

Institute of Thermomechanics
Academy of Sciences of the Czech Republic

THERMODYNAMIC ANALYSIS OF THE EFFICIENCY OF PEM FUEL CELLS

Frantisek Marsik and Tomas Nemeč

Institute of Thermomechanics v.v.i. CAS
Dolejšková 5, 182 00 Praha 8, Czech Republic,
marsik@it.cas.cz, nemeč@it.cas.cz

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- 1 Model description
- 2 Thermodynamic analysis
 - Characteristic length
 - Efficiency



www.minihydrogen.dk

Theoretical efficiency of a fuel is defined as in the gas-liquid operation mode, i.e. the evaporation heat is included

$$\eta_{teor} = \frac{W_{max}}{\Delta H_{ref}} = \frac{-\Delta G_{ref}}{\Delta H_{ref}} = \frac{237.13 \text{ kJ/mol}}{285.84 \text{ kJ/mol}} = 0.8295$$

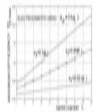
Taking into account the entropy increase evaluates, the corresponding Gibbs free enthalpy change is

$$\overline{\Delta G} = \overline{\Delta H} - T \overline{\Delta S} = \overline{\Delta H} - T \sigma(S) = \overline{\Delta H} + j_{H^+} F \nabla \phi + j_{H_2O} \nabla \mu_{H_2O}$$

$$W = j_{H^+} F \nabla \phi \quad \text{actual electric power}$$

$$j_{H_2O} \nabla \mu_{H_2O} \quad \text{the "lost power" of transport processes}$$

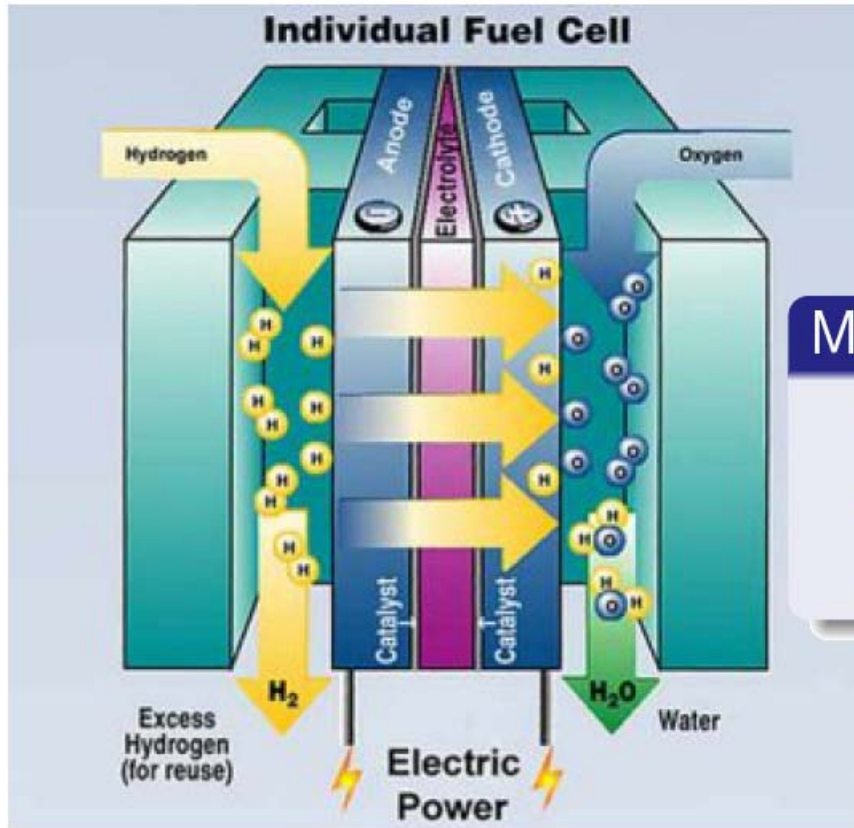
The relation of to the total efficiency to transport efficiency



is

$$\eta_{tot} = \frac{W_{el}}{\Delta H} = \frac{j_{H^+} F \nabla \phi}{\overline{\Delta G} + T \sigma(s)} = \frac{j_{H^+} F \nabla \phi}{\overline{\Delta G} - j_{H^+} F \nabla \phi - j_{H_2O} \nabla \mu_{H_2O}} = \frac{\eta_{tr}}{1 - 2\eta_{tr}}$$

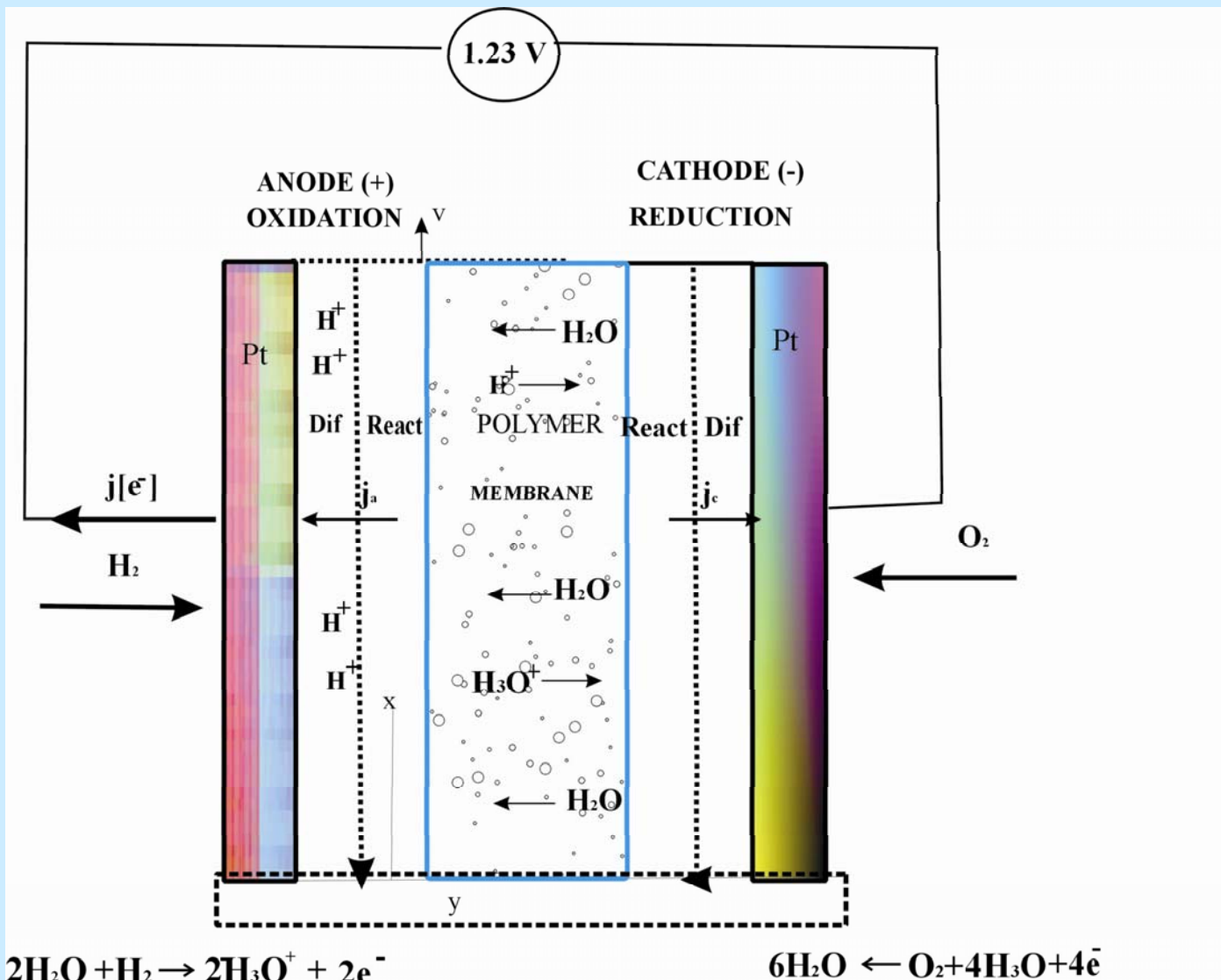
Simplified model



U.S. Department of Energy

Model assumptions

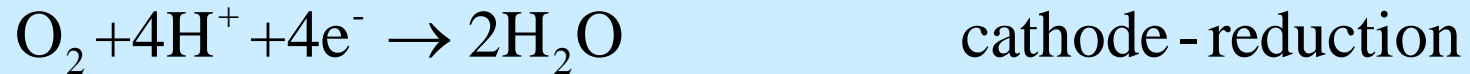
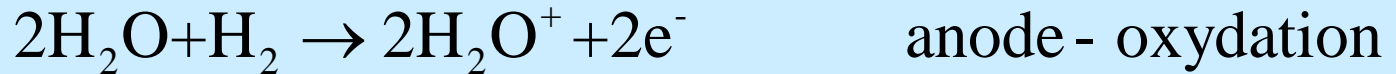
- One-dimensional reactor
- Homogeneous
- Constant reactant concentration



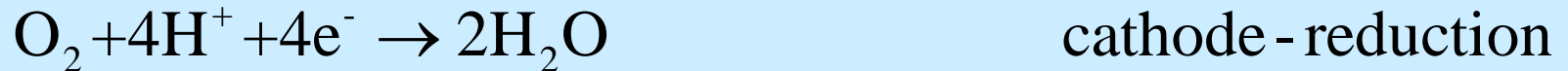
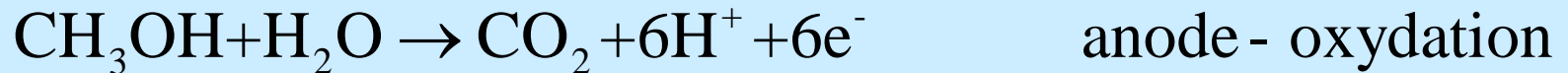
FUEL CELL

direct conversion chemical energy into electrical energy

Hydrogen Fuel Cell --- Proton Exchange Fuel Cell (PEFC)



Methanol Fuel Cell --- Direct Methanol Fuel Cell (DMFC)



Entropy production $\sigma(S)$ depends on the balance laws formulation

$$\sigma(S) = j_q^i \frac{\partial}{\partial x^i} \left(\frac{1}{T} \right) - \sum_{\alpha} j_{D_{\alpha}}^i \frac{\partial}{\partial x^i} \left(\frac{\mu_{\alpha}}{T} \right) + \frac{i_{\alpha e}^l}{F} \frac{\partial}{\partial x^l} \left(\frac{Z_{\alpha} F \phi}{T} \right) + \frac{1}{T} t_{dis}^{ij} \frac{\partial v_j}{\partial x^i} + \frac{1}{T} \sum r_{\rho} A_{\rho} \geq 0$$

Heat transfer
Mass & el. Charge (Z_{α}) transfer
friction
Chemical reactions

$$F = 9.6495 \cdot 10^7 \text{ [C/kmol]}$$

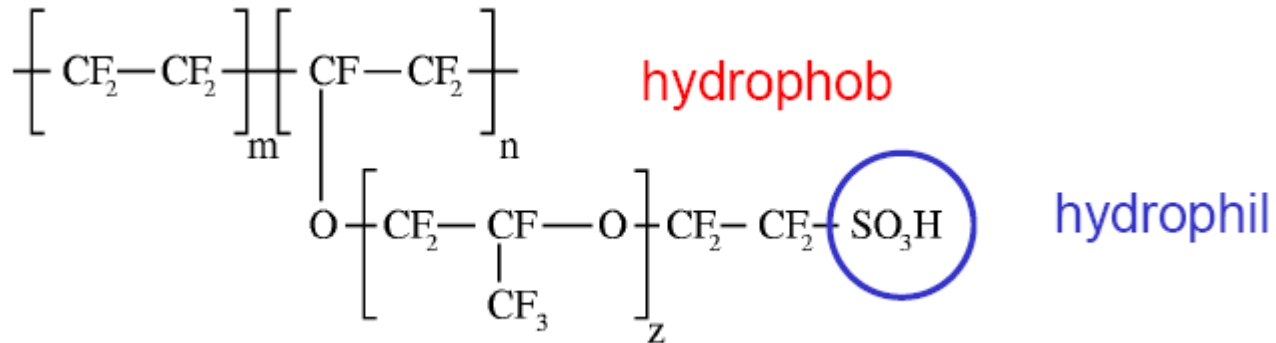
For isothermal case

$$j_{D_{\alpha}}^i = \rho_{\alpha} (v_{\alpha}^i - v^i), \text{ diffusion fluxes for } \alpha, \beta, = \text{H}_2\text{O}, \text{H}_3\text{O}^+, \text{H}_2, \text{H}^+, \text{O}_2$$

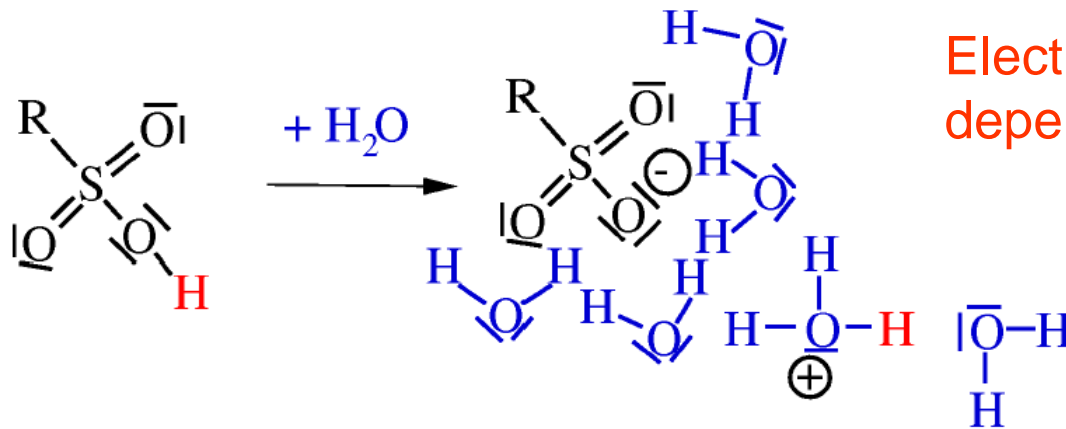
$$i_{\alpha e}^i = \rho_e (v_{\alpha e}^i - v^i), \text{ electric current of charged component } \alpha$$

$$r_{\rho} = \sum_{\sigma} L_{\rho\sigma} A_{\sigma}, \text{ chemical reaction rates for } \rho, \sigma = \text{cath, anode}$$

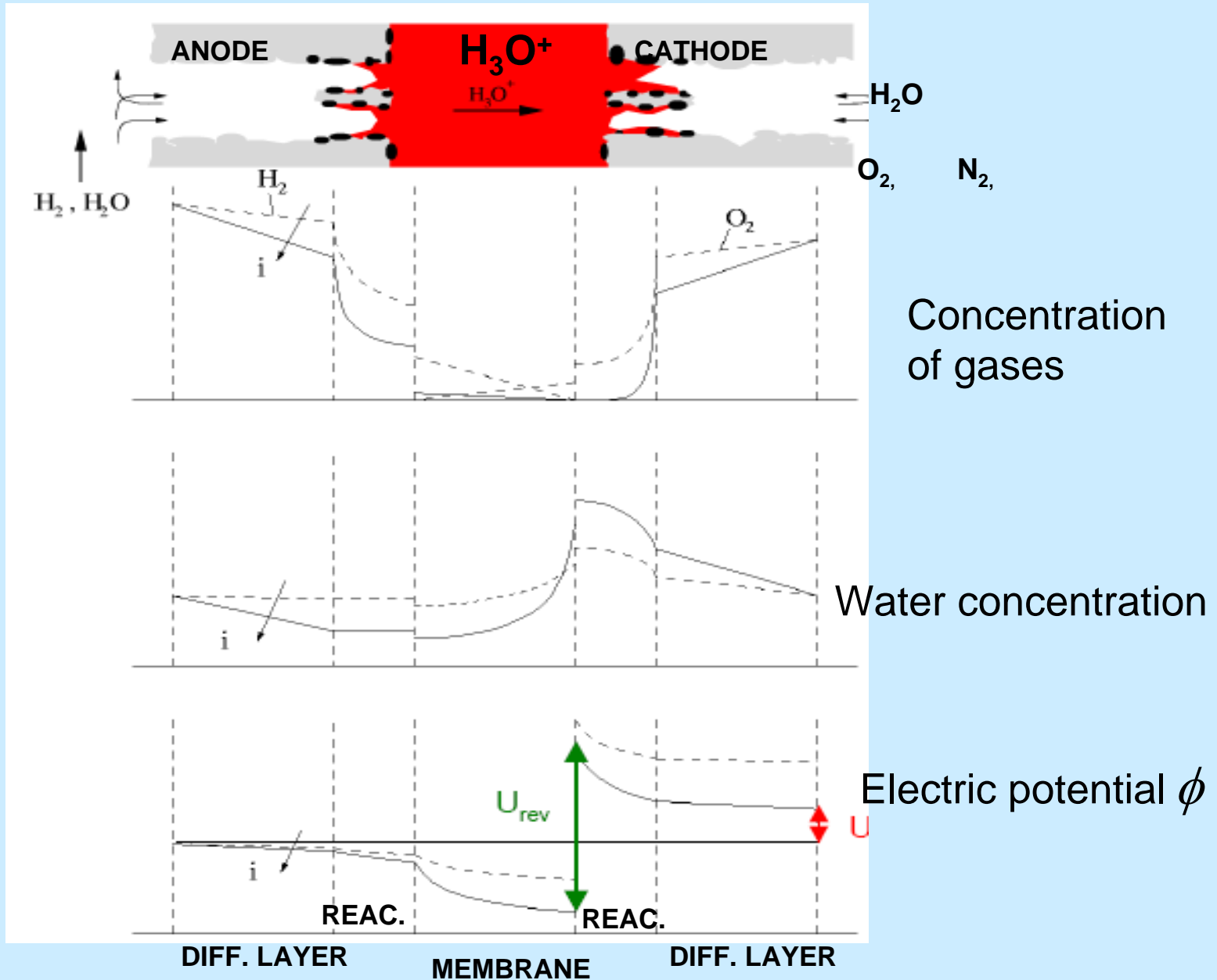
Nafion-Perfluorosulfonacid-polymer



SO₃H- complex induced dissociation by water



Distribution of all relevant quantities between electrodes by Frank Meier, Universität Stuttgart



Electro-chemical potential

$$\mu_{\alpha}(T, p, c_{\alpha}, \phi, \sigma) = \bar{\mu}_{\alpha}(T, p) + RT \ln \left(\frac{c_{\alpha}}{c_{0\alpha}} \right) + Z_{\alpha} F \phi + \frac{A_{\alpha}}{c_{\alpha}} \sigma \quad \left[\frac{\text{J}}{\text{kmol}} \right]$$

Reference pot.
of pure substance
Influence
of el. field

Influence of
concentration

Influence of
capillarity,
for water only
 $\alpha = \text{H}_2\text{O}$

$\sigma(c_{\alpha})$ water surface tension depends on a solute concentration c_{α}
on the surface A_{α} in 1 m^3 of the porous membrane

Thermodynamic analysis of transport processes

$$j_{D_w} \left[\frac{\text{kmol}}{\text{m}^2 \text{s}} \right] = L_{D_w} \left. \frac{\partial \mu_\alpha}{\partial c_w} \right|_\phi \frac{\partial c_w}{\partial y} + L_{we} \left. \frac{\partial \mu_\alpha}{\partial \phi} \right|_w \frac{\partial \phi}{\partial y}, \quad \text{water diffusion flux}$$

$$\frac{i}{F} \left[\frac{\text{kmol}}{\text{m}^2 \text{s}} \right] = L_{ew} \left. \frac{\partial \mu_\alpha}{\partial c_w} \right|_\phi \frac{\partial c_w}{\partial y} + L_{ee} \left. \frac{\partial \mu_\alpha}{\partial \phi} \right|_w \frac{\partial \phi}{\partial y} \quad \text{electric current}$$

$L_{ew} = L_{we}$... electrophoresis coefficients

Diff. coef.... $-L_{D_w} > 0$, conductivity $-L_{ee} > 0$,

physical dimension of all coef. are $\left[\frac{\text{kmol}^2}{\text{ms}} \right]$

Coupling coef. $q = \frac{L_{ew}}{\sqrt{L_{D_w} L_{ee}}}$, ... close relation to electrophoresis

Chemical potential of simplified model is

$$\mu_{\alpha}(c_{\alpha}, \phi) = \bar{\mu}_{\alpha}(T = \text{const}, p = \text{const}) + RT \ln \left(\frac{c_{\alpha}}{c_{0\alpha}} \right) + Z_{\alpha} F \phi$$

and corresponding diffusion and electric fluxes are

$$j_{D_w} \left[\frac{\text{kmol}}{\text{m}^2 \text{s}} \right] = L_{D_w} \frac{RT}{c_w} \frac{\partial c_w}{\partial y} + L_{we} ZF \frac{\partial \phi}{\partial y}, \quad \text{water diffusion flux } L_{D_w} \left[\frac{\text{kmol}^2}{\text{Jms}} \right], L_{ee} \left[\frac{\text{kmol}^2}{\text{Jms}} \right]$$

$$\frac{i}{F} \left[\frac{\text{kmol}}{\text{m}^2 \text{s}} \right] = L_{ew} \frac{RT}{c_w} \frac{\partial c_w}{\partial y} + L_{ee} ZF \frac{\partial \phi}{\partial y} \quad \text{electric current, } L_{we} \left[\frac{\text{kmol}^2}{\text{Jms}} \right] = L_{ew} \left[\frac{\text{kmol}^2}{\text{Jms}} \right]$$

Water diffusion flux through membrane or catalyst layers depends on coupling coefficient q

$$j_{D_w} = L_{D_w} \frac{RT}{c_w} (1 - q^2) \frac{\partial c_w}{\partial y} + q \sqrt{\frac{L_{D_w}}{L_{ee}}} \frac{i}{F}$$

from experiments (H. van Bussel *et al.*, 1998) and analysis (A. Kulikovski, 2003)

$$j_{D_w} = -D_{wl}(\lambda) \frac{\partial c_w}{\partial y} + n_d(\lambda) \frac{i}{F}, \quad \lambda \square \frac{c_{\text{H}_2\text{O}}}{c_{\text{SO}_3^-}} \square \frac{c_w}{c_{\text{H}^+}} = \Lambda \left(\frac{p_v}{p_{v,\text{sat}}} \right)$$

Extreme “efficiency” of electric power depends on electrophoresis
coef. q^2 only

$$\frac{\text{electric power}}{\text{total dissipation}} = \frac{\delta q + \delta^2}{1 + 2\delta q + \delta^2} \Bigg|_{\substack{\text{max} \\ q \in (-1,1)}} = 1 \pm \frac{q^2}{2\sqrt{1-q^2} \left(1 \pm \sqrt{1-q^2}\right)},$$

in all operating modes $\delta q < 0$,

$$\text{for } \delta = \sqrt{\frac{L_{ee}}{L_{D_w}}} \times \left\{ \frac{\text{electric intensity}}{\text{water gradient}} \right\} = -\frac{1 \pm \sqrt{1-q^2}}{q}.$$

Conclusion

I.) for $q > 0$, $\delta \propto \left\{ \frac{\text{electric intensity}}{\text{water gradient}} \right\} < 0$, i.e., $\frac{\partial \phi}{\partial y} > 0$, $\frac{\partial c_w}{\partial y} < 0$,

standard fuel cell operation

II.) for $q < 0$, $\delta \propto \left\{ \frac{\text{electric intensity}}{\text{water gradient}} \right\} > 0$, i.e., $\frac{\partial \phi}{\partial y} > 0$, $\frac{\partial c_w}{\partial y} > 0$,

electrolysis

Water content λ has close connection to the coupling coefficient q representing the diffusion flux through membrane or catalyst layers

$$j_{D_w} = L_{D_w} \frac{RT}{c_w} (1 - q^2) \frac{\partial c_w}{\partial y} + q \sqrt{\frac{L_{D_w}}{L_{ee}}} \frac{i}{F}$$

From the comparison with the experiments (H. van Bussel *et al.*, 1998) and corresponding analysis (A. Kulikovski, 2003) we have

$$j_{D_w} = -D_{wl}(\lambda) \frac{\partial c_w}{\partial y} + n_d(\lambda) \frac{i}{F},$$

where $\lambda = \frac{c_{\text{H}_2\text{O}}}{c_{\text{SO}_3^-}} = \frac{c_w}{c_{\text{H}^+}} = \Lambda \left(\frac{p_v}{p_{v,sat}} \right)$ is water content and

$$D_{wl}(\lambda) = D_{\text{H}_2\text{O}}(\lambda) = -L_{D_w} \frac{RT}{c_w} (1 - q^2), \quad q \sqrt{\frac{L_{D_w}}{L_{ee}}} = n_d(\lambda)$$

Typical operational conditions

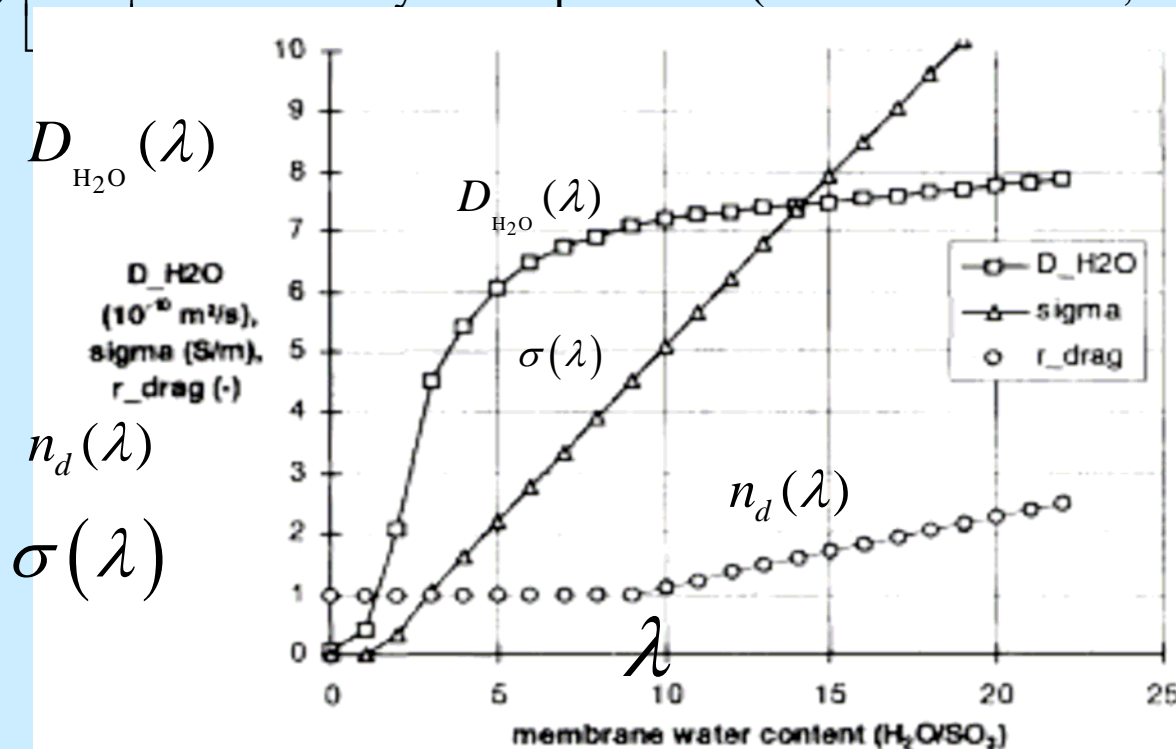
$$c_{\text{H}_2\text{O}} \approx c_{\text{H}_3\text{O}^+} \quad \text{and water content is } \lambda \approx \frac{c_{\text{H}_2\text{O}}}{c_{\text{SO}_3^-}} \approx \frac{c_w}{c_{\text{H}^+}} = \Lambda \left(\frac{p_v}{p_{v,\text{sat}}} \right)$$

$c_{\text{SO}_3^-}$ [kmol/m³]- concentration of sulphonic acid groups and $c_{\text{H}_2\text{O}} = c_{\text{SO}_3^-}$

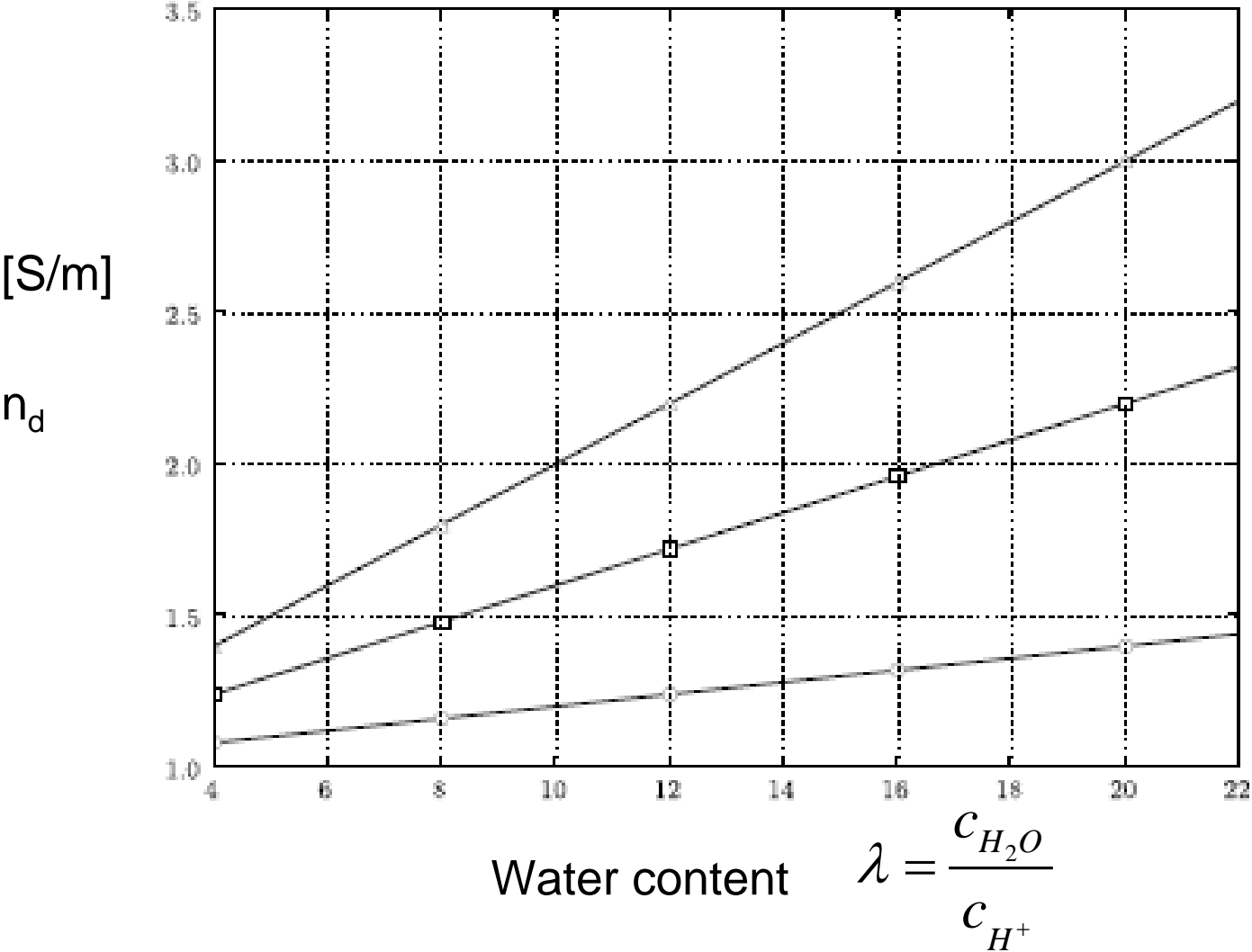
Water concentration is $c_w = c_{\text{H}_2\text{O}} = \lambda c_{\text{SO}_3^-}$

Diffusion coefficient is defined by $j_{D_w} = -D_{w1}(\lambda) \frac{\partial c_w}{\partial y} + n_d(\lambda) \frac{i}{F}$ or $j_{D_{\text{H}_2\text{O}}} = -D_{\text{H}_2\text{O}}(\lambda) \frac{\partial c_{\text{H}_2\text{O}}}{\partial y}$

$D_{\text{H}_2\text{O}}(\lambda) \left[\frac{\text{m}^2}{\text{s}} \right]$ is estimate by the experiments (H. van Bussel *et al.*, 1998)



Electroosmotic drag coefficient n_d applied in calculations



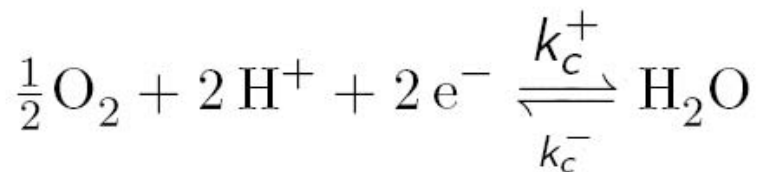
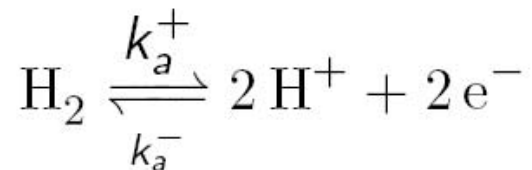
Relation between water diffusion $D_{\text{H}_2\text{O}}$ conductivity $\sigma(\lambda)$

drag coefficient $n_d(\lambda)$, coupling coefficient q

and water content λ

$$10^3 n_d(\lambda) = \frac{qF}{\sqrt{1-q^2}} \sqrt{\frac{Z\lambda D_{\text{H}_2\text{O}}(\lambda) c_{\text{SO}_3^-}}{\sigma(\lambda) RT}}$$

Applied chemical reaction for thermodynamical analysis



Mass balance equations

$$\frac{\partial c_{\text{H}_2\text{O}}}{\partial t} = w_c - \nabla \cdot \mathbf{j}_{\text{H}_2\text{O}}$$

$$\frac{\partial c_{\text{H}^+}}{\partial t} = 2w_a - 2w_c - \nabla \cdot \mathbf{j}_{\text{H}^+}$$

Anode/cathode reaction rates

$$w_a = k_a^+ c_{\text{H}_2} - k_a^- c_{\text{H}^+}^2$$

$$w_c = k_c^+ c_{\text{O}_2}^{\frac{1}{2}} c_{\text{H}^+}^2 - k_c^- c_{\text{H}_2\text{O}}$$

Modal analysis

Perturbations of the stationary solution $\bar{c}_{\text{H}_2\text{O}}$, \bar{c}_{H^+}

$$\begin{aligned}c_{\text{H}_2\text{O}} &= \bar{c}_{\text{H}_2\text{O}} + c_{\text{H}_2\text{O}}^0 \exp(kx - \omega t) \\c_{\text{H}^+} &= \bar{c}_{\text{H}^+} + c_{\text{H}^+}^0 \exp(kx - \omega t)\end{aligned}$$

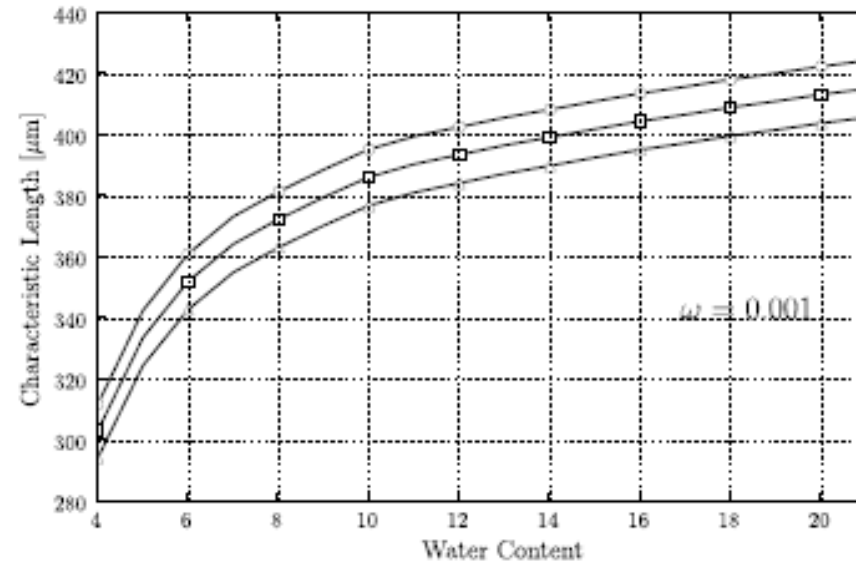
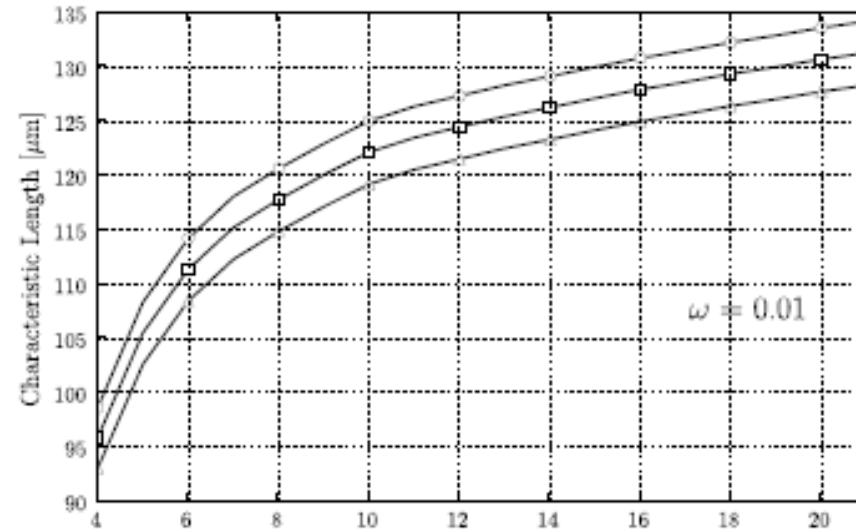
A non-zero perturbation amplitudes $c_{\text{H}_2\text{O}}^0$, $c_{\text{H}^+}^0$ condition gives the **dispersion relation** between k and ω

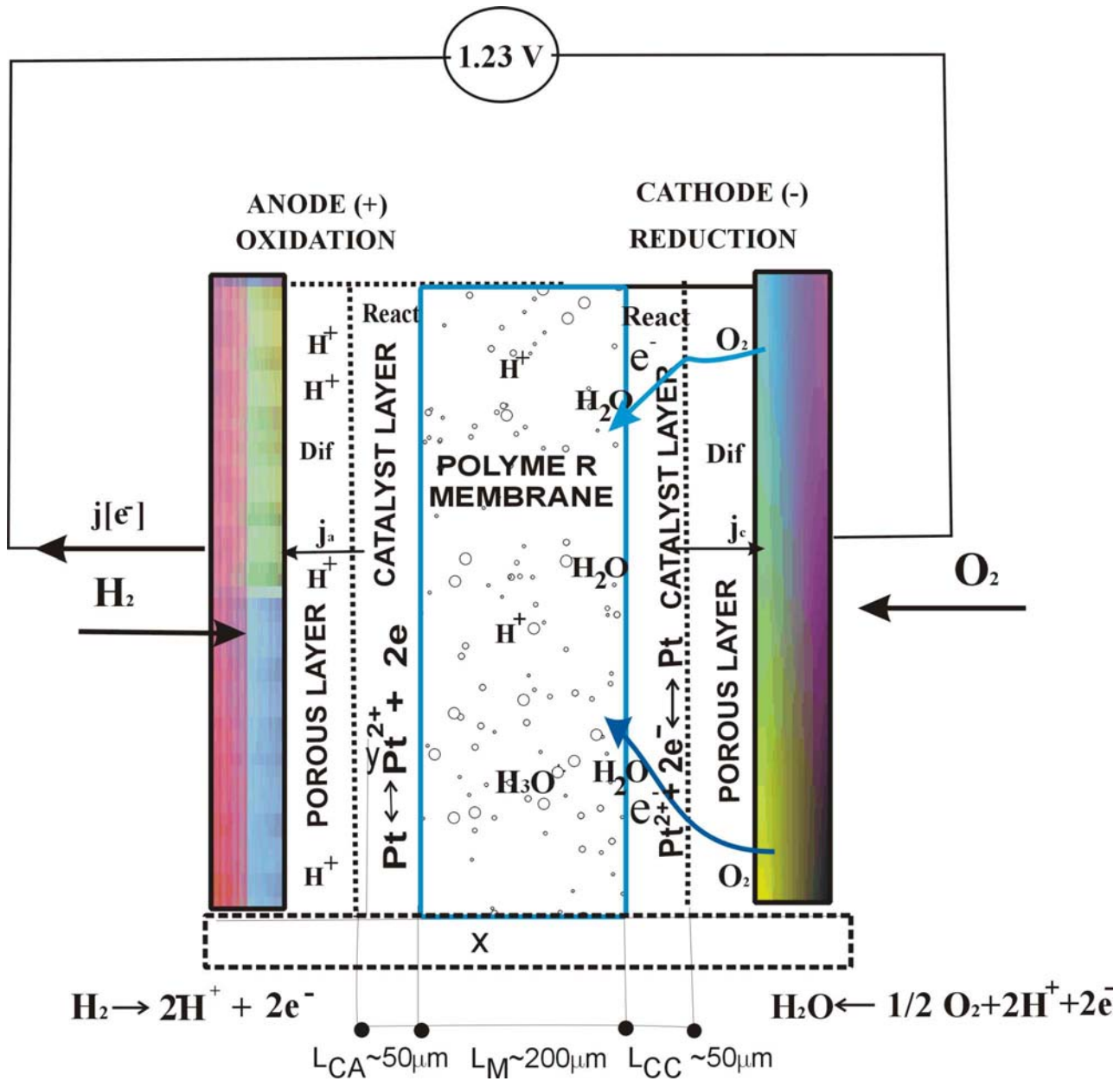
Characteristic membrane thickness L_{ch} [μm]

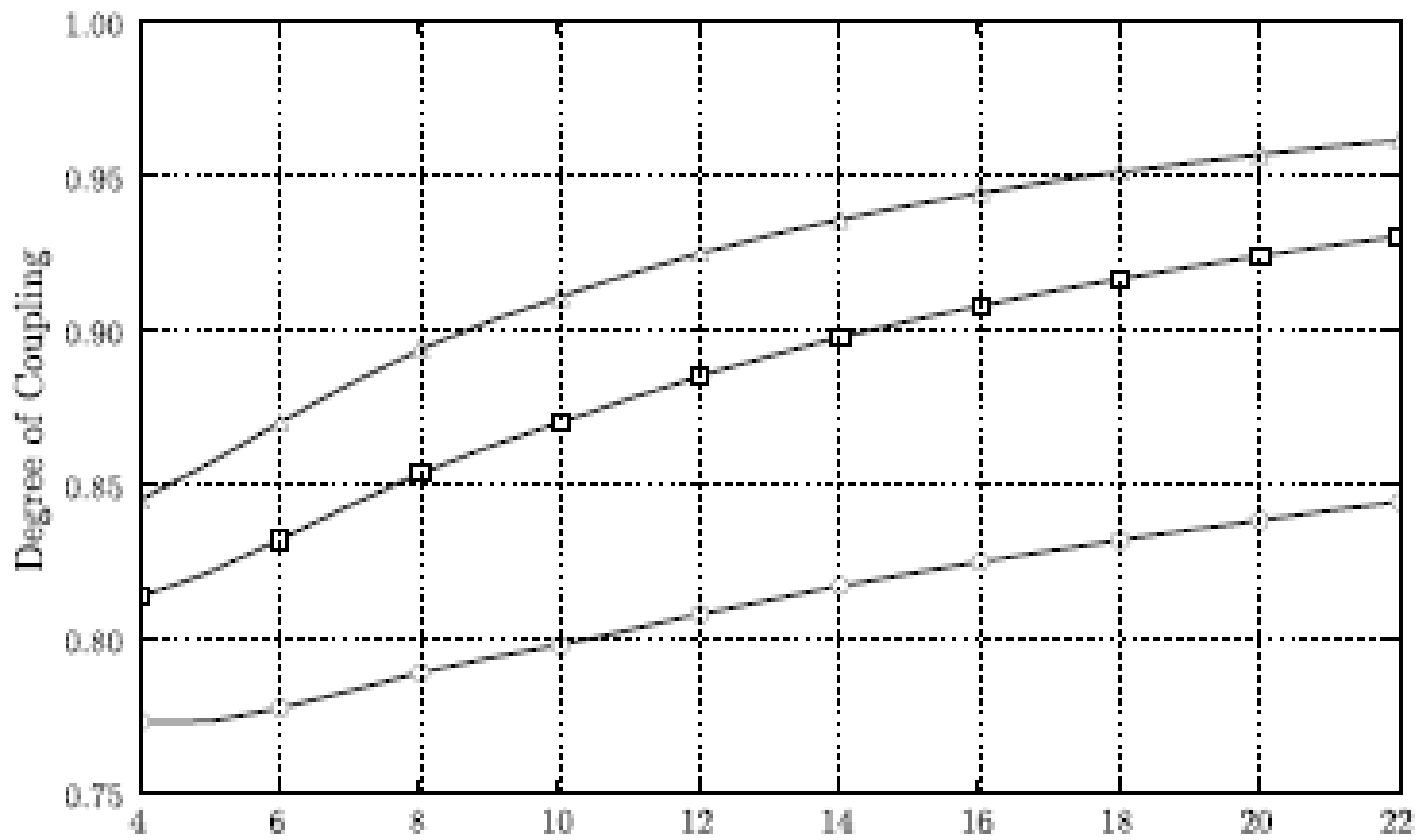
Characteristic damping time $\tau_{ch} = 1/\omega$ [s]

$$\omega = 4\sqrt{k_a^+ k_c^+ c_C^{1/2} c_{\text{H}_2\text{O}}},$$

$$l_{ch} = \frac{\pi}{2} \sqrt{\frac{D_{\text{H}_2\text{O}} \left(1 - \frac{n_d}{2}\right)}{\omega}}$$







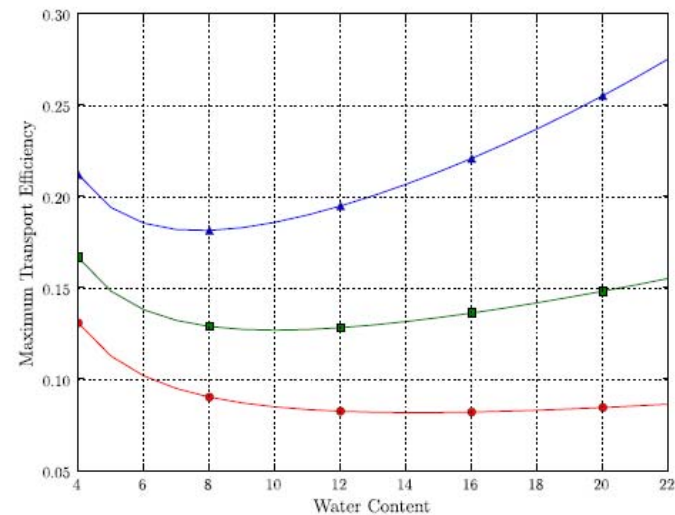
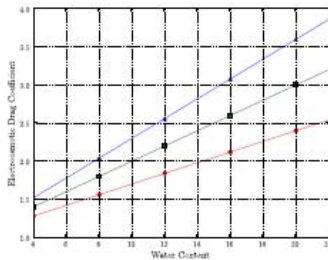
Water content $\lambda = \frac{C_{H_2O}}{C_{H^+}}$

Efficiency of transport processes

$$\eta_{tr} = \frac{\mathbf{j}_{H^+} \cdot F \nabla \phi}{-\mathbf{j}_{H_2O} \cdot \nabla \mu_{H_2O}} \approx \frac{W_{el}}{\Delta G_{tr}}$$

Maximum efficiency

$$\eta_{tr,max} = \left(\frac{1 - \sqrt{1 - q^2}}{q} \right)^2$$



Theoretical efficiency of a fuel is defined as in the gas-liquid operation mode, i.e. the evaporation heat is included

$$\eta_{teor} = \frac{W_{max}}{\Delta H_{ref}} = \frac{\Delta G_{ref}}{\Delta H_{ref}} = \frac{237.13 \text{ kJ/mol}}{285.84 \text{ kJ/mol}} = 0.8295$$

Taking into account the entropy increase evaluates, the corresponding Gibbs free enthalpy change is

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$$W = j_{H^+} F \nabla \phi \quad \text{actual electric power}$$

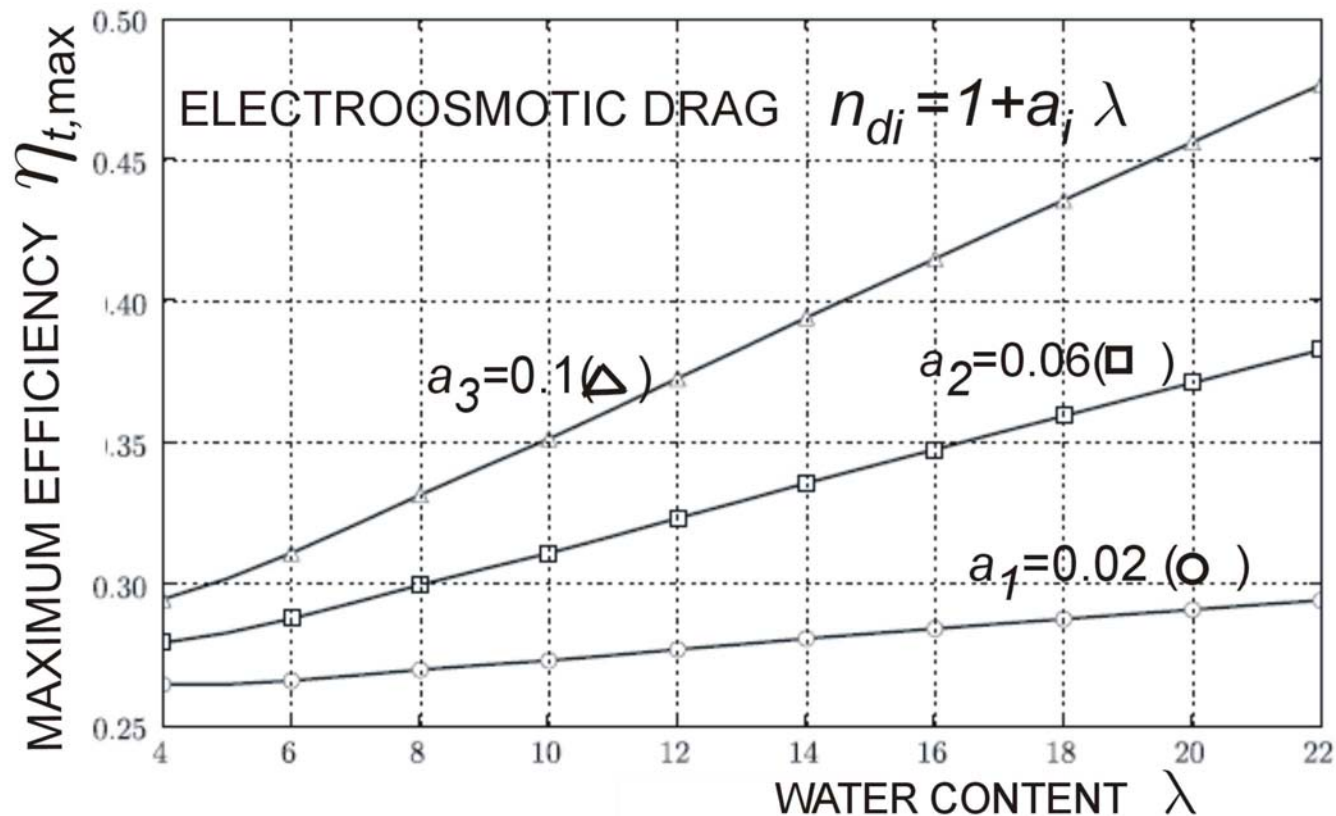
$$j_{H_2O} \nabla \mu_{H_2O} \quad \text{the "lost power" of transport processes}$$

The relation of the thermal efficiency η_t to the total efficiency η_{teor}

$$\eta_t = \frac{W_{el}}{\Delta H} = \frac{W_{el}}{\Delta G} \frac{\Delta G}{\Delta H} = \eta_t \eta_{teor},$$

$$\eta_t = \frac{j_{H^+} F \nabla \phi}{\overline{\Delta G} + T \sigma(s)} = \frac{j_{H^+} F \nabla \phi}{\overline{\Delta G} - j_{H^+} F \nabla \phi - j_{H_2O} \nabla \mu_{H_2O}}$$

$$\varepsilon = \frac{\text{electric power}}{\text{total dissipation}} = \frac{\delta q + \delta^2}{1 + 2\delta q + \delta^2} \Bigg|_{\substack{\max \\ q \in (-1,1)}} = 1 \pm \frac{q^2}{2\sqrt{1-q^2} \left(1 \pm \sqrt{1-q^2}\right)},$$



SUMMARY

Conclusion for fuel cells following from the thermodynamics analysis:

- The gradients of electric potential and water concentration can be both conformal (electric power generation) and opposite (electrolysis).
- The characteristic dimension of polymer membrane is in a certain relation to the water concentration and water diffusivity.
- Total efficiency is in the close relation to transport efficiency, which is a function of the water content