Modeling of Transport and Degradation Processes in Polymer Electrolyte Membranes

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Overview

Motivation

Improved Fuel Cells

↑

EC / DOE Targets

Performance | Cost | Durability

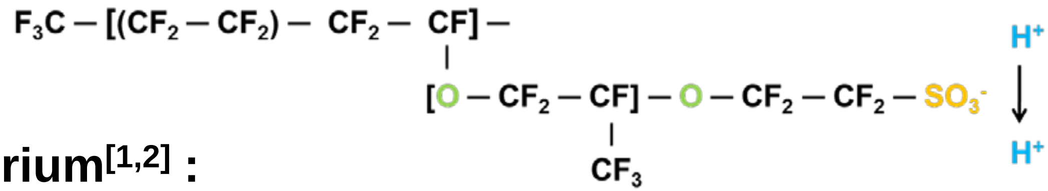
↑

Fuel Cell Modeling

Component	Degradation phenomena
GDL	Loss of hydrophobicity
CL	Loss of active surface area, carbon corrosion, ionomer degradation
PEM	Membrane thinning, loss of conductivity, pin-hole formation

Sorption Model[1]

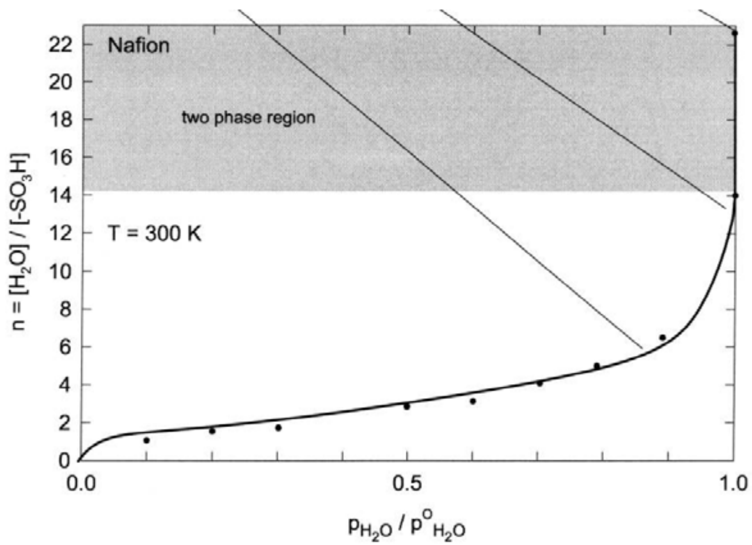
- **Nafion®:**



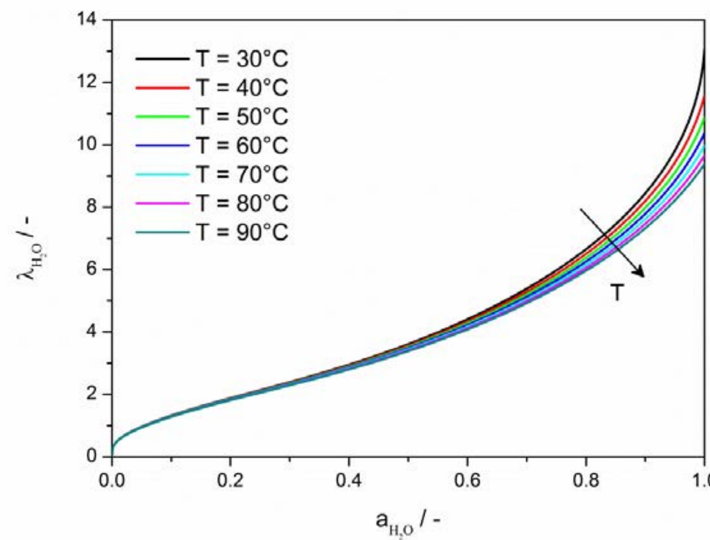
- **Chemical equilibrium[1,2] :**

$\mu_{H^+} + \mu_{H_2O} = \mu_{H_3O^+}$ → $$\frac{\lambda_{H_3O^+}}{\left(1-\lambda_{H_3O^+}\right)\left(\lambda_{H_2O}-\lambda_{H_3O^+}\right)}\exp\left(\Phi_1\lambda_{H_3O^+}\right)\exp\left(\Phi_2\lambda_{H_2O}\right)=K_1$$

$\mu_{H_2O,mem} = \mu_{H_2O,vapor}$ → $$a_{H_2O}=K_2\left(\lambda_{H_2O}-\lambda_{H_3O^+}\right)\exp\left(\Phi_2\lambda_{H_3O^+}\right)\exp\left(\Phi_3\lambda_{H_2O}\right)$$



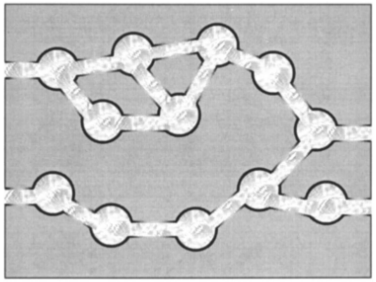
[3]: Kreuer et al., Chem. Rev., 2004



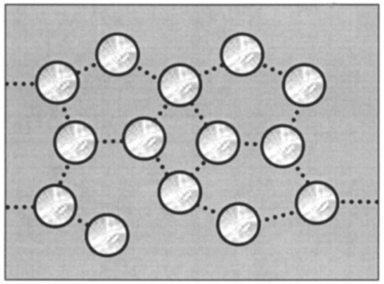
[1]: Meyers, Newman, J. Electrochem. Soc., 2002.
[2]: Weber, Newman, J. Electrochem. Soc., 2004.

Transport Model[1]

- **Conservation equations:** $$\frac{\partial x}{\partial t} - \nabla \cdot \mathbf{y} - z = 0$$
- **Chemical potential:** $$\mu_{\mathrm{H_2O}} = RT \ln a_{\mathrm{H_2O}} + \overline{V}_{\mathrm{H_2O}} p$$
- **Charge:** $$\mathbf{i} = S\left(-\kappa \nabla \Phi - \frac{\kappa \xi_l}{F} \nabla \mu_{\mathrm{H_2O}}\right) + (1-S)\left(-\kappa \nabla \Phi - \frac{\kappa \xi_v}{F} \nabla \mu_{\mathrm{H_2O}}\right)$$
- **Water:** $$\mathbf{N}_{\mathrm{H_2O}} = S\left[-\frac{\kappa \xi_l}{F} \nabla \Phi - \left(\alpha_l + \frac{\kappa \xi_l^2}{F^2}\right) \nabla \mu_{\mathrm{H_2O}}\right] + (1-S)\left[-\frac{\kappa \xi_v}{F} \nabla \Phi - \left(\alpha_v + \frac{\kappa \xi_v^2}{F^2}\right) \nabla \mu_{\mathrm{H_2O}}\right]$$



Expanded channels

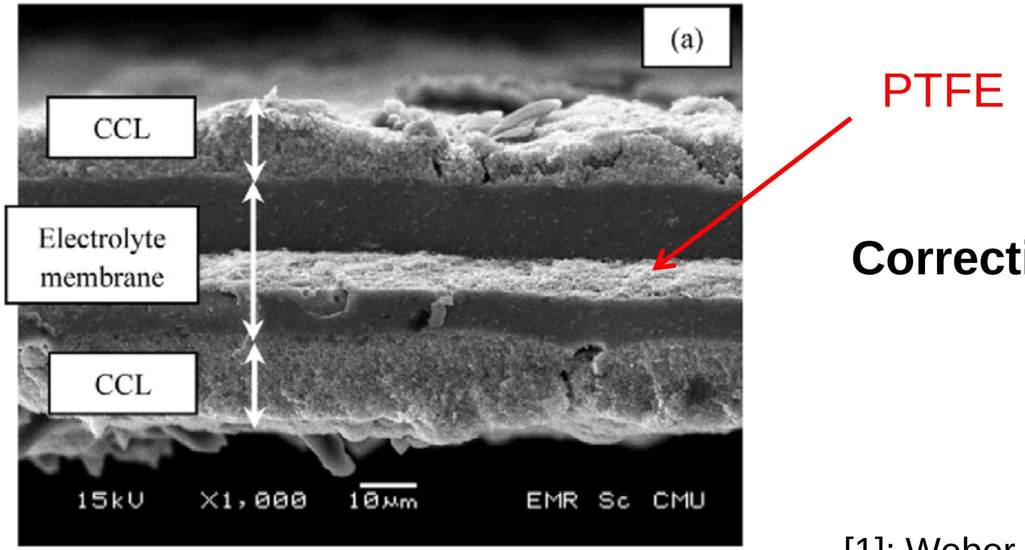


Collapsed channels

[1]: Weber, Newman, J. Electrochem. Soc., 2004.

Transport Model[1]

- **Gas transport:** $\mathbf{N}_\alpha = S\left(-\psi_{l,\alpha}\nabla p_\alpha\right) + (1-S)\left(-\psi_{v,\alpha}\nabla p_\alpha\right)$
- **Additional species:** $\mathbf{N}_\alpha = -D_\alpha \nabla C_\alpha$ and Henry's Law
- **Nafion®XL with PTFE reinforcement[2]:**



Correction of transport parameters:

$$x_{eff} = x\phi^{1.5}$$

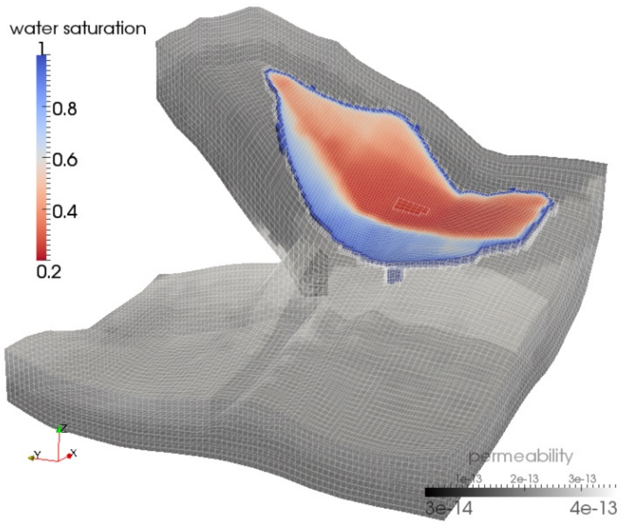
[1]: Weber, Newman, J. Electrochem. Soc., 2004.
[2]: Punyawudho et al., *Int. J. Hydrogen Energ.*, 2014.

Modeling Software: DuMu^X

DuMu^X

What is DuMu^X ?
- DuMu^X[1] = DUNE [2] for Multi-{Phase, Component, Scale, Physics,…} flow and transport in porous media
- Developed at the Institute for Modelling Hydraulic and Environmental Systems, University of Stuttgart
- Open source software

Possibilities:
- Free source code access (C++)
- 1D-3D
- Multi-Physics
- Different discretization methods
- Adaptive grids
- …

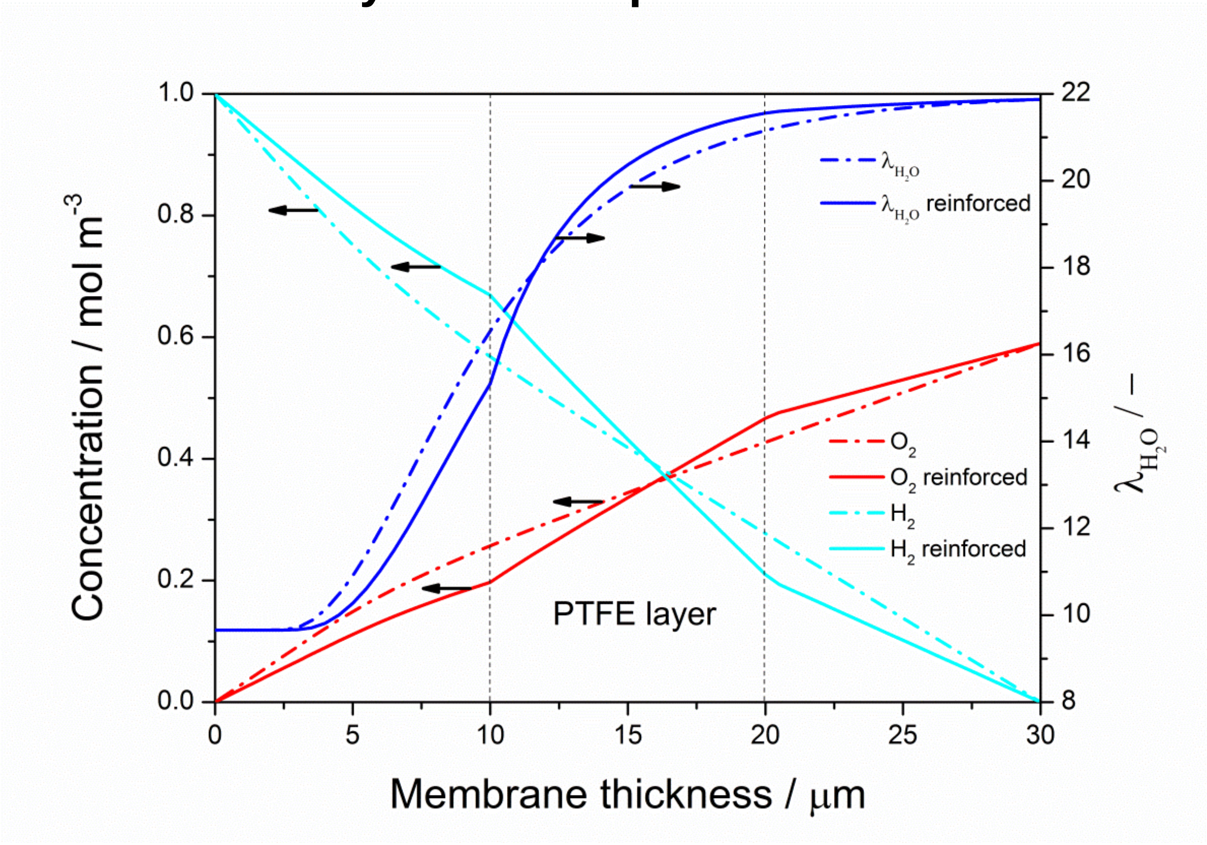


Underground storage of CO_2

[1] http://www.dumux.org/ [2] http://www.dune-project.org/

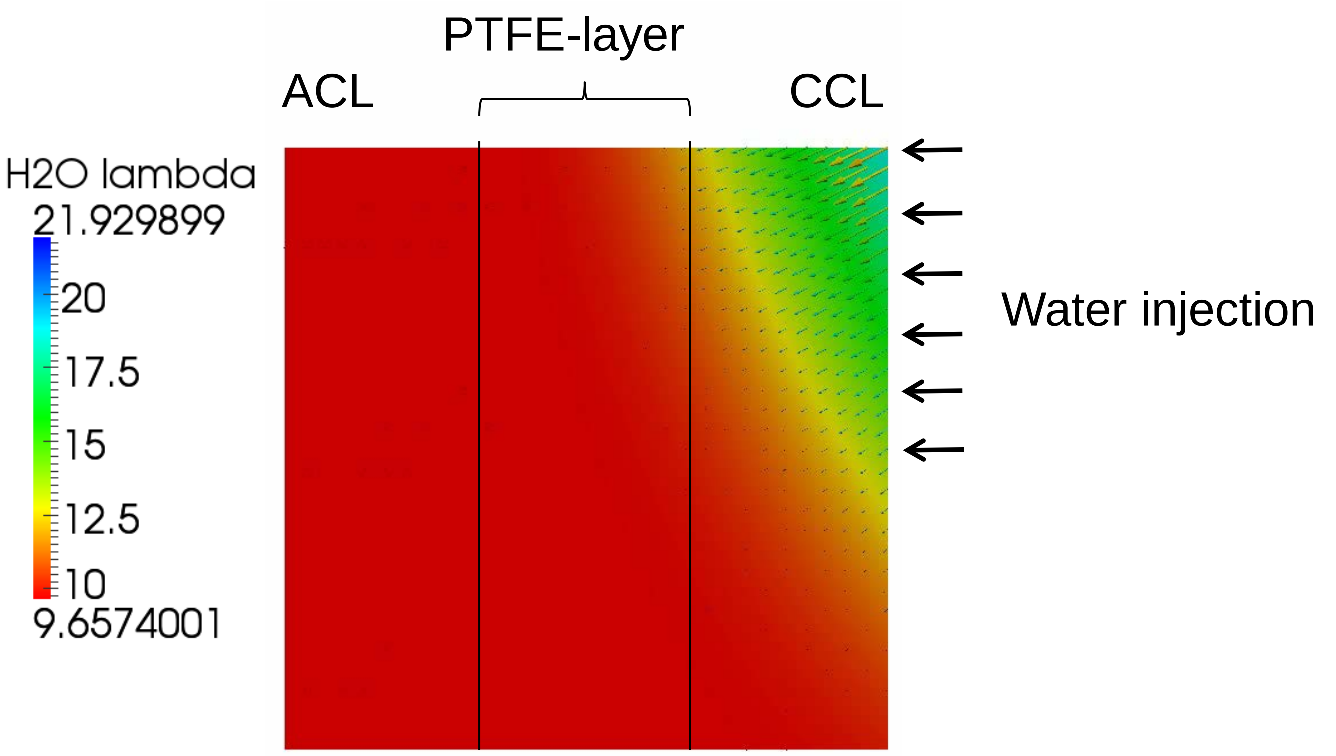
Transport Model: Preliminary Results

- **Influence of the PTFE layer on the species concentrations:**

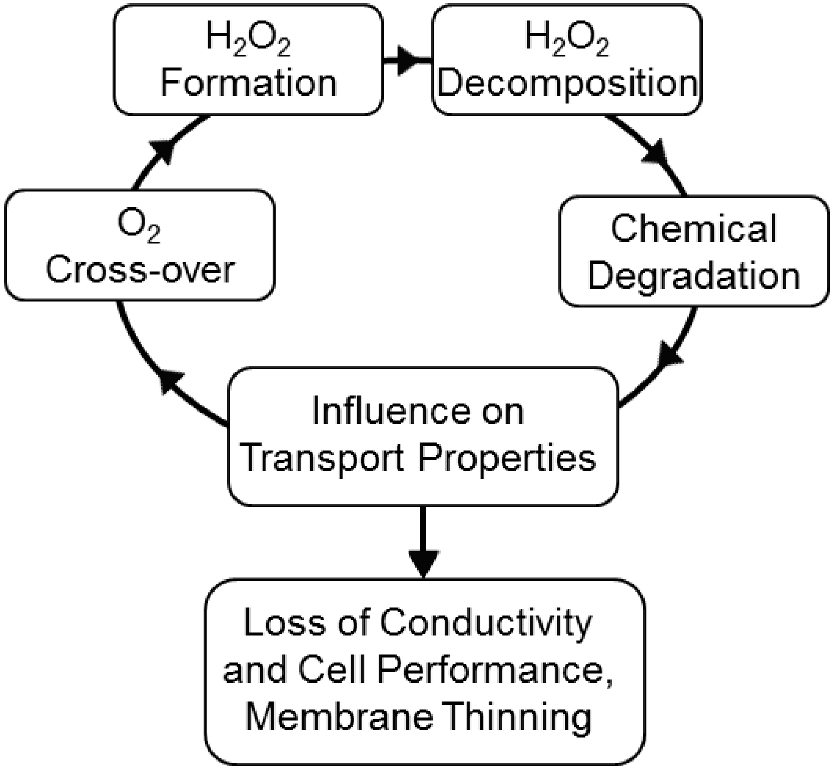


Transport Model: Preliminary Results

- **2D transient simulation of the water content:**



Degradation Model



Degradation Model: Radical formation[1]

Nr.	Reaction	k
1	$H_2O_2 \rightarrow 2HO\bullet$	$1.2\cdot10^{-7}$ / s^{-1}
2	$HO\bullet + H_2O_2 \rightarrow HOO\bullet + H_2O$	$2.7\cdot10^{7}$ / M^{-1} s^{-1}
3	$HOO\bullet + H_2O_2 \rightarrow HO\bullet + H_2O + O_2$	≤ 1 / M^{-1} s^{-1}
4	$HO\bullet + H_2 \rightarrow H\bullet + H_2O$	$4.3\cdot10^{7}$ / M^{-1} s^{-1}
5	$H\bullet + O_2 \rightarrow HOO\bullet$	$1.2\cdot10^{10}$ / M^{-1} s^{-1}
6	$2HOO\bullet \rightarrow H_2O_2 + O_2$	$8.6\cdot10^{5}$ / M^{-1} s^{-1}
7	$Fe^{2+} + H_2O_2 + H^+ \rightarrow Fe^{3+} + HO\bullet + H_2O$	63 / M^{-2} s^{-1}
8	$Fe^{2+} + HO\bullet + H^+ \rightarrow Fe^{3+} + H_2O$	$2.3\cdot10^{8}$ / M^{-2} s^{-1}
9	$Fe^{2+} + HOO\bullet + H^+ \rightarrow Fe^{3+} + H_2O_2$	$1.2\cdot10^{6}$ / M^{-2} s^{-1}
10	$Fe^{3+} + HOO\bullet \rightarrow Fe^{2+} + O_2 + H^+$	$2\cdot10^{4}$ / M^{-1} s^{-1}
11	$Fe^{3+} + H_2O_2 \rightarrow Fe^{2+} + HOO\bullet + H^+$	$4\cdot10^{-5}$ / M^{-1} s^{-1}

Reactions 1-6:
Radical formation from H_2O_2, H_2 and O_2

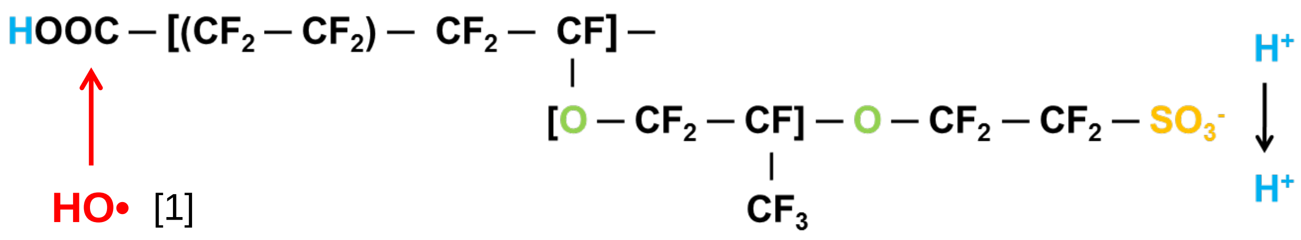
Reactions 7-11:
Fenton's reactions

Fe ion-level < 40ppm
→$HO\bullet$ mainly from reaction 1
Fe ion-level > 40ppm
→$HO\bullet$ mainly from reaction 7

Reduction $Fe^{3+} \rightarrow Fe^{2+}$
mainly via reaction 10

[1]: Gubler et al., *J. Electrochem. Soc.*, 2011.

Degradation Model: Mechanisms



[1]

- **Unzipping**

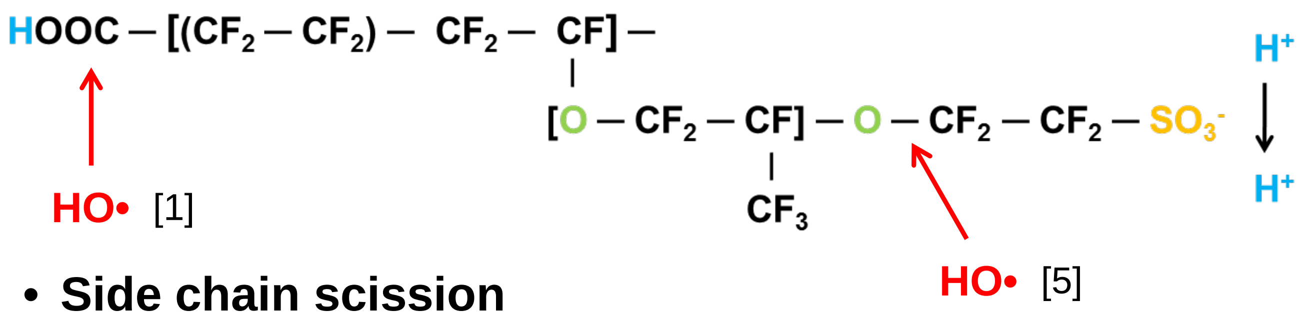
$$\sim CF_2COOH + 2 \cdot OH \xrightarrow{k_u} \sim COOH + CO_2 + 2\,HF$$ [2]

- **Rate constant at 25°C:**
  $k_u = 7.3 \cdot 10^2$ / $m^3\ mol^{-1}\ s^{-1}$ [3]

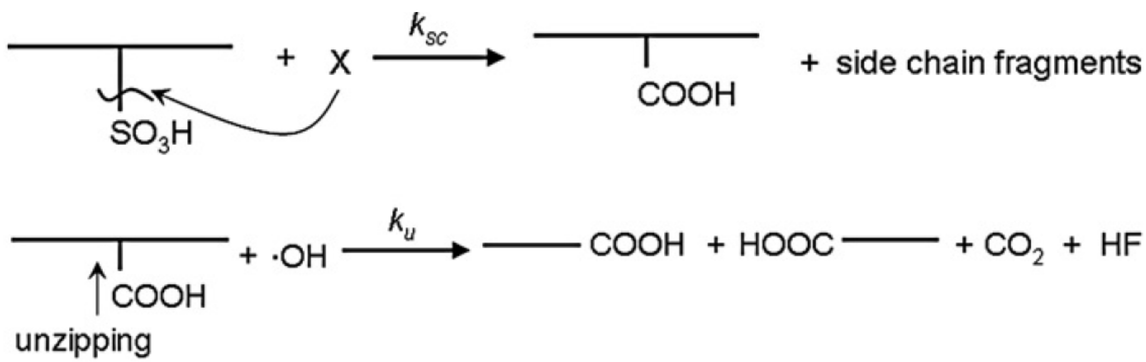
Activation energy:
$E_{act,u} \approx 70$ kJ mol^{-1} [4]

[1]: Curtin et al., *J. Power Sources*, 2004.
[2]: Xie, Hayden, *Polymer*, 2007.
[3]: Dreizler, Roduner, *Fuel Cells*, 2012.
[4]: Gubler et al., *J. Electrochem. Soc.*, 2011.
[5]: Ghassemzadeh et al., *J. Am. Chem. Soc.*, 2013.

Degradation Model: Mechanisms



- **Side chain scission**



[2]

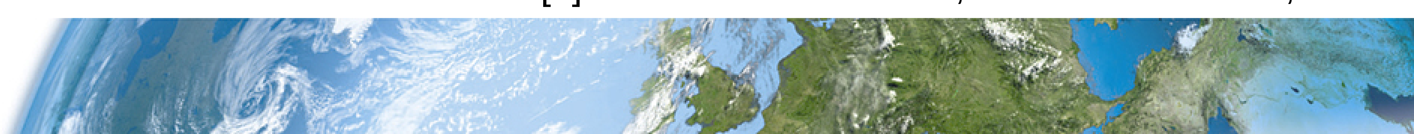
- **Rate constant at 25°C:**

  $k_u = 3.7 \cdot 10^3$ / m^3 mol^{-1} s^{-1} [3]

Activation energy:

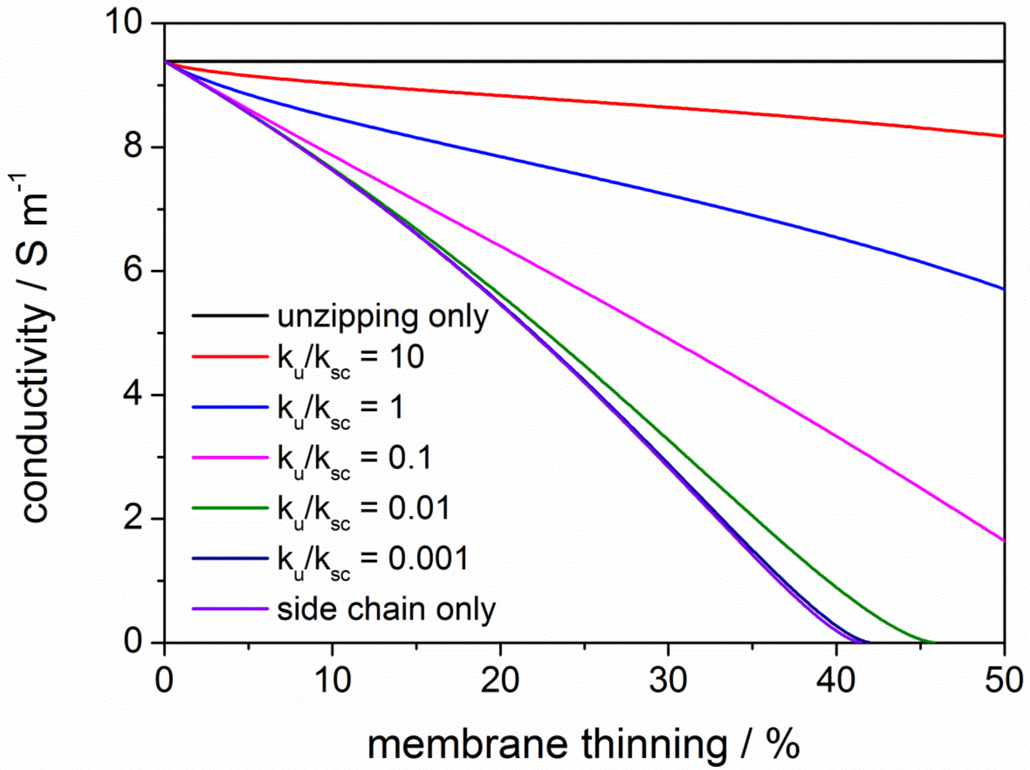
$E_{act,sc}$ = **???**

[1]: Curtin et al., *J. Power Sources*, 2004.
[2]: Xie, Hayden, *Polymer*, 2007.
[3]: Dreizler, Roduner, *Fuel Cells*, 2012.
[4]: Gubler et al., *J. Electrochem. Soc.*, 2011.
[5]: Ghassemzadeh et al., *J. Am. Chem. Soc.*, 2013.



Degradation Model: Results

- **Effect of unzipping and side chain scission transport properties:**



Determination of $E_{act,sc}$ from membrane thickness and conductivity (IEC) measurements

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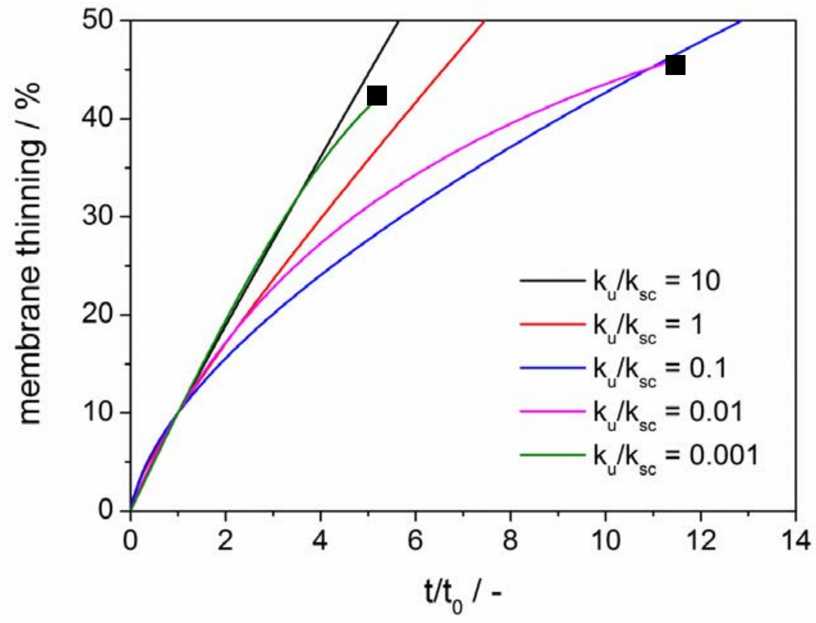
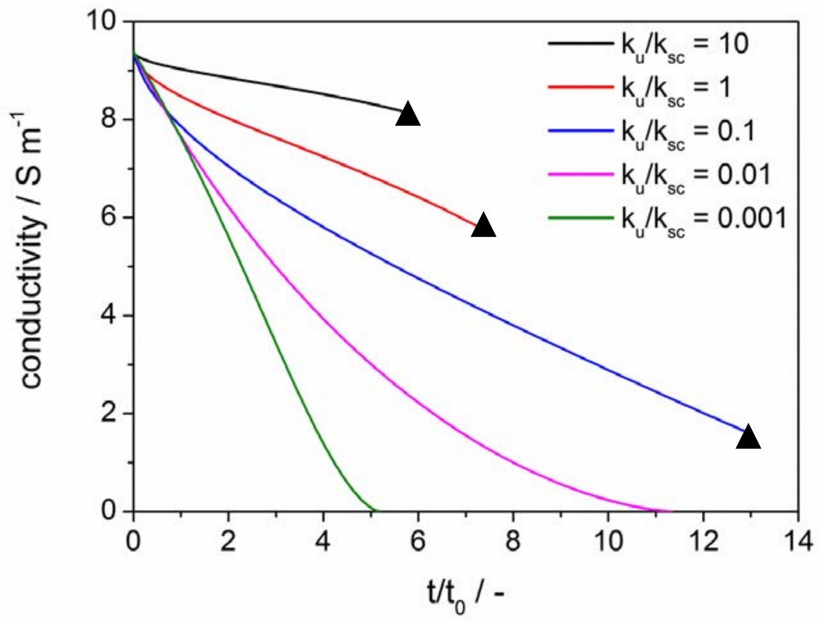
Degradation Model: Results

- **Membrane thinning and change of conductivity for different ratios of k_u/k_{sc}:**

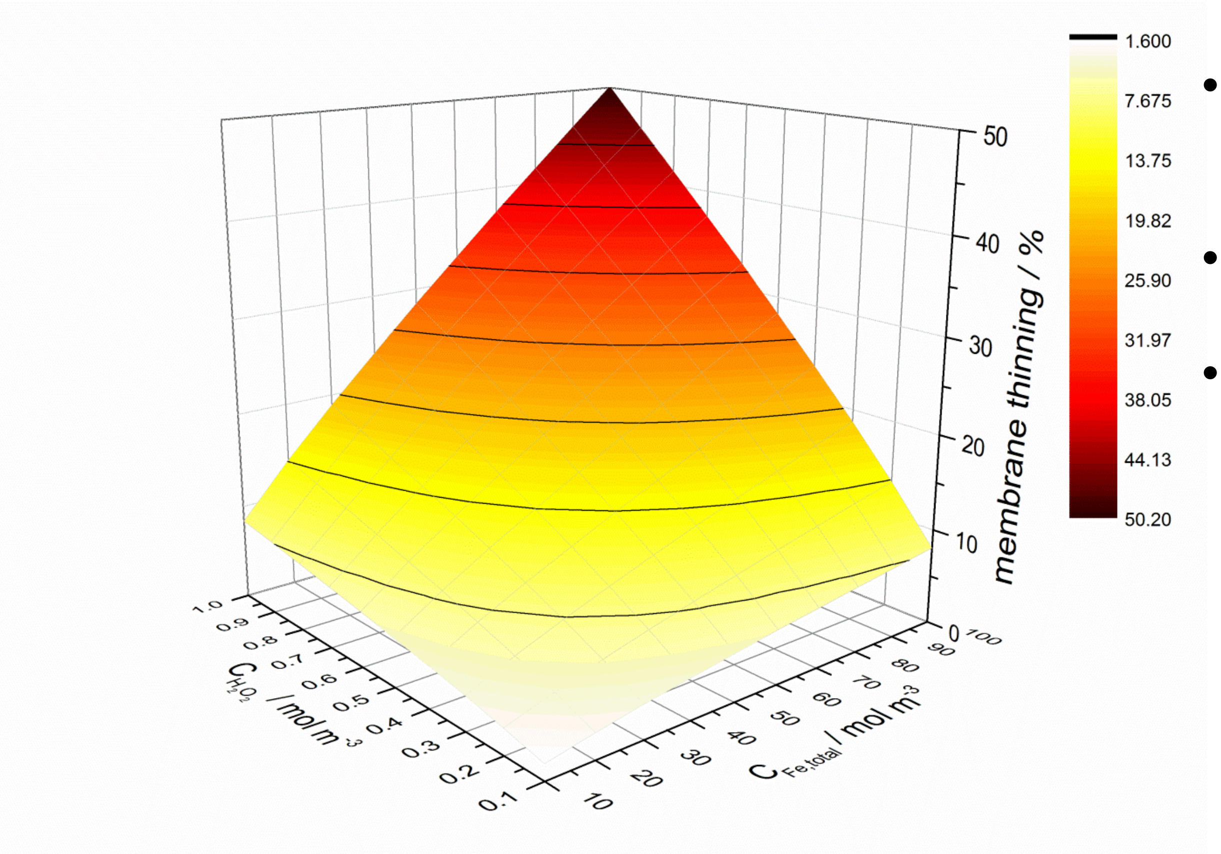




■: complete loss of conductivity ▲: membrane thickness = 50 %

Degradation Model: Results

- **Influence of H_2O_2 and Fe ions concentrations:**



- Degradation strongly depends on H_2O_2 and Fe concentration
- Fe concentration unknown ☹
- Additional mechanism for reduction of Fe^{3+}?

Summary

Achievements:

- 2D transient model for transport and degradation processes in PEM
- Coupling of degradation and transport properties

Future work:

- Coupling of the PEM model to electrode, GDL and channel
- Validation of the degradation model

→Determination of kinetic parameters of chemical degradation processes

Thank you for your attention

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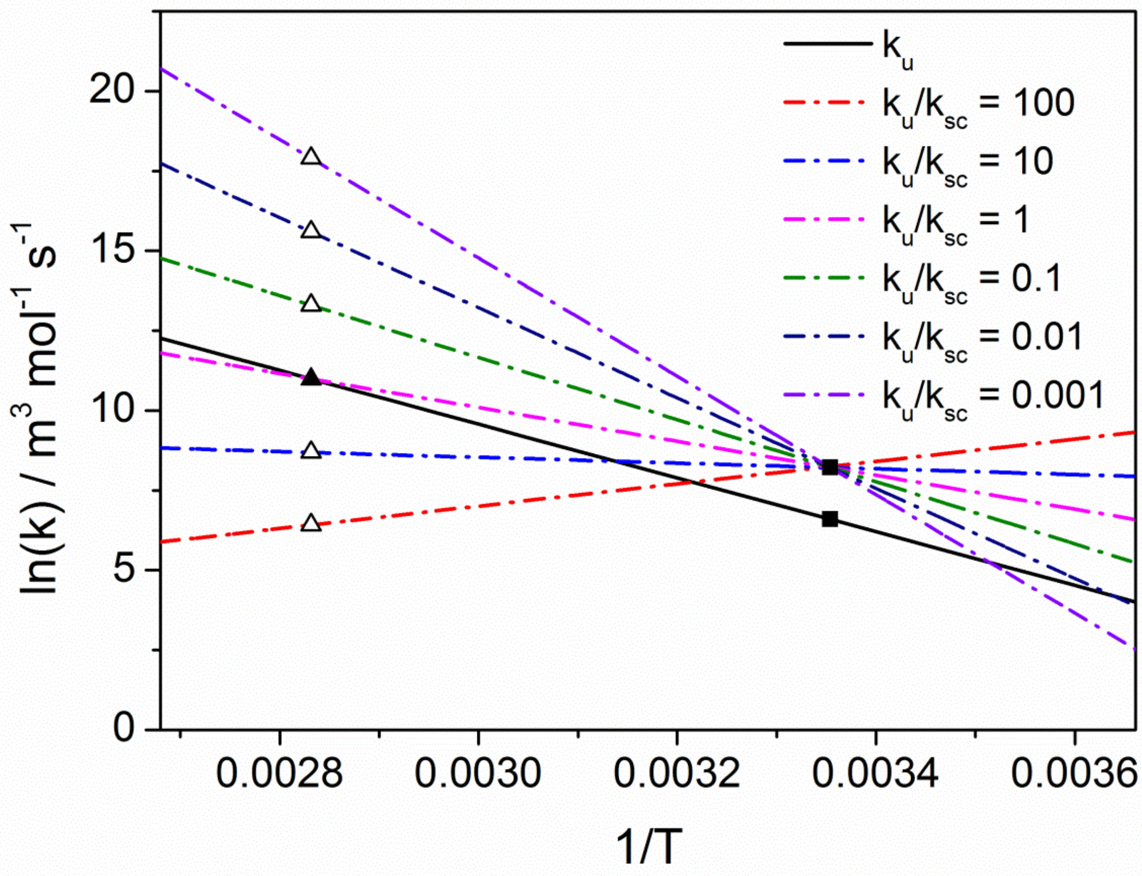
Degradation Model



■: determined by [1]

▲: extrapolated with $E_{act} \approx 70$ kJ [2]

[1]: Dreizler, Roduner, *Fuel Cells*, 2012.

[2]: Gubler et al., *J. Electrochem. Soc.*, 2011.