entropy production  $\mathcal{P}(S) = \int_V \sigma(s) d\nu \geq 0$  is always positive and corresponding heat is continuously removed from the system by the heat flux  $\mathcal{J}_q(S)$ . The entropy production  $\mathcal{P}(S) \geq 0$  is compensated by the flux of the negative entropy (fuel delivery) which is composed from the enthalpy flux  $\mathcal{J}_{Dh}(S) \geq 0$  or from the Gibbs free enthalpy flux  $\mathcal{J}_{Dg}(S) \geq 0$ .

# Efficiency power dependency – global approach I

Energy conversion in **the closed cycle at constant enthalpy**.

**Electrolyser** – the incoming energy flux contains the energy  $\dot{W}_{1e}$  needed for the chemical reactions (e.g., water decomposition) and corresponding heat loss is  $\dot{Q}_{1out}$ , so that  $\dot{Q}_{1in} = \dot{Q}_{1out} + \dot{W}_{1e}$ .

**FC** – the outgoing energy  $\dot{W}_{2e}$  contains the electric power accompanied by the heat  $\dot{Q}_{2out}$ , so that  $\dot{Q}_{2in} = \dot{Q}_{2out} + \dot{W}_{2e}$ .



# Definitions of efficiencies I

For the  $\Delta S_{ir} = 0$  the maximum possible efficiency of a chemical transformation is

$$\eta_{th} = \frac{-\tilde{W}_e}{\Delta H} = \frac{\Delta G}{\Delta H} + \frac{S_{eq}\Delta T}{\Delta H} \bigg|_{T=const} = \frac{\Delta G}{\Delta H}.$$

The incoming power is  $\dot{\Delta H}_{in} = V_{eq\ T,p} z_e F \dot{N}_{H_2\ in}$  and measured outgoing power is  $\dot{W}_{act} = V_{cell} I$ . The measured actual efficiency by means of the polarization curve is

$$\begin{aligned} \eta &= -\frac{\dot{W}_{act}}{\dot{\Delta H}_{in}} = \frac{\dot{\Delta G}_{in}}{\dot{\Delta H}_{in}} \left( 1 + \frac{T \dot{\Delta S}_{ir}}{\dot{\Delta G}_{in}} \right) \\ &= -\frac{\dot{W}_{nv}}{\dot{\Delta H}_{in}} \frac{\dot{W}_{act}}{\dot{W}_{nv}} = \eta_0 \eta_m = \frac{V_{cell}}{V_{eq\ T,p}} \frac{\dot{N}_{H_2\ in}}{\dot{N}_{H_2\ act}} = \frac{V_{cell}}{V_{eq\ T,p}} \underbrace{\frac{I}{z_e F \dot{N}_{H_2\ act}}}_{\text{fuel utilization}}. \end{aligned}$$

$V_{eq\ T,p} = -\frac{\Delta G}{2F} = 1.184$  V is equilibrium cell potential at temperature  $T = 353$  K, pressure

$p = 101.3$  kPa for pure hydrogen and air. Theoretical efficiency  $\eta_{th} = \frac{V_{eq\ T,p}}{1.482} = 0.7989 \simeq 0.8$ .

## Definitions of efficiencies II – efficiency splitting

The hypothetical (endoreversible) FC efficiency is defined as

$$\eta_0 = -\frac{\dot{\bar{W}}_{nv}}{\dot{\bar{\Delta H}}_{in}}.$$

We consider that hypothetical FC ( PEM especially) convert all incoming Gibbs free enthalpy into electric power, i.e.,  $\dot{\bar{W}}_{nv} = -\dot{\bar{\Delta G}}_{in}$  and is connected with the reactants delivery and products outflow and does not depend on the actual chemical energy transformation. The membrane efficiency is

$$\eta_m = \frac{\dot{\bar{W}}_{act}}{\dot{\bar{W}}_{nv}} = -\frac{\dot{\bar{W}}_{act}}{\dot{\bar{\Delta G}}_{in}} = 1 + \frac{T \dot{\bar{\Delta S}}_{ir}}{\dot{\bar{\Delta G}}_{in}} \leq 1$$

and describes the transformation of the chemical energy  $\dot{\bar{\Delta G}}_{in}$  into electric energy through the dissipation  $T \dot{\bar{\Delta S}}_{ir}$ .

## Efficiency power dependency – global approach II

We suppose the closed cycle, it means that the change of the total enthalpy is zero ( $\dot{H} = 0$ ) and the energy balance becomes

$$\dot{Q}_{in} - \dot{Q}_{out} = \dot{W}_e = -T \Delta \dot{S} + \overline{\Delta \dot{H}} = -\dot{W}_e,$$

$$\text{for efficiency } \eta = \frac{\dot{W}_e}{\dot{Q}_{in}}$$

$$\text{heat fluxes are } \dot{Q}_{in} = \frac{\dot{W}_e}{\eta}, \quad \dot{Q}_{out} = \frac{1 - \eta}{\eta} \dot{W}_e.$$

The final form of the [entropy balance for the electrochemical device](#) is

$$\frac{\dot{Q}_{in}}{T_3} - \frac{\dot{Q}_{in}}{T_4} + \frac{\dot{W}_e}{T_4} - \frac{\overline{\Delta \dot{G}_{in}}}{T_4} = 0, (-\mathcal{P}(S) \leq 0).$$

# Efficiency power dependency – global approach III

The heat and enthalpy fluxes between the different temperatures are driven by the temperature gradients  $\int_{\partial V} (\mathbf{j}_q + \sum_{\alpha} \mathbf{j}_{D_{\alpha}} h_{\alpha}) \mathbf{da} = \mathcal{J} \sim \nabla T$ ,

$$\dot{Q}_{in} = \mathcal{J}_{q3} + \mathcal{J}_{Dh3} = \gamma_H (T_1 - T_3), \quad \dot{Q}_{out} = \mathcal{J}_{q2} + \mathcal{J}_{Dh2} = \gamma_L (T_4 - T_2),$$

for  $\gamma_H = \alpha_H + \beta_H, \quad \gamma_L = \alpha_L + \beta_L$ .

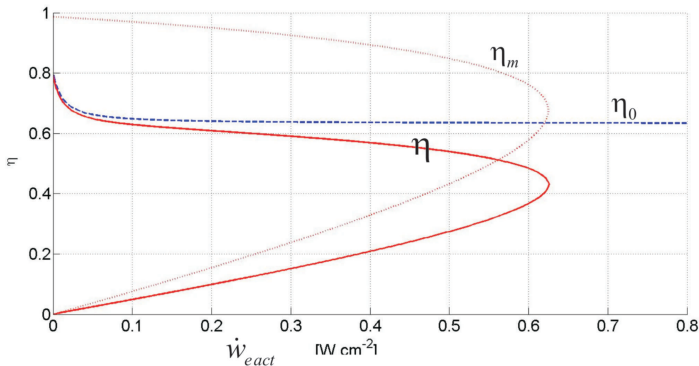
The relation between the total efficiency  $\eta = \dot{W}_{e\ act} / \dot{Q}_{in}$  and the actual electric power is **the relation between the total efficiency  $\eta$  and the actual electric power** is

$$\dot{W}_{e\ act} = \frac{\eta[(1 - \eta_m)\eta - \tau\eta_m]}{\eta_m(1 - \eta) + \gamma_0\eta} \quad \text{for} \quad \eta = \eta_0\eta_m, \quad \gamma_0 = \frac{\gamma_L}{\gamma_H + \gamma_L} < 0$$

## Typical form of the efficiencies

The comparison of the FC efficiencies for typical HFC with

$$\eta_{th} = 0.8, \dot{W}_{e,ref} = \gamma_H \gamma_0 T_1 = 2 \text{ W cm}^{-2}, \gamma_0 = -0.5, \gamma_H = -0.01$$



$$\eta = \eta_0 \eta_m|_{\eta_m \rightarrow 1} = \eta_0, \text{ and } \eta_0(\dot{w}_{nv} \gg 0) \simeq \frac{\eta_{th}}{1 - \gamma_0},$$

$$\text{for } \tau = \eta_{th}(1 - \eta_m)|_{\eta_m \rightarrow 1} \text{ and } \gamma_0 < 0$$

## Maximum efficiency and maximum power of FC

For the open circuit conditions ( $\dot{w}_{e\ act} \rightarrow 0$ ) the membrane efficiency goes to the value  $\eta_m = 1 - (\tau/\eta_{th})$ .

$$\left. \frac{\partial \dot{w}_{e\ act}}{\partial \eta_m} \right|_{\gamma_0=0, \eta_0 \rightarrow \eta_{th}, \tau \rightarrow 0} = 0, \quad \eta_{m\ max} = \frac{1 - \sqrt{1 - \eta_{th}}}{\eta_{th}}$$
$$\text{where } \eta = \eta_0 \eta_m = \left. \frac{\tau \eta_m}{1 - \eta_m} \right|_{\eta_m \rightarrow 1} = \eta_0 |_{\eta_m \rightarrow 1} = \eta_{th}$$

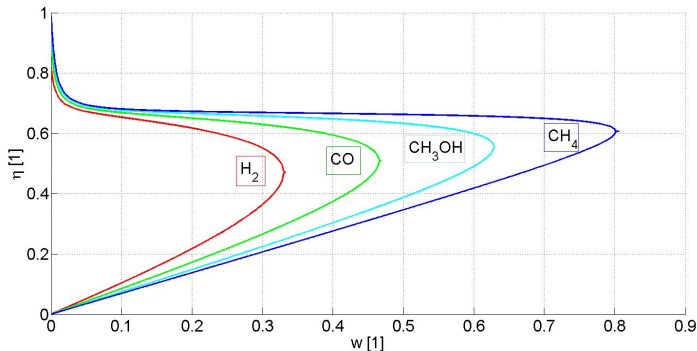
Theoretical maximum efficiency of the membrane depends on the  $\eta_{th}$  only and the corresponding theoretical maximum power output is

$$\dot{w}_{e\ max} = (1 - \sqrt{1 - \eta_{th}})^2$$

and depends as well on the  $\eta_{th}$  only.

# Maximal FC efficiency

Dependence of the efficiency  $\eta = \eta_0 \eta_m$  on the power density  $\dot{w}_{e, act}$  for  $\dot{W}_{e, ref} = 1 \text{ W cm}^{-2}$ ,  $\dot{W}_{e, max} = 1 \text{ W cm}^{-2}$ ,  $\gamma_0 = -0.5$  for the different fuels.



Theoretical maximum efficiency of the membrane depends on the  $\eta_{th}$  only

$$\left. \frac{\partial \dot{w}_{e, act}}{\partial \eta_m} \right|_{\gamma_0=0, \eta_0 \rightarrow \eta_{th}, \tau \rightarrow 0} = 0, \quad \eta_{m, max} = \frac{1 - \sqrt{1 - \eta_{th}}}{\eta_{th}}$$

$$\text{where } \eta = \eta_0 \eta_m = \frac{\tau \eta_m}{1 - \eta_m} \Big|_{\eta_m \rightarrow 1} = \eta_0 |_{\eta_m \rightarrow 1} = \eta_{th}$$

## Maximal FC efficiency for different fuels

Reaction	enthalpy $-\Delta H$ [kJ mol <sup>-1</sup> ]	Gibbs enthalpy $-\Delta G$ [kJ mol <sup>-1</sup> ]	efficiency $\eta_{th} = \frac{\Delta G}{\Delta H}$ [1]	max. effic, [1]	max. power [1]
$\text{H}_2 + 1/2\text{O}_2 \rightarrow \text{H}_2\text{O}_{liq}$	286.0	237.13	0.829	0.707	0.343
$\text{H}_2 + 1/2\text{O}_2 \rightarrow \text{H}_2\text{O}_{gas}$	241.8	228.6	0.946	0.811	0.589
$\text{CO} + 1/2\text{O}_2 \rightarrow \text{CO}_2$	283.1	257.2	0.909	0.768	0.487
$\text{CH}_3\text{OH} + 3/2\text{O}_2 \rightarrow \text{CO}_2 + 2\text{H}_2\text{O}_{liq}$	726.6	702.5	0.967	0.846	0.669
$\text{CH}_4 + 2\text{O}_2 \rightarrow \text{CO}_2 + 2\text{H}_2\text{O}_{gas}$	802.4	800.9	0.999	0.969	0.937

## Coupling coefficient definition

For water activity  $a_w$  in PEM and for electric potential  $\phi$  the coupling between water diffusivity and proton conductivity is

$$\mathbf{j}_{D_w} = -\rho D_w \nabla a_w - \frac{L_{wH^+} F}{T M_{H^+}} \nabla \phi \quad \text{water flux}$$

$$\mathbf{j}_{DH^+} = i_e \frac{M_{H^+}}{F} = -\frac{L_{H^+w} R}{M_w a_w} \nabla a_w - \frac{M_{H^+} \sigma_p}{F} \nabla \phi \quad \text{proton flux}$$

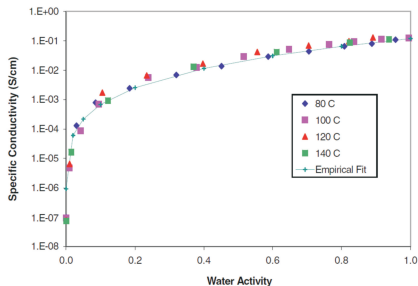
For Grotthus mechanism is  $L_{wH^+} \rightarrow L_{wH_3O^+}$ . The cross coefficient

$$L_{H_3O^+w} = q \frac{M_{H_3O^+}}{F} \sqrt{\frac{\rho_w M_w T}{R} D_w \sigma_p}$$

represents the electro-osmotic coupling by the "coupling coefficient"  $q$ .

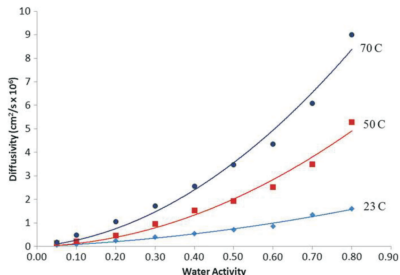
# Proton conductivity and water diffusivity dependence on water activity $a_w$ in PEM without coupling

Benziger J. et al : *Struct Bond* **141**: 85-113, 2011



Proton conductivity of Nafion as a function of water activity at different temperatures. The empirical fit to the data is given by

$$\sigma_p = 1.3 \cdot 10^{-7} \exp(14a_w^{0.2}) \text{ S/cm}$$



Effective diffusion coefficient of water in EW 1100 Nafion as a function of water activity and temperature and can be fitted

$$D_w = 0.265a_w^2 \exp(-3343/T) \text{ cm}^2/\text{s}$$

# Membrane efficiency and electro-osmotic coupling

Coupling coefficient  $q$

$$q = \frac{\hat{L}_{H^3O^+w}}{\sqrt{\hat{L}_{ww}\hat{L}_{H^3O^+w}}} = \frac{F L_{H^3O^+w}}{M_{H^3O^+} \sqrt{\frac{\rho_w M_w T}{R} D_w(a_w, T) \sigma(a_w)}}$$

$L_{H^3O^+w}$  is unknown electro-osmotic coefficient

Force ratio  $y$

$$y = \frac{\sqrt{L_{H^3O^+H^3O^+}} X_e}{\sqrt{L_{ww}} X_w} = \sqrt{\frac{M_w \rho_w \sigma_p}{\rho^2 R T D_w} \frac{\nabla \phi}{\nabla a_w}}$$

# Maximal efficiency and maximal coupling

The unknown dependance between thermal efficiency  $\eta_m(y, q)$  and electro-osmotic coupling  $q$  (or  $L_{H_3O^+ w}$ ) is determined from the maximum condition

$$\frac{d\eta_m}{dy} = 0, \quad \text{i.e.,} \quad y_1 = \frac{-1 + \sqrt{1 - q^2}}{q} \quad \text{and} \quad y_2 = \frac{-1 - \sqrt{1 - q^2}}{q}$$

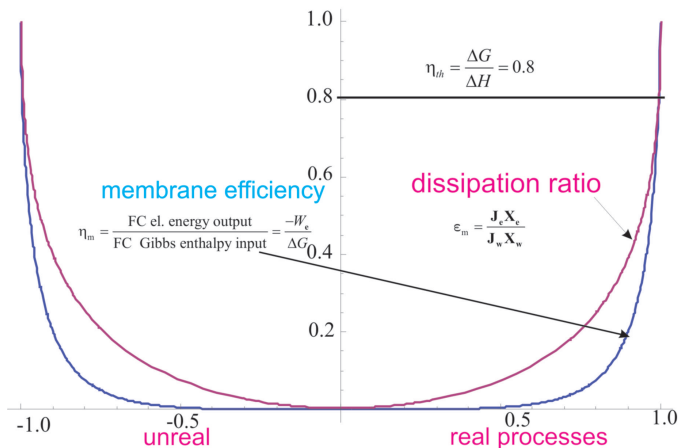
$$\eta_{m \max} = \frac{q^2 - 2 + 2\sqrt{1 - q^2}}{3q^2 - 4 + \sqrt{1 - q^2}} = \frac{y_1^2}{y_1^2 + y_2^2 - 1} \quad \text{and} \quad \epsilon_{e.w \max} = \frac{-1 + \sqrt{1 - q^2}}{q} = y_1$$

Maximum coupling condition for Hydronium ions  $H^3O^+$

$$y_1 = \sqrt{\frac{M_w \rho_w \sigma_p}{\rho^2 R T D_w}} \frac{\nabla \phi}{\nabla a_w} < 0 \quad \text{for} \quad q \in (0, 1)$$

Water concentration gradient (e.g.,  $\nabla a_w \sim \frac{da_w}{dx}$ ) has to have the opposite direction to the potential gradient  $\nabla \phi \sim \frac{d\phi}{dx}$ .

# Coupling coefficient–efficiency dependence

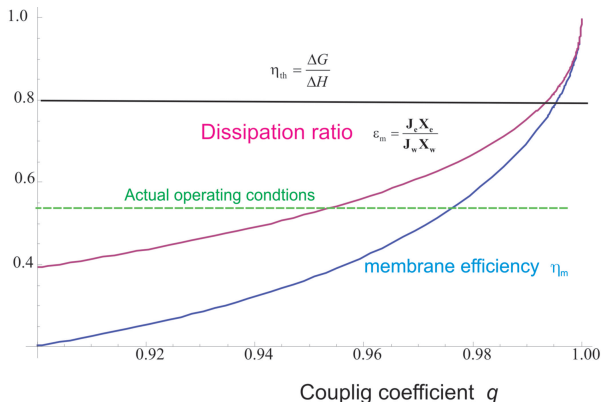


Coupling coefficient

$$q = \frac{F L_{H_3O^+,w}}{M_{H_3O^+} \sqrt{\frac{\rho_w M_w T}{R} D_w(a_w, T) \sigma_p(a_w)}}$$

The influence of coupling coefficient on the values of the thermal efficiency of Hydrogen fuel cell and on the efficiency of PEM.

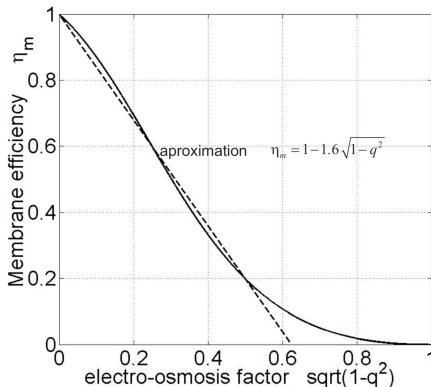
# FC efficiencies close to operating conditions



The thermal and PEM efficiencies close to the operation conditions. Coupling coefficient  $q$  is really very close to 1.

# Coupling influence on proton conductivity and water diffusivity

The coupling coefficient  $q$  depends on the thermal efficiency  $\eta_m$  and consequently on the power  $w$  and influences strongly the proton conductivity and water diffusivity.



$$\mathbf{i} = -\sqrt{1-q^2}\sigma_p(a_w)\nabla\phi$$

$$\mathbf{J}_w = -\rho_{w0}\sqrt{1-q^2}D_w(a_w)\nabla a_w$$

# Polarization curve - Input data

Polarization curve ( $V, i$ ) follows directly from the general formula for  $\dot{W}_{e, act} = \dot{W}_{e, act}(\eta, \eta_m, \tau, \gamma_0)$  putting

$$\eta = \frac{-i V_{cell}}{\dot{\Delta H}_{in}}, \quad \dot{\Delta H}_{in} = V_{th\ T, p} z_e F \dot{N}_{H_2\ in} = -i V_{th\ T, p}, \quad \dot{W}_{e\ act} = \frac{i V_{cell}}{\dot{W}_{e\ ref}}, \quad \text{for } \dot{W}_{e\ ref} = \gamma_H \gamma_0 T_1$$

- ▶  $V_{th\ T, p} = -\frac{\Delta H}{2F} = \frac{284.18}{2 \cdot 96.485} = 1.473\text{ V}$  is the electric potential corresponding to the higher heating value at actual temperature  $T = 353\text{ K}$ , pressure  $p = 101.3\text{ kPa}$  and fuel concentration (pure Hydrogen and Air)
- ▶  $V_{eq\ T, p} = -\frac{\Delta G}{2F} = 1.184\text{ V}$  is equilibrium cell potential at actual temperature  $T = 353\text{ K}$ , pressure  $p = 101.3\text{ kPa}$  and fuel concentration (pure Hydrogen and Air). Corresponding theoretical efficiency (open circuit performance) is  $\eta_{th} = \frac{V_{eq\ T, p}}{1.473} = 0.8038 \simeq 0.8$ .
- ▶  $z_e$  is number of exchanged electrons (for  $H_2$ ,  $z_e = 2$ ) and  $\dot{N}_{H_2\ act}$  [mol/cm<sup>-2</sup>s] is actual fuel ( $H_2$ ) consumption (utilized fuel only).
- ▶ The total incoming power is  $\dot{\Delta H}_{in} = V_{th\ T, p} z_e F \dot{N}_{H_2\ in}$ ,  $\dot{\Delta G} = V_{eq\ T, p} z_e F \dot{N}_{H_2\ act}$  is into the electric power converted part, and measured outgoing power density is  $i V_{cell} = \dot{W}_{e\ act} \dot{W}_{e\ ref}$  [Wcm<sup>-2</sup>].

## Polarization curve-Implicit form

Implicit relation between voltage and current density

$$V_{cell} = \frac{V_{th} T, p}{2} \left[ \frac{\tau \eta_m}{(1 - \eta_m)} - \frac{(\eta_m - \gamma_0) i V_{cell}}{(1 - \eta_m) \dot{W}_{e ref}} \right] \times \\ \left( 1 - \sqrt{1 + \frac{4(1 - \eta_m) \eta_m \dot{W}_{e act}}{[\dot{W}_{e act}(\eta_m - \gamma_0) - \tau \eta_m]^2}} \right)$$

The membrane efficiency  $\eta_m$  is calculated from the general formula, when the transport processes are neglected, i.e.,  $\gamma_0 = 0$ . Explicit form  $V_{cell} = V_{cell}(i, \dot{W}_{e ref}, V_{th} T, p, \eta_{th}, \tau, \gamma_0, \sigma_p, l_{mol})$  we find putting

$$V_{cell} = \eta V_{th} T, p \quad \text{and} \quad \dot{W}_{e act} = \frac{i V_{cell}}{\dot{W}_{e ref}}$$

## Including the coupling and internal resistance

Coupling  $q$  between proton current and water flux is expressed by actual electric power

$$\begin{aligned}\dot{W}_{e, act} &= iV_{cell} = \dot{W}_{e, act} \dot{W}_{e, ref} = -\sqrt{1-q^2}\sigma_p V_{cell} \frac{\partial\phi}{\partial x} \\ &\simeq \sqrt{1-q^2}\sigma_p \left( \frac{V_{cell}^2}{l_m} \right)\end{aligned}$$

$l_m$  is the thickness of PEM

Electro-osmotic factor  $\sqrt{1-q^2}$  is replaced by the approx. formula

$\eta_{m, coupl} = 1 - 1.6\sqrt{1-q^2}$  so that the coupling is described by

$$\eta_{m, coupl} = 1 - \frac{1.6 \dot{W}_{e, act} \dot{W}_{e, ref}}{\sigma_p \left( \frac{V_{cell}^2}{l_m} \right)}$$

and included in the final PEM efficiency

$$\eta_{m, f} = \eta_m \eta_{m, coupl}$$

The passive resistance  $R_i$  [ $\Omega$ ] coming from the connecting wires and the electrodes and GDL (no from the PEM)

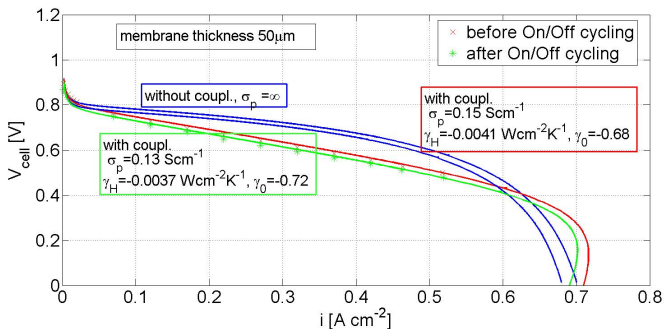
$$V_{cell, f} = V_{cell} - iR_i$$

# Comparison with the experiments

Accelerating test procedure according to JRC Scientific and Technical Reports  
Test Module PEFC SC 5-4

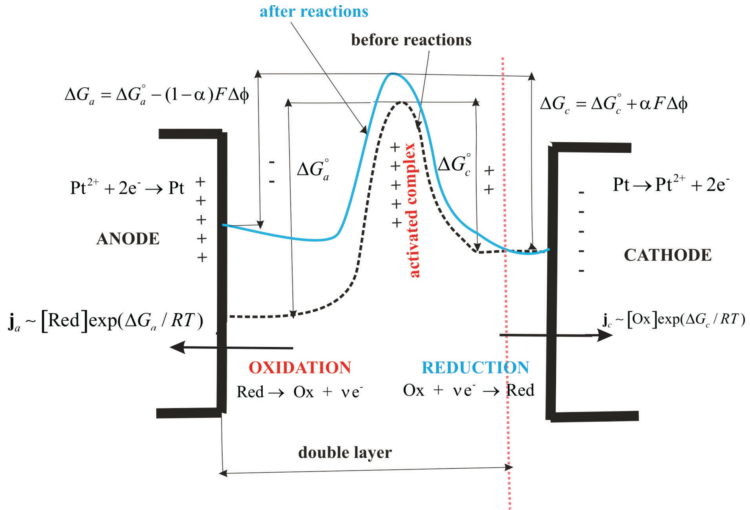
The tested cell provided PaxiTech and is marked as MEA S50-5L with area  $50 \text{ cm}^2$

catalyst 70 % Pt/C, catalyst loading  $0.5 \text{ mg Pt}\cdot\text{cm}^{-2}$  and membrane thickness  $50 \mu\text{m}$ .



# Reverse flow study

The existence of the double layer changes the potential between the electrodes. For very low supply of the fuel (open circuit conditions) the anodic current is higher than cathodic current



## Reverse flow study-Butler-Volmer equation

the exchange current density depends on the actual concentrations of fuels (in our case the Hydrogen and Oxygen) and transfer coefficients  $\alpha_a$ ,  $\alpha_c$ , i. e.,

$$i_0 = 2Fk_a n_{O_2}^{0.5} \exp \left[ \frac{\alpha_a F V_{eq\ T,p}}{RT_1} \right] = 2Fk_c n_{H_2} \exp \left[ \frac{-\alpha_c F V_{eq\ T,p}}{RT_1} \right] \quad (4)$$

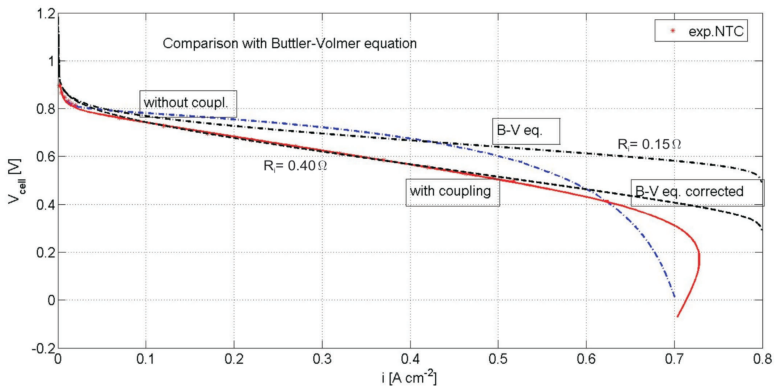
where  $n_{H_2}$ ,  $n_{O_2}$  [mol/m<sup>3</sup>] are fuel concentrations,  $k_a$ ,  $k_c$  [1/s] are the unknown reaction rates (activity of the catalysts layers),  $F = 96.485$  [C/mol],  $R = 8.314$  [J/(mol K)]. The concentration of [O<sub>2</sub>] is used instead of the unknown concentration of [H<sup>+</sup>].

For the loaded FC the electrode potential changes from its zero current value  $V_{eq\ T,p}$  to the actual value  $V_{cell}$  and the Butler-Volmer equation has usual form

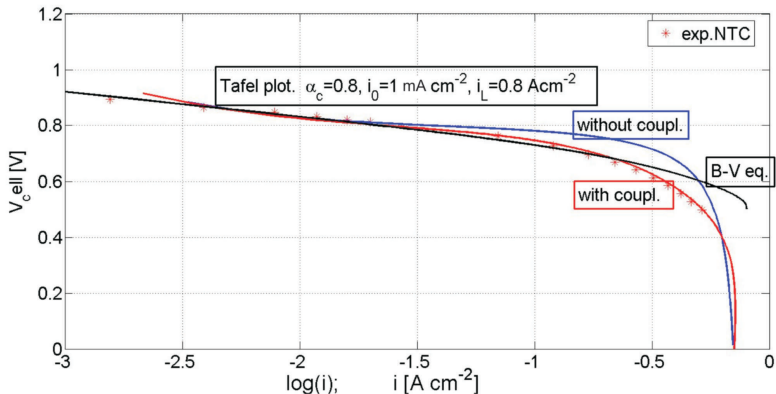
$$i = i_0 \left[ \exp \left[ \frac{\alpha_a F (V_{cell} - V_{eq\ T,p})}{RT_1} \right] - \exp \left[ \frac{-\alpha_c F (V_{cell} - V_{eq\ T,p})}{RT_1} \right] \right]$$

where the difference  $V_{cell} - V_{eq\ T,p}$  is called **overpotential**.

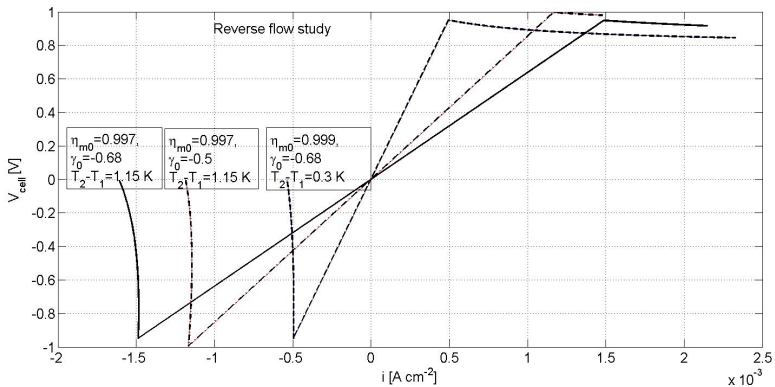
# Butler-Volmer study



# Transfer coefficient



# Reverse flow-Thermodynamic theory



# Summary

- ▶ The splitting of the work on the volumetric and non-volumetric get new possibility to formulate electro-chemical processes
- ▶ Close to the steady state is the entropy production compensated by the decrease of entropy and entropy flux is "almost" constant
- ▶ The efficiency of the energy transformations depends on the power and has the maximum. This analysis offers to find the optimal design and operation conditions.
- ▶ The coupling between different processes is self-regulated to reach the minimum entropy production (minimum entropy decrease)

# Some Relevant Publications I



Glansdorff P., Prigogine I.: Thermodynamic Theory of Structure, Stability and Fluctuations. Wiley/Interscience, 1971.



de Groot S.R. and Mazur P.: Non-Equilibrium Thermodynamics. North-Holland, Amsterdam, 1962.



Vukalovich M. P. and Novikov I.I.: Thermodynamics, Mashinostroenie, Moscow, 1972



Curson F.L., Ahlborn B.: Efficiency of a Carnot engine at maximum power output, American Journal of Physics, 43:22, 1975



De Vos A.: Endoreversible Thermodynamics of Solar Energy Conversion, Oxford University Press, 1992



Chambadal P.: Evolution et Applications du Concept d'Entropie, Dunod, Paris, Sec. 30, 1963