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Enhancement of Hydrogen Fuel Cell Efficiency by the Control a Water

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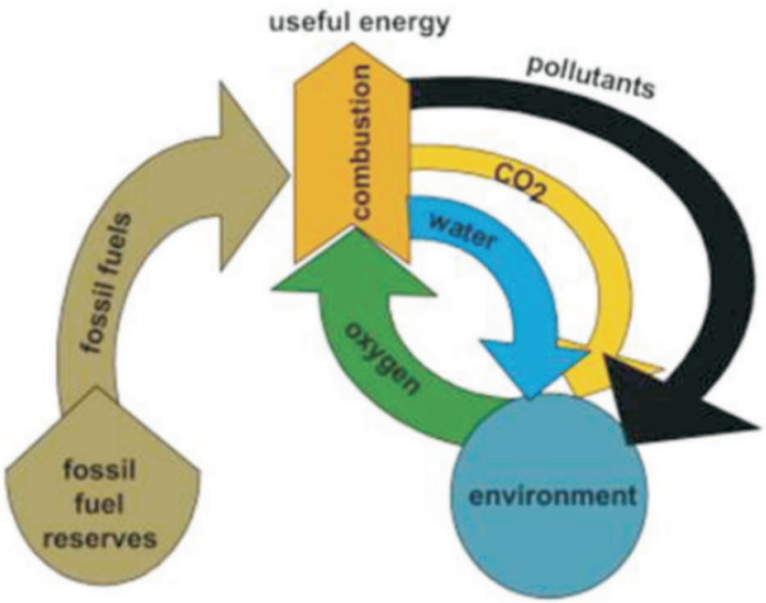
Outline

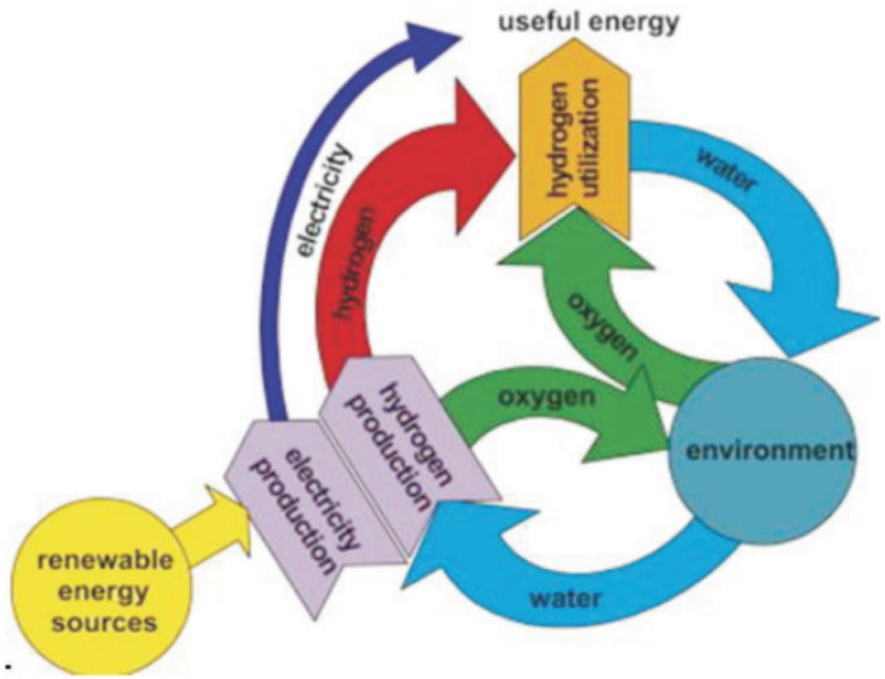
1. Energy conversion and its future modifications
2. Energy in chemical bounds
3. Fuel cells concept and its application
4. Low Temperature Hydrogen Fuel Cells
5. Theory of mixture
   - The entropy production
   - Thermodynamic forces and fluxes
6. Efficiency of HFC and maximum coupling
7. Efficiency enhancement by capillarity
8. Summary

Energy conversion and its future modifications

ENERGY CONVERSION

from Today to Future





Various energy forms

Balance of energy – I. Law of Thermodynamics

$$\Delta Q = \Delta U + \Delta W_{\text{mech+chem}} \qquad \ldots \quad \Delta Q = -\int_{\partial V} \mathbf{q}\, d\mathbf{a} \ \ldots \ \text{heat imput}$$

$$= \Delta H + \Delta W_{\text{non volume}} \qquad \ldots \qquad H = U + W_{\text{vol. work}} \ \ldots\text{enthalpy}$$

$$= \Delta H_{\text{c}} - \Delta_t p - \Delta_{\text{ir}} W_{\text{mech}} \qquad \ldots \ \Delta H_{\text{c}} = \int_V \rho h_{\text{c}} dv, \ \ \Delta_t p = \int_V \frac{\partial p}{\partial t} dv, \ \ \Delta_{\text{ir}} W_{\text{mech}} = \int_{\partial V} \mathbf{v} \cdot \mathbf{t}_{\text{dis}}\, d\mathbf{a},$$

$$h_{\text{c}} = \frac{\text{v}^2}{2} + u + \frac{p}{\rho} + \varphi \ \ldots \text{ total enthalpy-for convective problems}$$

Balance of entropy– II. Law of Thermodynamics

$$\Delta Q \le T \Delta S_{\text{eq}} + T \Delta S_{\text{ir}}, \qquad \Delta Q = T \Delta S_{\text{eq}}$$

$$T \Delta S_{\text{ir}} \ge 0$$

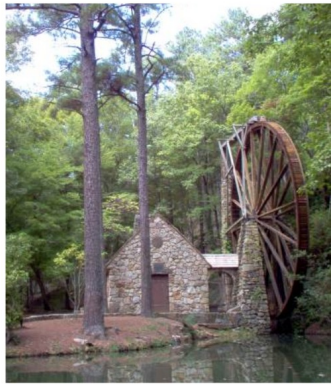
Various form of energy utilization

$$\Delta Q = \Delta U + \Delta W_{\text{mech+chem}} \qquad \text{for } \Delta U = 0 \quad (T = \text{const})$$

$$\Delta Q = \Delta W_{\text{chem}} \qquad \text{...combustion}$$

$$\Delta Q = 0, \quad \Delta W_{\text{mech}} = 0, \qquad \text{for } \Delta U = 0 \quad (T = \text{const})$$

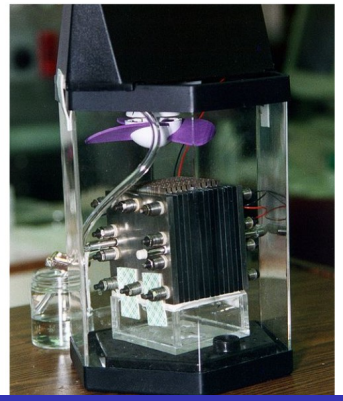
$$\Delta W_{\text{pot}} + \Delta W_{\text{mech}} = 0 \text{...conversion of mechanical energies}$$



$$\Delta Q = T\Delta S = \Delta H + \Delta W_{\text{nonvolume}} = \Delta H - \Delta G - S\Delta T,$$

$$\text{for } \Delta W_{\text{non volume}} = W_{\text{e}} \quad \text{...electric work}$$

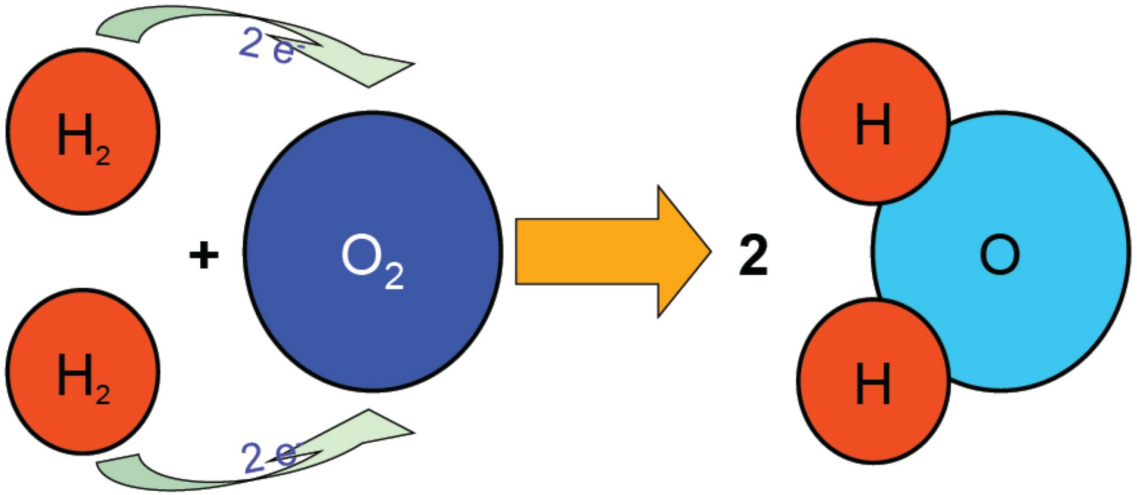
$$\eta_{teor} = \frac{\Delta G}{\Delta H} = \frac{\Delta H - T\Delta S - S\Delta T}{\Delta H} = \frac{W_e - S\Delta T}{\Delta H}$$



Energy in chemical bounds

Energy of chemical reactions

$$\Delta Q = \Delta H + \Delta W_{\text{non volume}}$$



Fuel + Oxidant → Product

The fuel will be oxidized during combustion

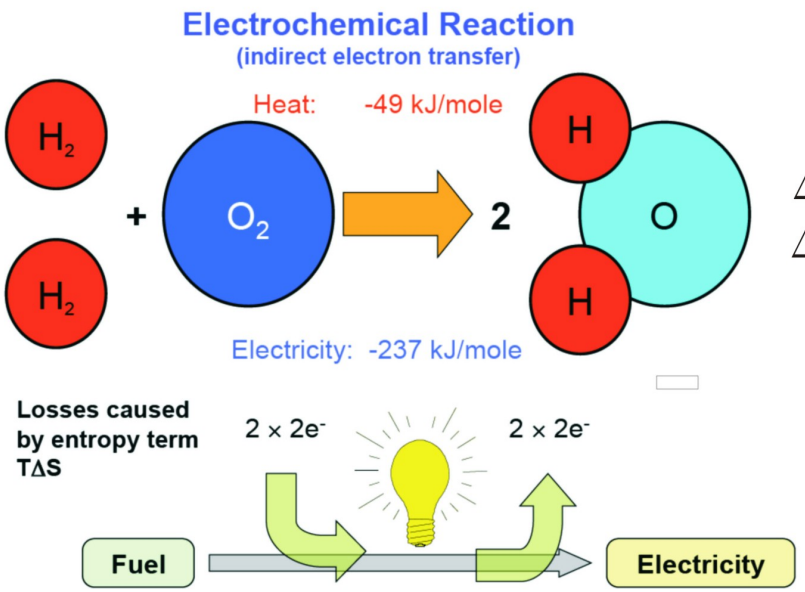
Oxidation from a chemical point of view means loss of electrons

The oxidant will be reduced during combustion

Reduction from a chemical point of view means gain of electrons

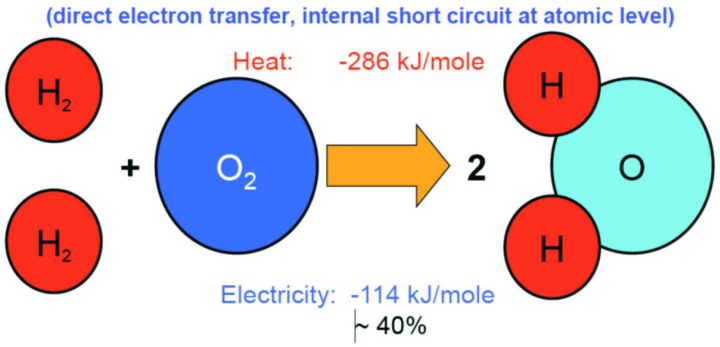
Therefore: Combustion is associated with the ecxhange of electrons!

Efficiency of fuel combustion

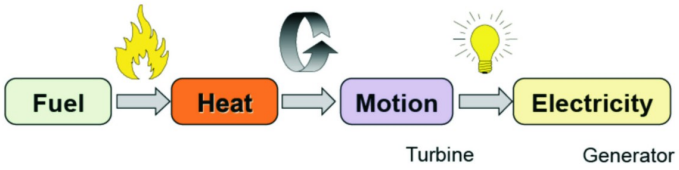


ΔH=-286 kJ/mol
ΔG=-237.13 kJ/mol

$$\eta_{\text{Fuel Cell}} = \frac{\Delta G}{\Delta H} = \left[1 + \frac{T\Delta S}{\Delta G}\right]^{-1} \sim 80\%$$



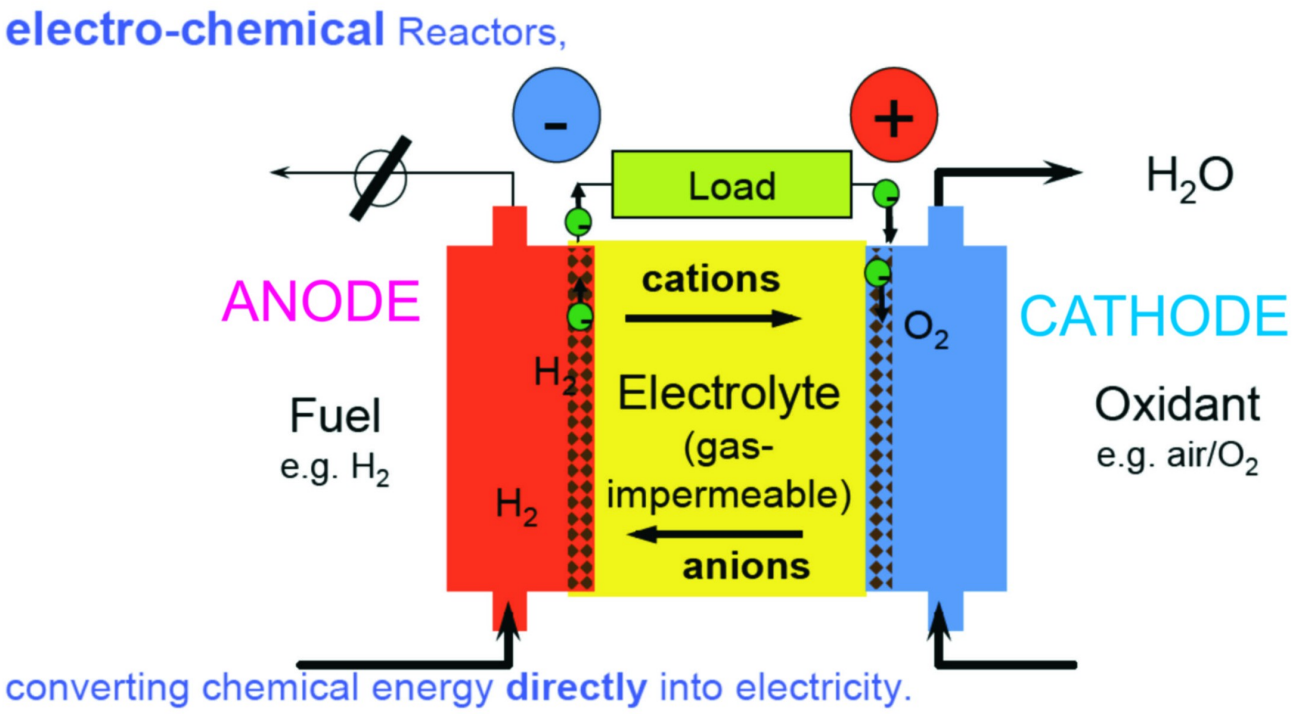
$$\eta_{\text{Carnot}} = 1 - \frac{T_{\text{out}}}{T_{\text{in}}}$$



Performance of fuel cells

FUEL CELL CONCEPT

Oxidation and reduction are realized at the two different places; anode and cathode



Fuel tested for everyday application

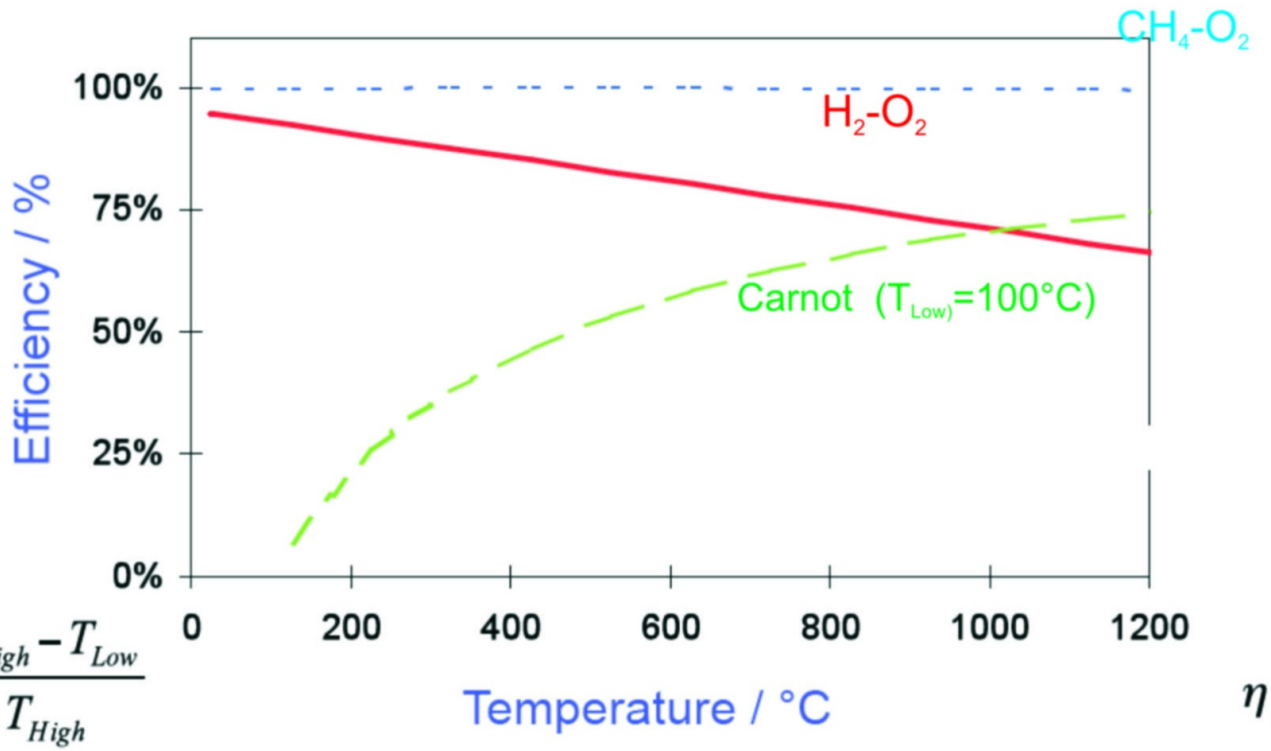
Thermodynamic efficiency for different reactions

$$\eta_t = \frac{\text{useful energy output}}{\text{energy input}} = \frac{W_e\ (\text{electric work})}{\Delta H\ \ (\text{heat of combustion})} \Rightarrow \text{in the best case} = \frac{\Delta G}{\Delta H},$$

$$\eta_{th} = \frac{\Delta G}{\Delta H} = \frac{\Delta H - T\Delta S - S\Delta T}{\Delta H} = \frac{W_e - S\Delta T}{\Delta H} = \eta_t(q)\big(1-\delta(q)\big) \text{ for } \delta(q) = \frac{S\Delta T}{W_e}$$

Reaction	n	$-\Delta H^0$ [kJ mol^{-1}]	E^0_H [V]	$-\Delta G^0$ [kJ mol^{-1}]	E_0 [V]	η_{th}
$H_2 + 1/2\ O_2 \rightarrow H_2O_{liq}$	2	286,0	1,482	237,13	1,229	0,829
$H_2 + 1/2\ O_2 \rightarrow H_2O_{gas}$	2	241,8	1,253	228,6	1,185	0,946
$CO + 1/2\ O_2 \rightarrow CO_2$	2	283,1	1,467	257,2	1,333	0,909
$CH_3OH + 1\ 1/2\ O_2 \rightarrow CO_2 + 2\ H_2O_{liq}$	6	726,6	1,255	702,5	1,214	0,967
$CH_4 + 2\ O_2 \rightarrow CO_2 + 2\ H_2O_{gas}$	8	802,4	1,039	800,9	1,038	0,999

Thermal efficiency versus Temperature



$$\eta_{Carnot} = \frac{T_{High} - T_{Low}}{T_{High}}$$

$$\eta_{FuelCell} = \frac{\Delta G}{\Delta H}$$

We expect high efficiency at low temperature when using hydrogen,
And we would be happy to use methane directly.

Low Temperature Hydrogen Fuel Cells-LTHFC

Thermodynamic analysis of the transport processes in the Hydrogen Fuel Cells (HFC) is oriented to the following items:

- to formulate adequate theory of mixture, which include such internal processes like capillary flow and swelling
- to derive the entropy production for the HFC and to define all relevant thermodynamic forces and fluxes
- to estimate the maximum efficiency of the HFC and especially of the Polymer Electrolyte Membrane (PEM)
- to find the maximum coupling between diffusion flux end electric flux
- to estimate the possible enhancement by the capillary action of water

Standard electrochemical analysis of fuel cells

Net current density as a function of Gibbs free enthalpy at the cathode and anode surface

$$j = j_a - j_c = Fk_a[\mathrm{Red}] - Fk_c[\mathrm{Ox}], \quad k_a = A_a \exp\left[-\frac{\Delta G_a}{RT}\right],$$

$$k_c = A_c \exp\left[-\frac{\Delta G_c}{RT}\right]$$

Zero current potential E_0 is defined for $j = 0$

$$j_0 = \underbrace{FA_a[\mathrm{Red}]\exp\left[-\frac{\Delta G_a}{RT}\right]}_{\text{anodic current}} = FA_a[\mathrm{Red}]\exp\left[-\frac{\Delta G_a^0 - (1-\alpha)F\Delta\phi}{RT}\right] =$$

$$= \underbrace{FA_c[\mathrm{Ox}]\exp\left[-\frac{\Delta G_c}{RT}\right]}_{\text{cathodic current}} = FA_c[\mathrm{Ox}]\exp\left[-\frac{\Delta G_c^0 + \alpha F\Delta\phi}{RT}\right]$$

To satisfy this condition we define the overpotential η

$$\Delta\phi = E_0 + \eta$$

Transfer coeff. $\alpha \simeq 0.5$

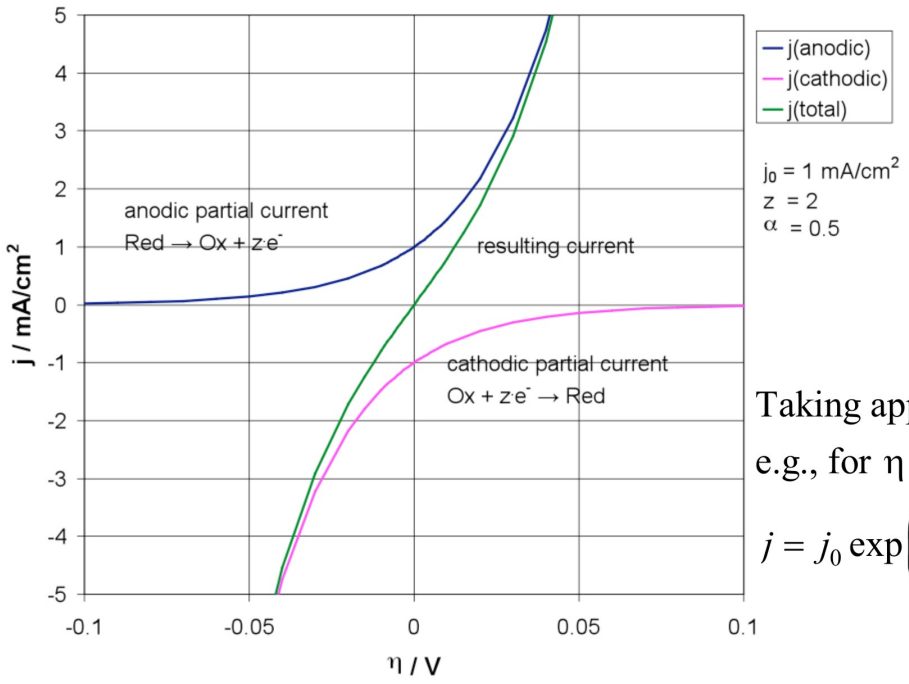
Standard electrochemical analysis of fuel cells

The Butler-Volmer Equation
Charge transfer between the electrodes

$$j(\eta) = j_0 \left\{ \exp\left[\frac{z\alpha F\eta}{RT}\right] - \exp\left[\frac{z(1-\alpha)F\eta}{RT}\right] \right\}$$

j_0 ... exchange current density

Current-Voltage-Curve Dominated by Charge Transfer

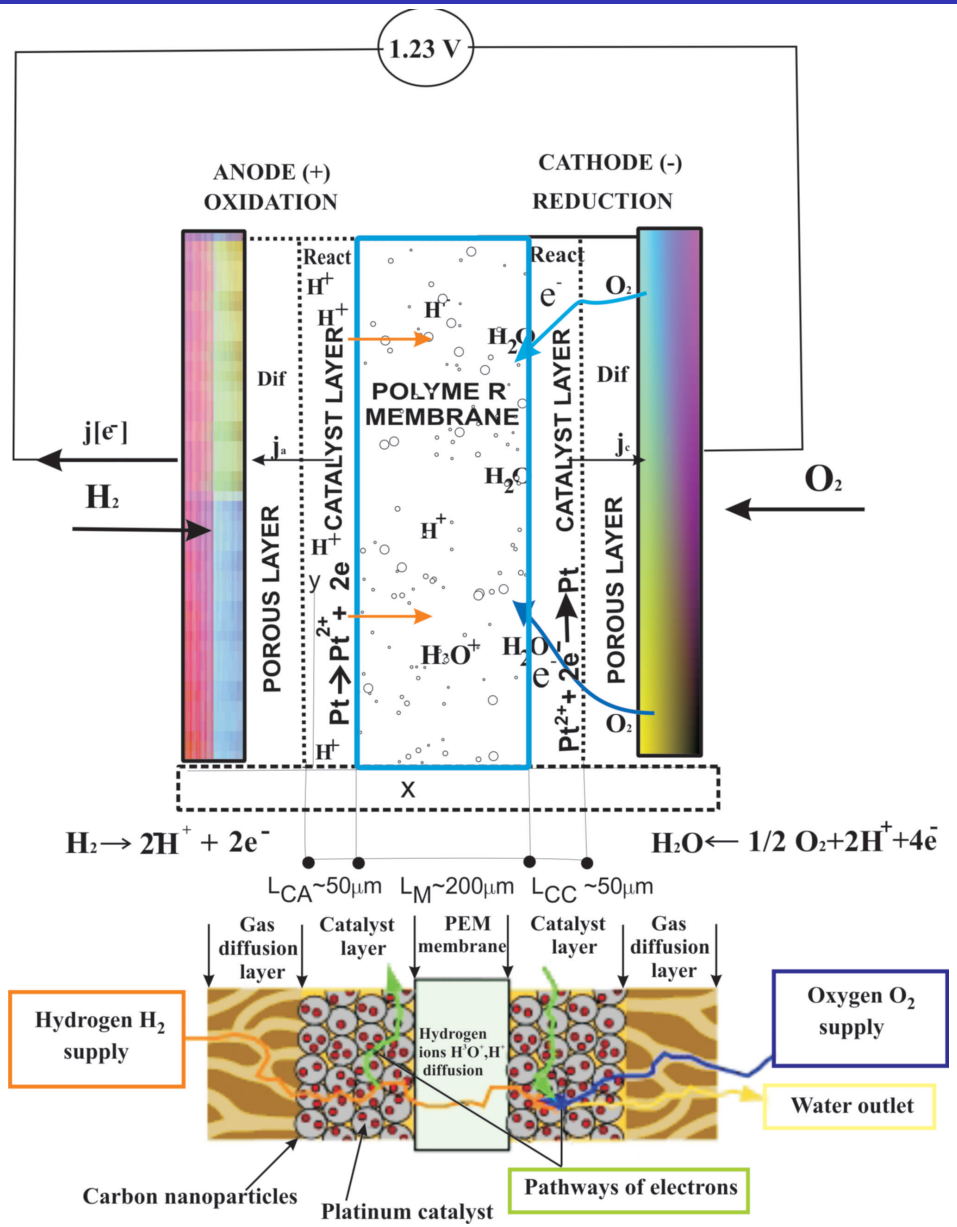


Taking approx. $e^x \doteq 1 + x$,

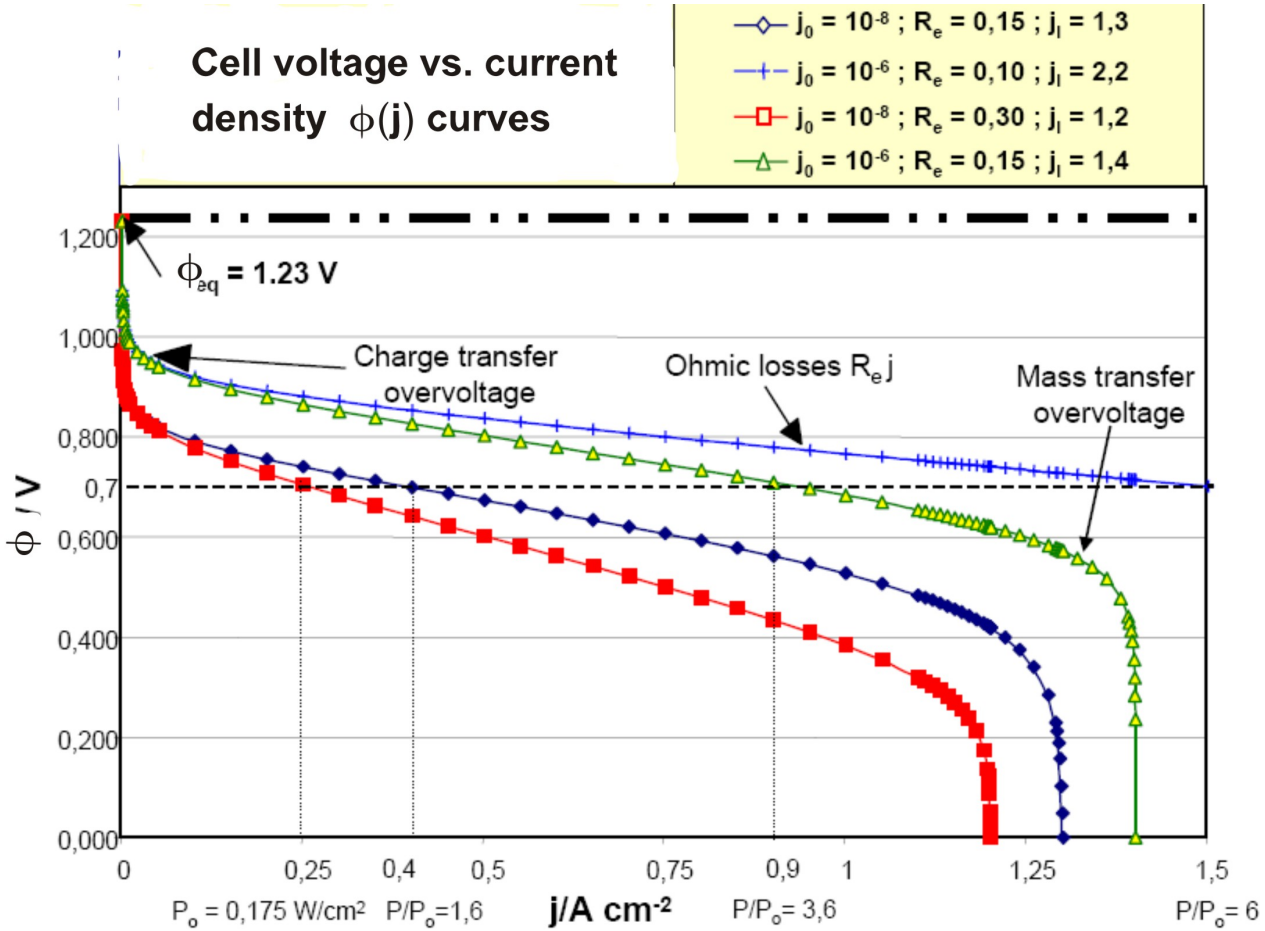
e.g., for $\eta \geq 50\,\mathrm{mV}$

$$j = j_0 \exp\left(\frac{\alpha F\eta}{RT}\right)$$

HFC structure and corresponding relevant processes.



Standard fuel cell measurement



$$\phi(j) = \phi_c(j) - \phi_a(j) - R_e j = \phi_{eq} - (|\eta_c(j)| + |\eta_a(j)| + R_e |j|)$$

Theory of mixture

Gibbs definition of entropy

$$T\dot{s} = \dot{u} - \frac{\mathbf{t}_{el}}{\rho}\dot{\mathbf{e}} - \sum \mu_\alpha \dot{w}_\alpha \tag{1}$$

where $\dot{()}$ is material (Euler) derivative.
All extensive quantities for mixture depends on a mass fraction

$$w_\alpha = \frac{\rho_\alpha}{\rho}, \quad \text{for} \quad \rho_\alpha = M_\alpha c_\alpha, \quad \rho = \sum_\alpha \rho_\alpha \tag{2}$$

Here ρ_α $\left[\mathrm{kg/m^3}\right]$ is density, c_α $\left[\mathrm{kmol/m^3}\right]$ is molar concentration and M_α $[\mathrm{kg/kmol}]$ is molecular mass of chemical component α. Analogously is introduced volume fraction

Internal energy, deformation and entropy

$$u = \sum_\alpha w_\alpha u_\alpha, \quad \mathbf{e} = \sum_\alpha w_\alpha \mathbf{e}_\alpha, \quad s = \sum_\alpha w_\alpha s_\alpha \tag{3}$$

Euler deformation tensor $\mathbf{e}$ is symmetrical tensor for solids and it shrinks for fluids in the $\mathrm{tr}\,\mathbf{e} = e_{(1)}$ and then the specific volume can be replaced by

$$\frac{e_{(1)}}{\rho} \Rightarrow v = \frac{1}{\rho} = \sum_\alpha w_\alpha v_\alpha \tag{4}$$

Stress tensor has different form for solids

$$\mathbf{t}_{el} = p\left(e_{(1)}, T\right)\mathbf{I} + \overset{(o)}{\mathbf{t}}_{el} \tag{5}$$

and for fluids

$$\mathbf{t}_{el} = -p(\rho, T)\mathbf{I} \tag{6}$$

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Entropy flux and entropy production.

Entropy flux is

$$\mathbf{j}(s) = \frac{(\mathbf{j}_q - \sum_\alpha \mathbf{j}_{D_\alpha}\mu_\alpha + \sum \mathbf{j}_{D\alpha}(u_\alpha \mathbf{I} - \mathbf{t}_\alpha/\rho_\alpha))}{T} \tag{7}$$

and entropy production

$$\sigma(s) = \left[\mathbf{j}_q + \sum \mathbf{j}_{D\alpha}(u_\alpha - \frac{\mathbf{t}_\alpha}{\rho_\alpha})\right] \nabla\left(\frac{1}{T}\right) + \left[\mathbf{t}_{dis} - \sum_\alpha \rho_\alpha \mathbf{v}_{D_\alpha} \otimes \mathbf{v}_{D_\alpha}\right] : \mathbf{d}$$
$$- \sum \mathbf{j}_{D_\alpha}\left[\nabla\left(\frac{\mu_\alpha}{T}\right) + \frac{\mathbf{F}_\alpha}{T} + \frac{\mathbf{\Gamma}_\alpha}{T}\right] + \sum_\rho \frac{\mathcal{A}_\rho \dot{\zeta}_\rho}{T} \geq 0 \tag{8}$$

The last inequality is an alternative form of ***II. law of thermodynamics***.

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Transport phenomena **J** and Driving forces **X**.

heat $\mathbf{j}_q$	$\nabla\left(\frac{1}{T}\right)$
visco-plastic	
- for solids $\mathbf{t}_{dis}\left(T, \mathbf{d}, \dot{\mathbf{t}}_{dis}\right)$	$\frac{\mathbf{d}}{T}$
- for fluids p_{dis}	$\frac{\mathrm{div}\mathbf{v}}{T}$
- viscosity $\mathbf{t}_{dis} - \sum_\alpha \rho_\alpha \mathbf{v}_{D_\alpha} \otimes \mathbf{v}_{D_\alpha}$	$\frac{\overset{(o)}{\mathbf{d}}}{T}$
- swelling $\mathbf{t}_{el\,\alpha} + \mathbf{t}_{dis\,\alpha}$	$-\mathbf{v}_{D\alpha}\nabla(\frac{1}{T})$
concentration diffusion $\mathbf{j}_{D_\alpha}$	$\left(\frac{\nabla\mu_\alpha}{T}\right)$
thermodiffusion $\mathbf{j}_{D_\alpha}$	$(u_\alpha - \mu_\alpha)\nabla\left(\frac{1}{T}\right)$
electric current $\mathbf{j}_{e,\alpha}$	$\frac{\mathbf{F}_\alpha}{T} = -\frac{z_\alpha F}{M_\alpha T}\nabla\varphi$
capillary flux $\mathbf{j}_{D_c}$	$\frac{\mathbf{\Gamma_c}}{T} = +\frac{1}{T}\nabla(\sigma \cdot a)$
chemical reaction and phase transition $\dot{\zeta}_\rho$	$\frac{\mathcal{A}_\rho}{T}$

Tab. 1. Independent thermodynamic forces and fluxes

General form of transport properties of PEM

General linearized form of all these processes for an isothermal state is

$$
\begin{aligned}
\mathbf{j}_{D_w} &= -\frac{L_{ww}}{T}\nabla\mu_w - \frac{L_{wH^+}F}{TM_{H^+}}\nabla\varphi - \frac{L_{wc}}{T}\nabla(\sigma a) \\
\mathbf{j}_{DH^+} &= j_e\frac{M_{H^+}}{F} = -\frac{L_{H^+w}}{T}\nabla\mu_w - \frac{L_{H^+H^+}F}{TM_{H^+}}\nabla\varphi - \frac{L_{H^+c}}{T}\nabla(\sigma a) \\
\mathbf{j}_c &= -\frac{L_{cw}}{T}\nabla\mu_w - \frac{L_{cH^+}F}{TM_{H^+}}\nabla\varphi - \frac{L_{cc}}{T}\nabla(\sigma a)
\end{aligned}
\tag{9}
$$

Here the fluxes $\mathbf{j}_{D_w}, \mathbf{j}_{DH^+}, \mathbf{j}_c$ have physical dimension $\left[\mathrm{kg/m^2s}\right]$ and electric current density $\mathbf{j}_e$ $\left[\mathrm{A/m^2}\right]$. All phenomenological coefficients

$$
\mathbf{L} = \begin{bmatrix} L_{ww}\,, & L_{wH^+}\,, & L_{wc} \\ L_{H^+w}\,, & L_{H^+H^+}\,, & L_{H^+c} \\ L_{cw}\,, & L_{cH^+}\,, & L_{cc} \end{bmatrix} \quad \left[\frac{\mathrm{kg\cdot K\cdot s}}{\mathrm{m^3}}\right] \tag{10}
$$

have the same physical dimension and the application of Onsager reciprocal relations $L_{ij} = L_{ji}$ is possible.

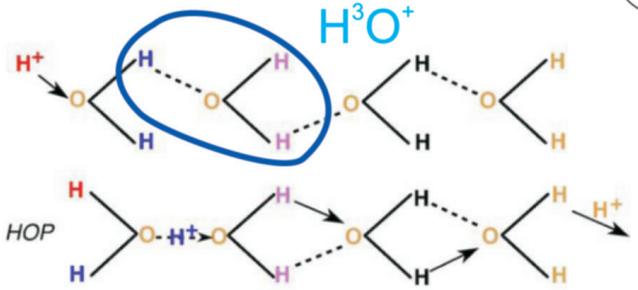
Coefficients of diffusion and conductivity in PEM

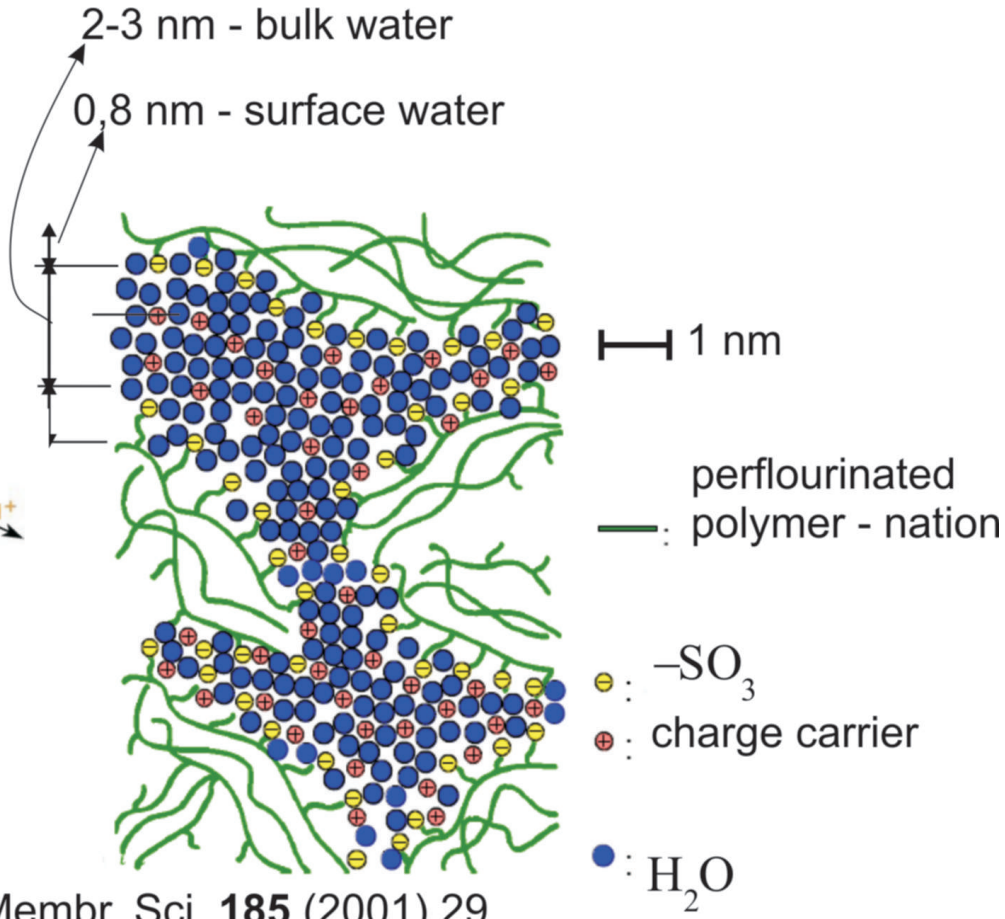
Diffusion coefficient
(Einstein-Smoluchowski)

$$D_{H^+} \approx \frac{l^2}{\kappa \tau_D}$$

$l[\mathrm{m}]$ mean step
$\tau_D\,[\mathrm{s}]$ mean time of a step
$\kappa = 2,4$ or 6 for $1,2$ or 3 dim.

Grotthus mechanism for water





Kreuer et. al., J. Membr. Sci. **185** (2001) 29

Coefficients for different molecular mechanisms

	surface diff.	Grotthus diff.	*En masse* diff.
step time τ [ps]	1610	1.5	5.78
step distance l_{mol} [nm]	0.255	0.255	0.28
Diffusion coef. D_α [cm^2/s]	0.006	7.22	2.26
Conductivity $\frac{\sigma_{H^+}}{w_{H^+}}$ [$\mathrm{S/cm}$] $M_{H^+} = 1,\ T = 360\,K$	0.057	2.24	0.703
Conductivity $\frac{\sigma_{H^3O^+}}{w_{H^3O^+}}$ [$\mathrm{S/cm}$] $M_{H^3O^+} = 19,\ T = 360\,K$	0.0003	0.12	0.037

Tab 2. Diffusion coefficients and electric conductivity for different mechanism are calculated by Einstein - Smoluchowski formula. The experimental values of the proton conductivity (see Choi P. at al. 2005) of the Nafion EW 1100 are very close to the value 0.12 S/cm for the hydronium ion $\mathrm{H_3O^+}$.

Fuel cell efficiency

The thermal efficiency $\eta_t = \frac{\text{electric output}}{\text{energy input}} = \frac{W_e}{\Delta H}$, where W_e is an electric work and $\frac{dW_e}{dt} = -\mathbf{i}\nabla\phi\,[\mathrm{W}]$ is generated electric power.
The maximal possible (theoretical) efficiency of a chemical transformation is formulated as $\eta_{theor} = \frac{\Delta G}{\Delta H}$. The thermal efficiency can be expressed from the balance of energy

$$T\Delta S = \Delta H - W_e \quad \text{or} \quad \eta_t = 1 - \frac{T\Delta S}{\Delta H}$$

applying the change of the Gibbs free enthalpy $\Delta G = \Delta H - T\Delta S - S\Delta T$. The theoretical efficiency is

$$\eta_{theor} = \frac{\Delta G}{\Delta H} = \frac{\Delta H - T\Delta S - S\Delta T}{\Delta H} =$$
$$\frac{W_e - S\Delta T}{\Delta H} = \eta_t(q)(1 - \delta(q)) \quad \text{for} \quad \delta(q) = \frac{S\Delta T}{W_e}$$

Thermal efficiency

Entropy production

$$\sigma(s) = \mathbf{t}_{dis} : \mathbf{d} - \mathbf{J}_w \mathbf{X}_w - \mathbf{J}_\mathrm{e} \mathbf{X}_\mathrm{e} + \sum_\rho \frac{\mathcal{A}_\rho \dot{\zeta}_\rho}{T} \geq 0$$

Thermal efficiency

$$\eta_t = \frac{W_e}{\Delta H} = \frac{-T\mathbf{X}_\mathrm{e}\mathbf{J}_\mathrm{e}}{\Delta H} = 1 - \frac{\mathbf{J}_w\mathbf{X}_w + \mathbf{J}_\mathrm{e}\mathbf{X}_\mathrm{e}}{\mathbf{X}_\mathrm{e}\mathbf{J}_\mathrm{e}} \eta_t = 1 - \frac{\eta_t}{\varepsilon}$$

where

$$\varepsilon = \frac{\mathbf{X}_\mathrm{e}\mathbf{J}_\mathrm{e}}{\mathbf{J}_w\mathbf{X}_w + \mathbf{J}_\mathrm{e}\mathbf{X}_\mathrm{e}} = \frac{\mathbf{X}_\mathrm{e}\mathbf{J}_\mathrm{e}}{\mathbf{J}_w\mathbf{X}_w} \left(1 + \frac{\mathbf{X}_\mathrm{e}\mathbf{J}_\mathrm{e}}{\mathbf{J}_w\mathbf{X}_w}\right)^{-1}$$

so that

$$\eta_t = \frac{\varepsilon}{\varepsilon + 1}$$

Membrane efficiency and coupling

The ratio

$$\eta_m = \frac{\mathbf{X}_e \mathbf{J}_e}{\mathbf{J}_w \mathbf{X}_w} = \frac{-W_e}{\Delta H_m} = \frac{\varepsilon}{1-\varepsilon} = \frac{\eta_t}{1-2\eta_t}$$

is the efficiency of the PEM only. ΔH_m is the change of the enthalpy of the consumed Hydrogen.
The corresponding electrical work in Volts for 1 mol of Hydrogen is
$\Delta H_m = 286.02[\mathrm{kJ/mol}]/(2 \cdot 96.48) = 1.481[V]$.
Coupling coefficient q and force ratio y

$$q = \frac{\hat{L}_{wH^3O^+}}{\sqrt{\hat{L}_{ww}\hat{L}_{H^3O^+H^3O^+}}}, \quad y = \frac{\sqrt{\hat{L}_{H^3O^+H^3O^+}}\mathbf{X}_e}{\sqrt{\hat{L}_{ww}}\mathbf{X}_w} = \frac{\sqrt{\hat{L}_{H^3O^+H^3O^+}}}{\sqrt{\hat{L}_{ww}}} \frac{ZF\nabla\phi}{\nabla(\mu_w + a\sigma)}$$

Maximal efficiency and maximal coupling

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

$$\eta_{t\,max} = \frac{y_1^2}{y_1^2 + y_2^2 - 1} \quad \text{and} \quad \eta_{m\,max} = y_1^2$$

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

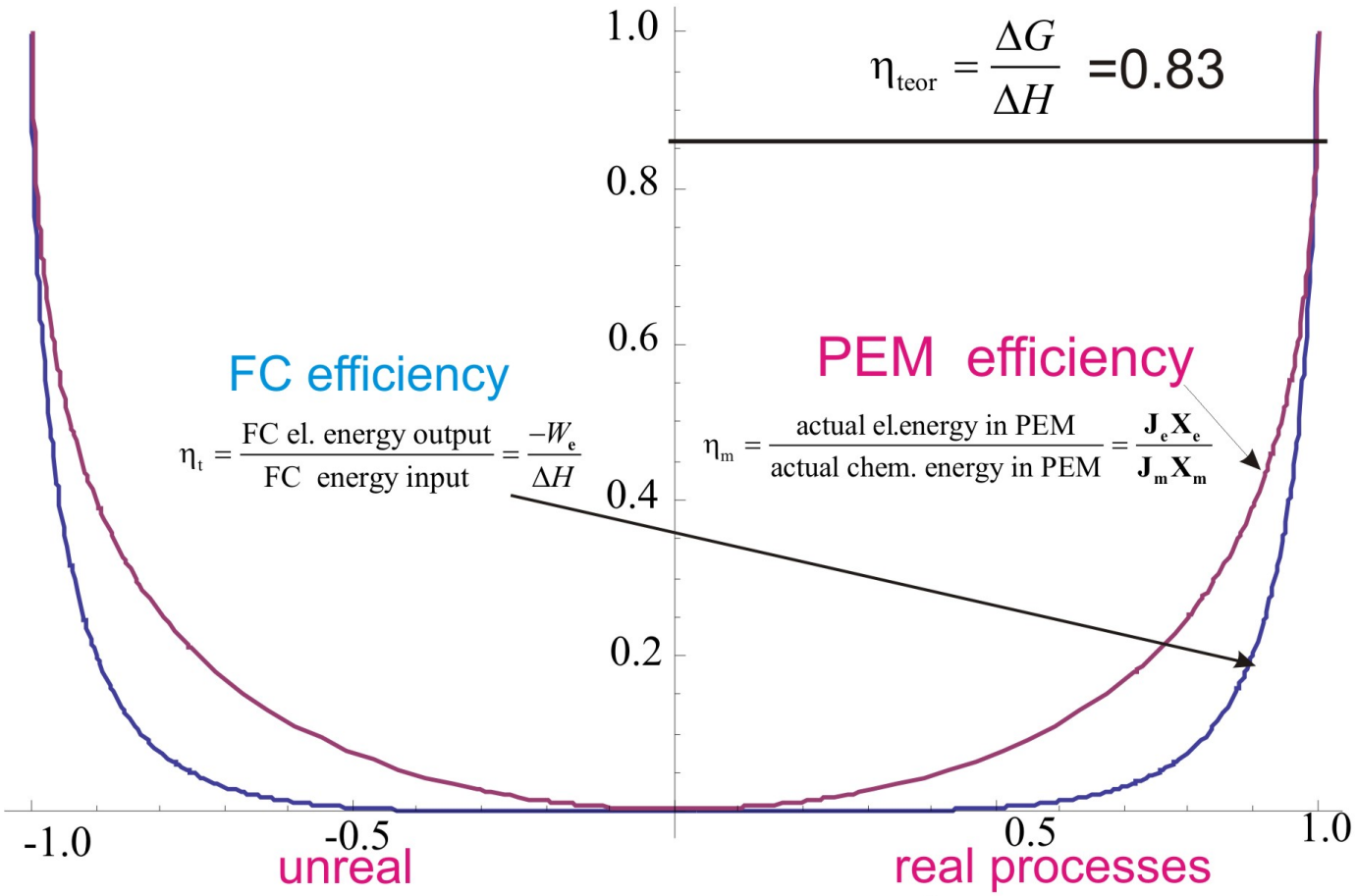
$$\mathbf{J}_{\mathrm{e}} = -\hat{L}_{H^3O^+w}\mathbf{X}_w = -\frac{\rho_{H^3O^+w} M_{H^3O^+} D_{H^3O^+}}{RT}\nabla(\mu_w + a\sigma)$$

Diffusion coefficients by Tab. 2 are $D_{H^3O^+} = 7.22 \cdot 10^{-5}\,\mathrm{cm}^2/\mathrm{s}$- Grotthus mechanism and for water we put $D_w = 2.26 \cdot 10^{-5}\,\mathrm{cm}^2/\mathrm{s}$ - this value corresponds to the self-diffusion . The coupling coefficient q is by the definition

$$q = \frac{\hat{L}_{H^3O^+w}}{\sqrt{\hat{L}_{ww}\hat{L}_{H^3O^+w}}} = \sqrt{\frac{(1-w_w)M_{H^3O^+}D_{H^3O^+}}{w_w M_w D_w}} = \sqrt{3.37\frac{1-w_w}{w_w}}$$

The maximum coupling $q = 1$ is reached for the $w_w = 0.77$, in the other words; the maximum coupling is reached when 23% of water is ionized to the Hydronium.

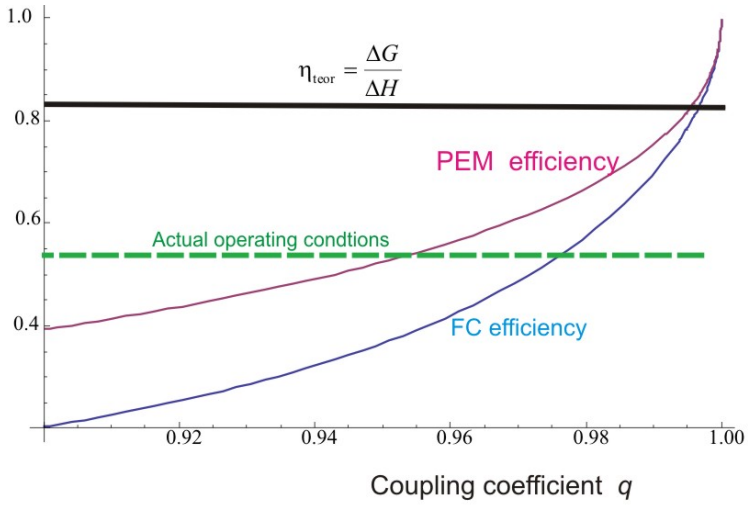
Coupling coefficient–efficiency dependence

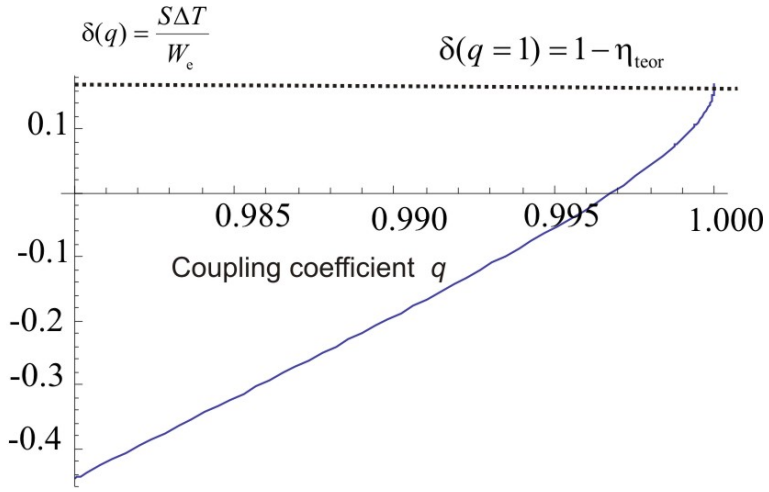


Coupling coefficient $q = \frac{L_{H^3O^+,w}}{\sqrt{L_{ww} L_{H^3O^+H^3O^+}}}$

Figure: 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; the relative losses $\delta(q)$ of the enthalpy ΔH express the multiple of the output electric power W_e.

Water transport enhanced by capillarity

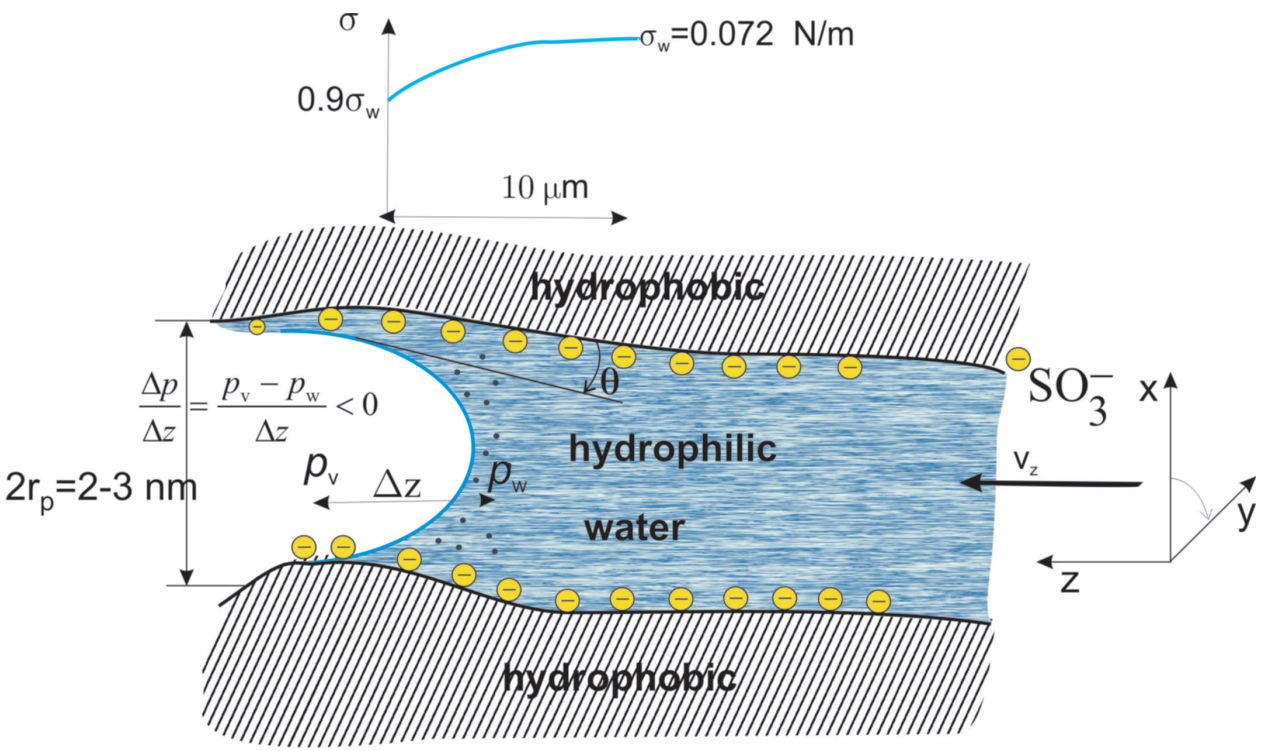
Capillary flux in the pore of the radius r_p is driven by surface tension σ_w of liquid water, which has the kinematic viskosity ν_w, is given by

$$j_c = -\frac{L_{cc}}{T}\frac{d(\sigma_w a_m)}{dz} = -\frac{r_p^2}{8\nu_w}\frac{d}{dz}\left(\sigma_w \frac{dA}{dV}\right) = -\frac{r_p^2}{8\nu_w}\frac{d}{dz}\left(\rho_m \sigma_w a_m\right)$$

and can be enhanced by the change of surface tension $\sigma_w(z)$ or by the membrane porosity $v_m(z)$ in the flow direction

$$\frac{d}{dz}\left(\sigma \frac{dA}{dV}\right) = \frac{d}{dz}\left(\sigma(z) v_m(z)\right) = v_m(z)\frac{d\sigma(z)}{dz} + \sigma(z)\frac{dv_m(z)}{dz} < 0$$

Surface tension drives the water in pores



$$j_c = -\frac{r_p^2}{8\nu_w}\frac{d}{dz}\left(\sigma\frac{dA}{dV}\right) =\sim 2\cdot 10^{-5}\frac{(\sigma(z+\Delta z)-\sigma(z))}{\sigma\Delta z}$$

$$\doteq 2\cdot 10^{-5}\frac{(0.9-1)}{10^{-5}}\,\frac{\mathrm{kg}}{\mathrm{m^2 s}} = 0.02\,\frac{\mathrm{g}}{\mathrm{cm^2 s}}$$

The experimental investigation of this phenomenon is in progress.

Summary

- the entropy production contains all relevant processes, including the water diffusivity, electric conductivity in membrane and capillary action of the water in membrane pores, the chemical reaction at the electrodes and structural changes (swelling) in the PEM are included.
- the thermal efficiency of the whole FC and the efficiency of the PEM are analyzed in detail and the conditions for their maximum are formulated
- from the condition for maximal coupling between water diffusion flux in the PEM and corresponding maximal electric density flux, the optimal concentration of Hydronium ions in water is specified
- the influence of capillarity of water for the typical Nafion membrane structure is appointed and possibilities of its enhancement are formulated

For Further Reading I

Němec T., Maršík, F., Mičan O.
The Charackteristic Thickness of Polymer Electrolyte Membrane and the Efficiency of Fuel Cell
Heat Transfer Engineering. **30**,(7), 574-581. 2009

Choi Pyoungho, Jalani Nikhil H., Datta Ravindra
Thermodynamics and Proton Transport in Nafion II. Proton diffusion Mechanisms and Conductivity
Journal of The Electrochemical Society, **152**,(3) E123-E130, 2005

Barbir F.
PEM Fuel Cells: Theory and Practice,
Elsevier Academic Press, Amsterdam, 2005

Jörissen L.
Introduction to Fuel Cells,
IZMIR, July 11-15, 2011

Mamut E.
Hydrogen Generation, IZMIR, July 11-15, 2011

For Further Reading II

Hydrogen & Fuel Cells Conference,
ZiNG CONFERENCES, Dec. 1/5, 2011, Mexico

Conference f-cell,
The fuel cell 11th Forum for Producers and Users, Sept. 26-27, 2011 Stuttgart, Germany.