Modeling of degradation mechanisms in low temperature fuel cells

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Motivation

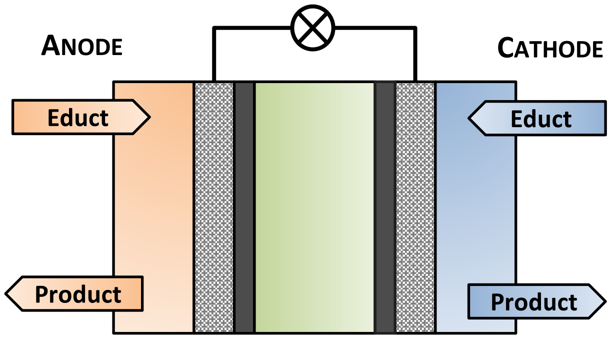
The development of predictive fuel cell models is of particular importance for the improvement of cell design and operating strategies.

"Prediction is very difficult, especially about the future."
Niels Bohr

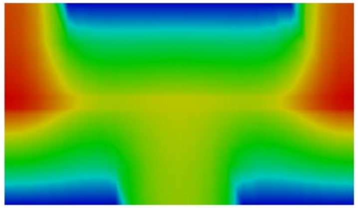
Why is it difficult to predict fuel cell degradation?

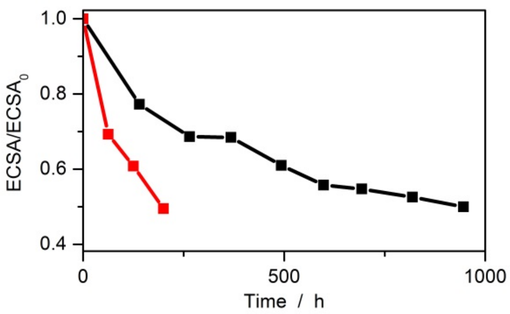
- Complex system: processes on very different time and length scales
- Details of the involved mechanisms often unknown
- Degradation depends on local conditions inside the cell
- Interplay of the degradation mechanisms

How to derive predictive models?



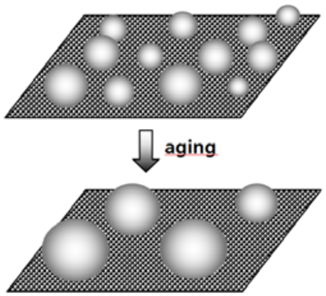
Multi-scale cell models

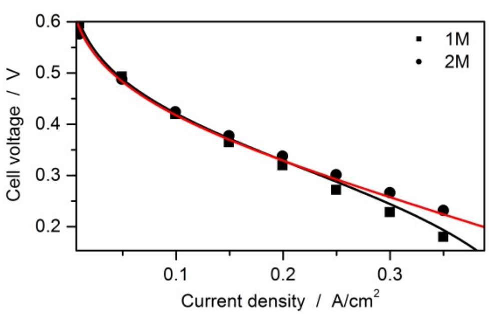


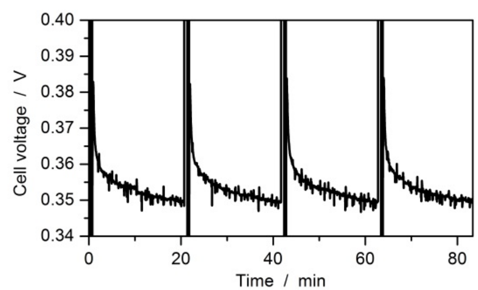


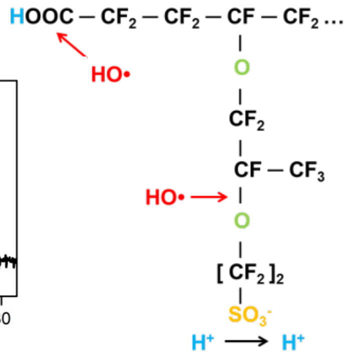
Model validation

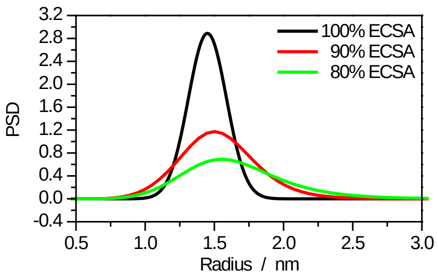
Degradation models









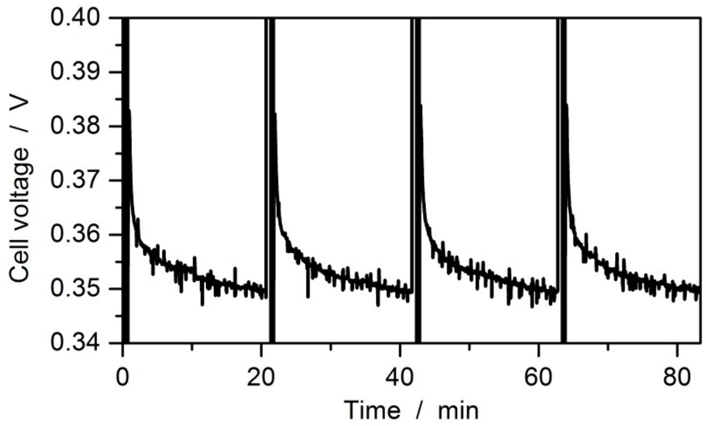


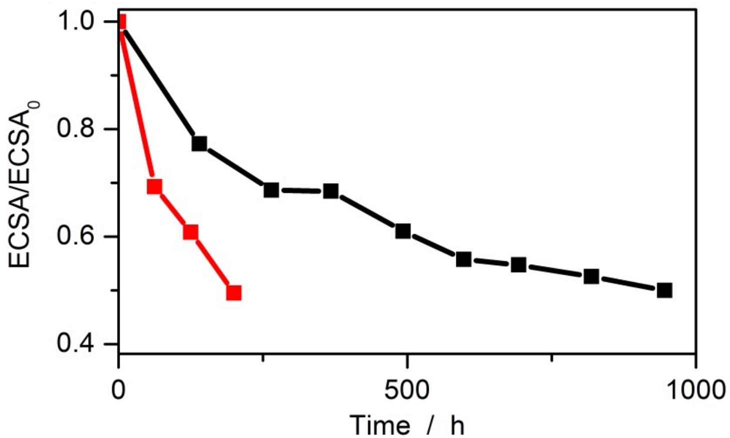
PART I – Catalyst degradation in DMFC

Reversible and irreversible degradation for DMFC: Experimental observations

- Experimental observation[1]: reversible and irreversible performance loss during operation
- Most of the loss can be recovered by short air stop (refresh procedure)
- Irreversible degradation is observed mainly at cathode side: loss of ECSA

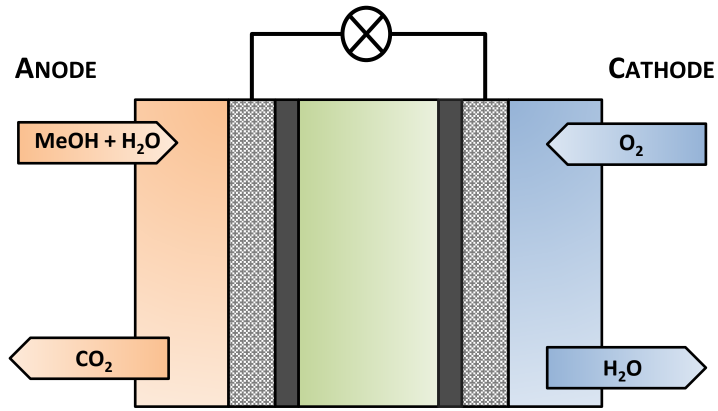
Questions:
- What are the mechanisms leading to reversible and irreversible degradation?
- How to describe the mechanisms by physical models?
- How can we avoid/reduce catalyst degradation?

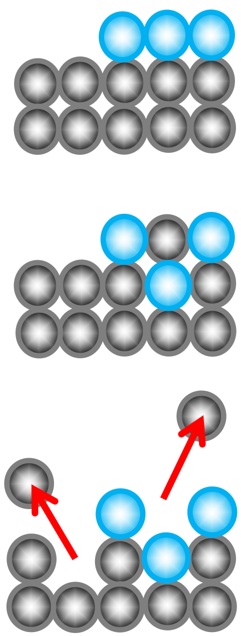


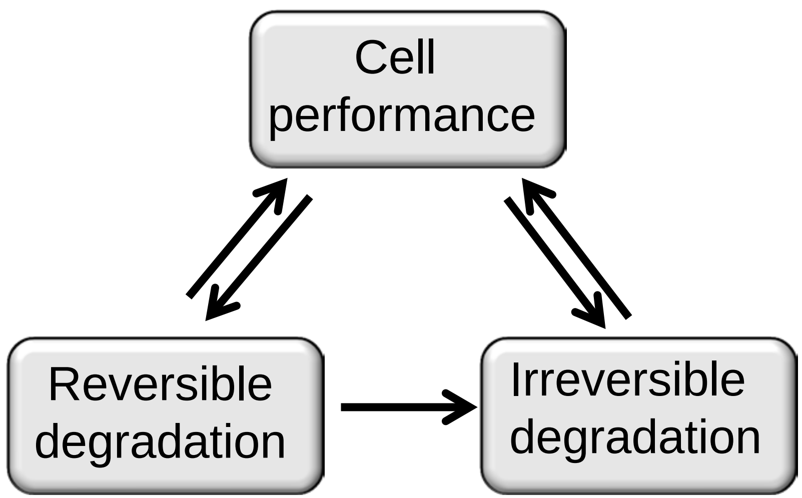


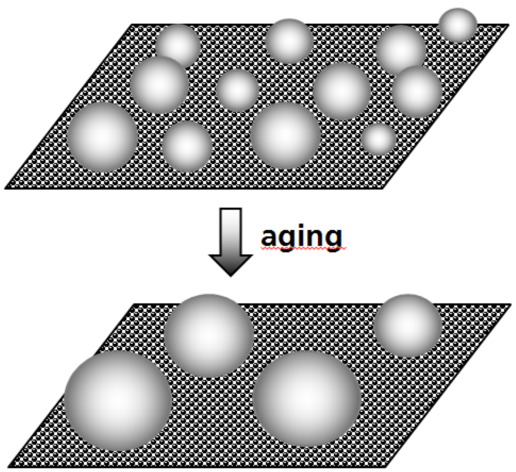
[1]: F. Bresciani et al., *Int. J. Hydrogen Energy* 39 (2014) 21647 -21656

Catalyst degradation in DMFC









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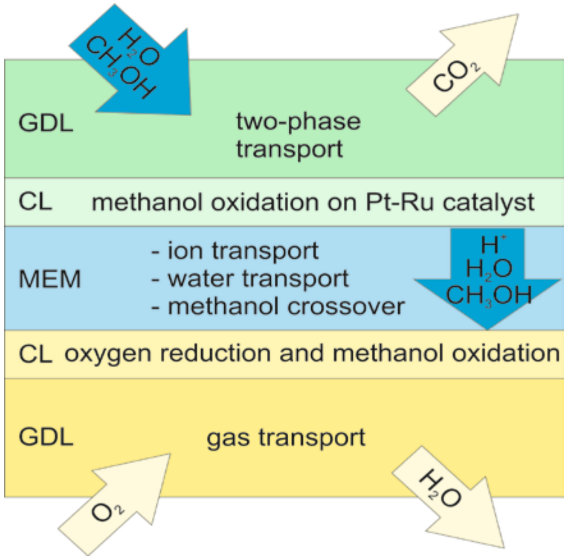
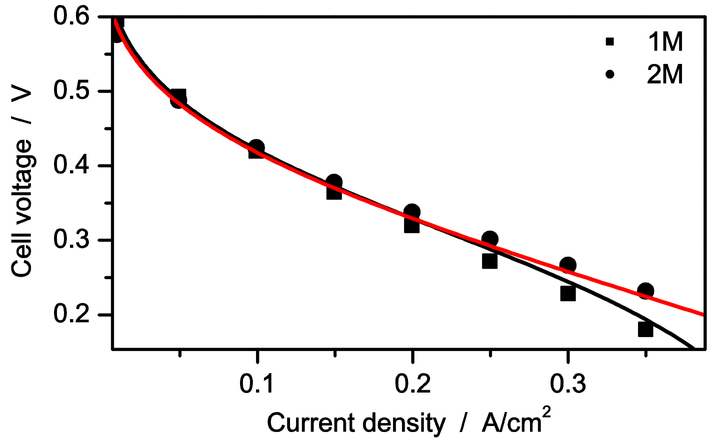
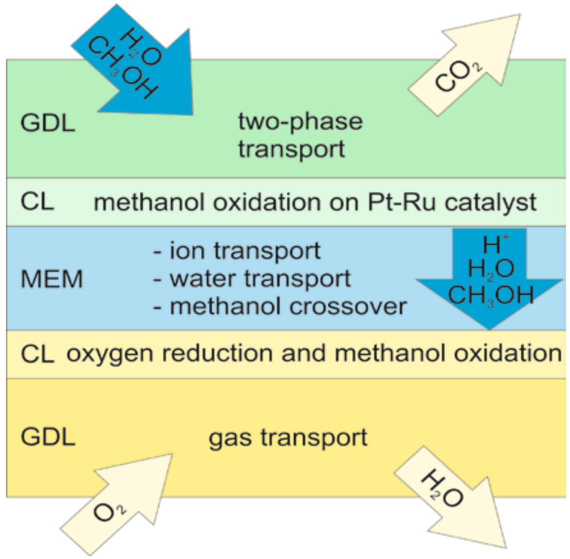
Catalyst degradation: DMFC cell model

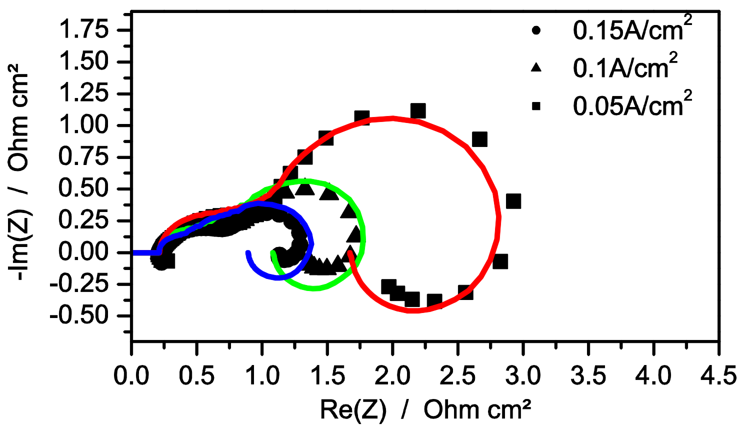
- Degradation rates depend on local conditions in the cell, e.g., local potential and local species concentrations.
- To obtain the local conditions coupling of the degradation with a cell model is needed
- The developed 1D cell model includes
  - Species transport through the layers
  - Multi-step reaction pathways for methanol oxidation and oxygen reduction reaction

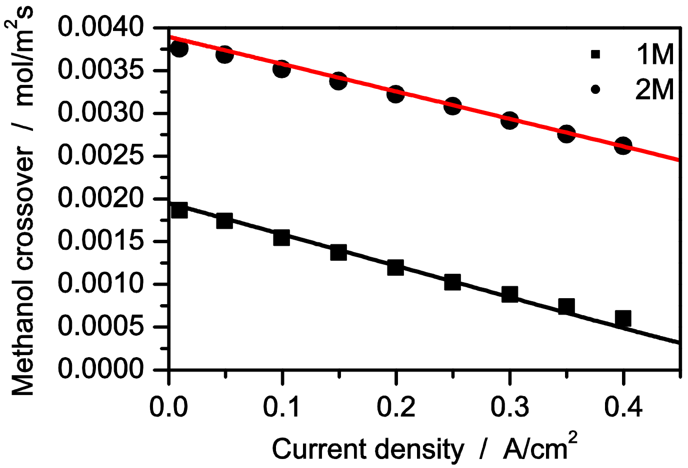


Catalyst degradation: DMFC cell model





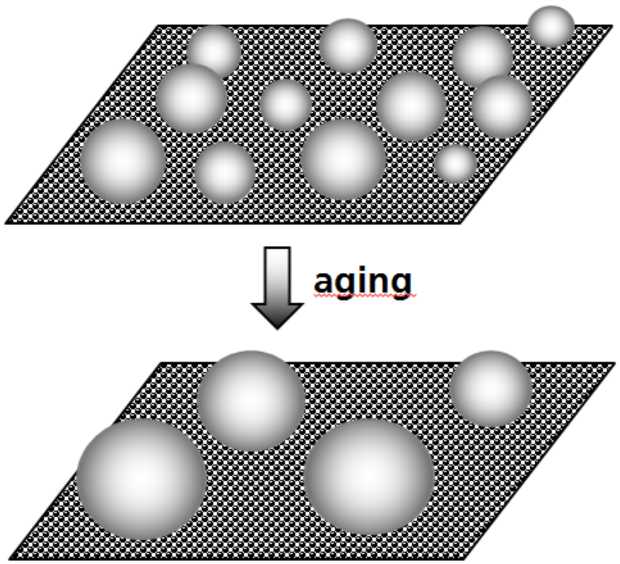




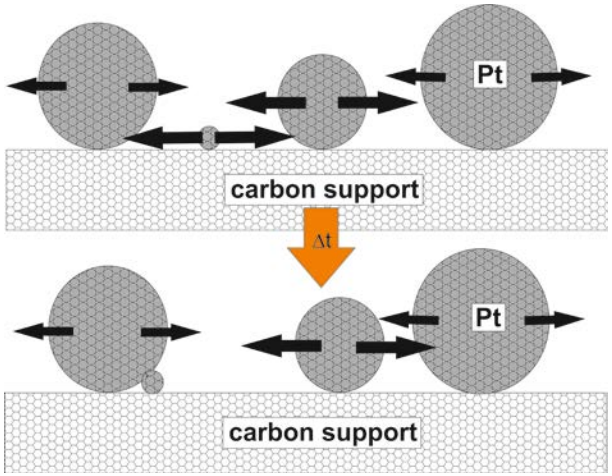
Catalyst degradation: Particle growth mechanism

- The loss of electrochemical active surface area (ECSA) at the cathode is mainly responsible for performance degradation
- Loss of ECSA is related to a growth of the platinum particles
- Different processes can contribute to the particle growth:
  - Ostwald ripening
  - Coalescence
- Key property for mathematical desciption: particle size distribution (PSD) $N(r)$
- Balance equation for PSD

$$\frac{\partial N(r,t)}{\partial t} + \frac{\partial}{\partial r}\left(N(r,t) \left.\frac{\partial r}{\partial t}\right|_{Ostwald} \right) = \left.\frac{\delta N(r,t)}{\delta t}\right|_{Coal}$$



Catalyst degradation: Coalescence mechanism



- Movement of the platinum particles on the carbon support can lead to coalescence of the particles
- The coalescence can be described by an integro-differential equation for the particle distribution:

$$\left.\frac{\delta N(r,t)}{\delta t}\right|_{Coal} = \underbrace{r^2 \int_0^r D(r')N(r',t)\frac{N((r^3-r'^3)^{1/3},t)}{(r^3-r'^3)^{2/3}}dr'}_{\text{Coalescence of two particles to one with size r}} - \underbrace{\int_0^\infty \big(D(r)+D(r')\big)N(r,t)N(r',t)dr}_{\text{Coalescence of a particle with size r}}$$

- Mechanisms for particle diffusion:
  - (i) Ion attachment/detachment[1]: $D(r) \sim r^{-1}$
  - (ii) Adatom diffusion[2] (high temp.): $D(r) \sim r^{-4}$

[1]: S.V. Khare, N.C. Bartelt, T.L. Einstein, *Physical Review Letters* 75 (1995) 2148
[2]: F. Behafarid, B.R. Cuenya, *Surface Science* 606 (2012) 908

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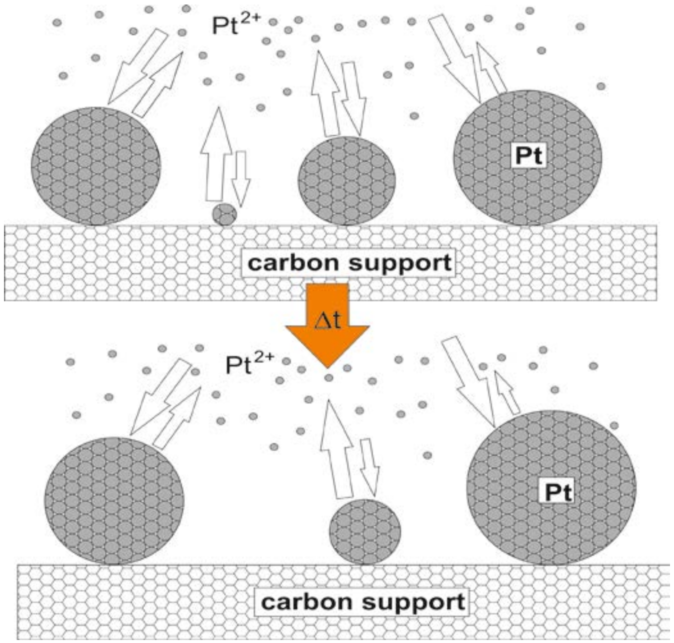
Catalyst degradation: Ostwald ripening

- Change of particle sizes due to Pt dissolution and precipitation
  $Pt \rightleftarrows Pt^{2+} + 2\,e^{-}$
- The particle stability depends on the particle size (surface energy):

$$\Delta\mu_{GT} = \mu(r) - \mu(\infty) = \frac{2\Omega\gamma}{r}$$

- Experimental observation: Degradation is accelerated by cycling.
- Explanation: The formation and reduction of platinum oxides play an important role for the dissolution

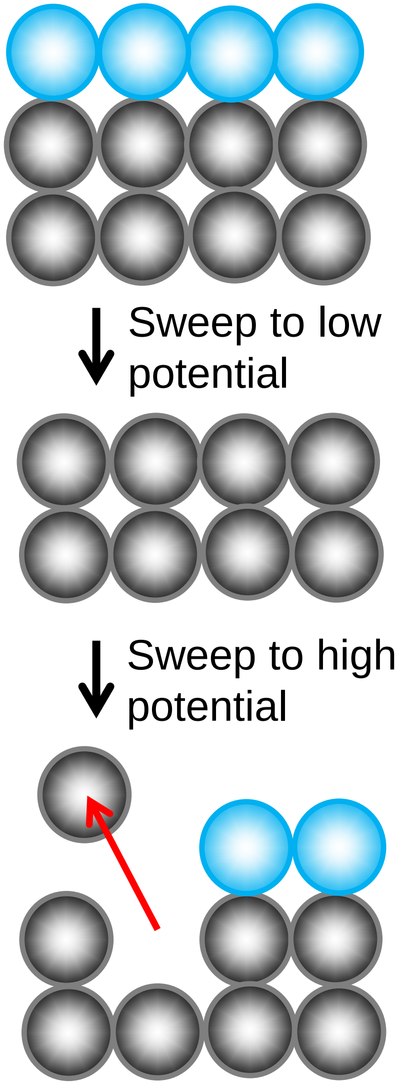
→ A model for the oxide formation is needed



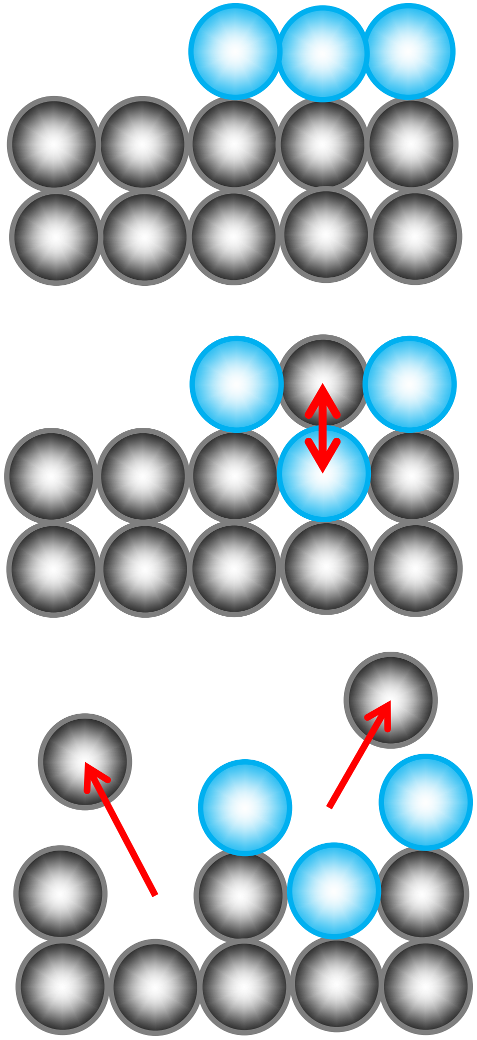
Catalyst degradation: Effect of platinum oxides

- Simple platinum oxide model:
  - Platinum oxides form a protective layer at high potentials, reducing the dissolution
    $Pt + H_2O \rightleftarrows PtO + 2H^+ + 2e^-$
  - At low potential the oxides are reduced
  - Going back to high potential leads to accelerated dissolution until the protective layer is formed again
    $Pt \rightleftarrows Pt^{2+} + 2\ e^-$

→Fast degradation expected after sweep from low to high potential



Catalyst degradation: Effect of platinum oxides

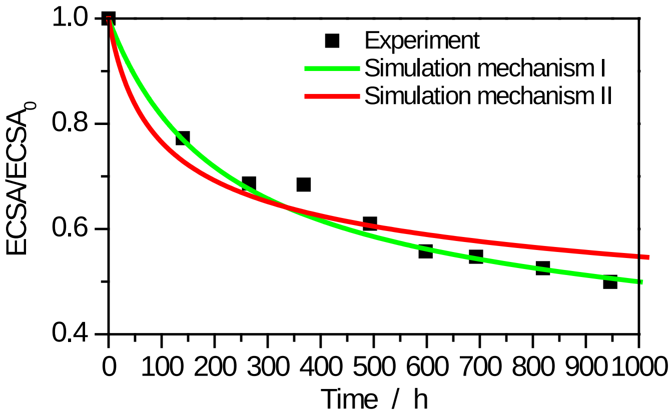


- Recent experiments show that faster dissolution occurs during sweep to low potentials [1] → contradiction to simple model!
- Advanced model:
  - Include the place exchange between platinum and oxygen atoms
    - $Pt + H_2O \rightleftarrows PtO_{surf} + 2H^+ + 2e^-$
    - $PtO_{surf} \rightleftarrows PtO_{bulk}$
    - $PtO_{bulk} + H_2O \rightleftarrows PtO_2 + 2H^+ + 2e^-$
  - Dissolution occurs also during the place exchange → accelerated degradation during sweep to low potentials
    - $PtO_{bulk} + 2\,H^+ \rightleftarrows Pt^{2+} + H_2O$

[1] A. A. Topalov et al., Chem. Sci. 5 (2014) 631

Catalyst degradation: Modeling the particle growth

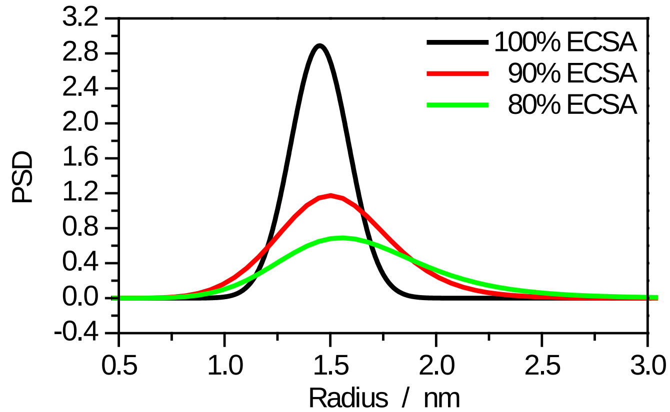
- The particle growth mechanisms lead to a change in the PSD and a loss of ECSA
- Time evolution of ECSA depends on the mechanism



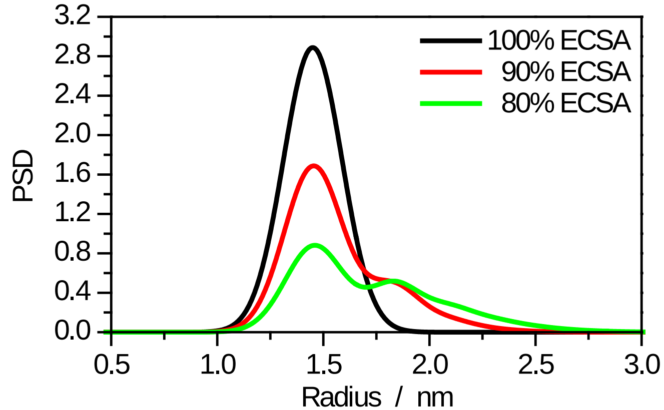
Catalyst degradation: Modeling the particle growth

- The particle growth mechanisms lead to a change in the PSD and a loss of ECSA
- Time evolution of ECSA depends on the mechanism
- The shape of the PSD also depends on the mechanism:
    - Tail at small particle sizes is formed during Ostwald ripening
    - Tail at large particle sizes and second peak is formed during coalescence

→Analyzing the PSD (e.g. with transmission electron microscopy) can help identifying the relevant degradation mechanism



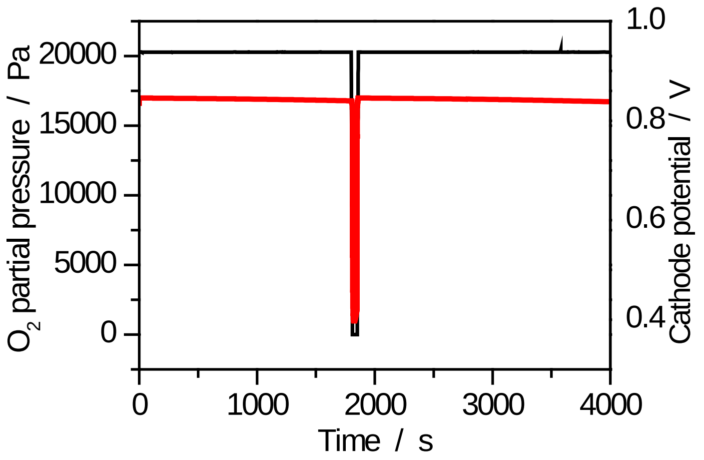
Ostwald ripening

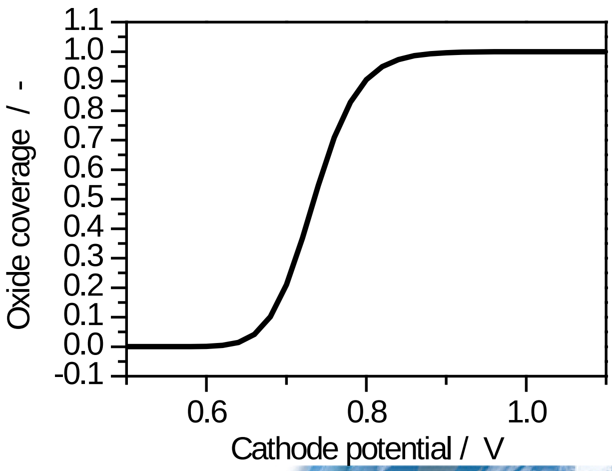


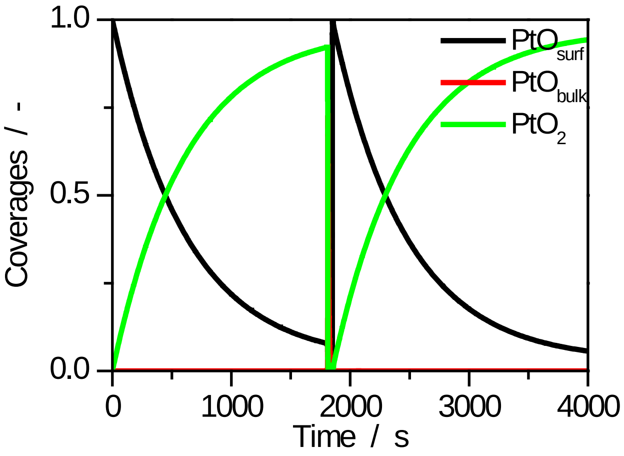
Coalescence

Catalyst degradation: Modeling the refresh procedure

- Recovery of reversible degradation is observed after stopping the air flow
- Oxygen starvation leads to low a cathode potential (due to methanol crossover)
- Low potential allows for reduction of platinum oxides
  →recovery of cell performance



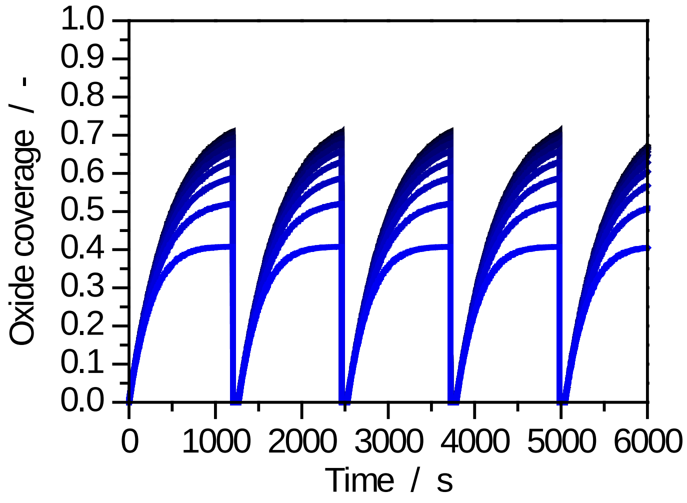


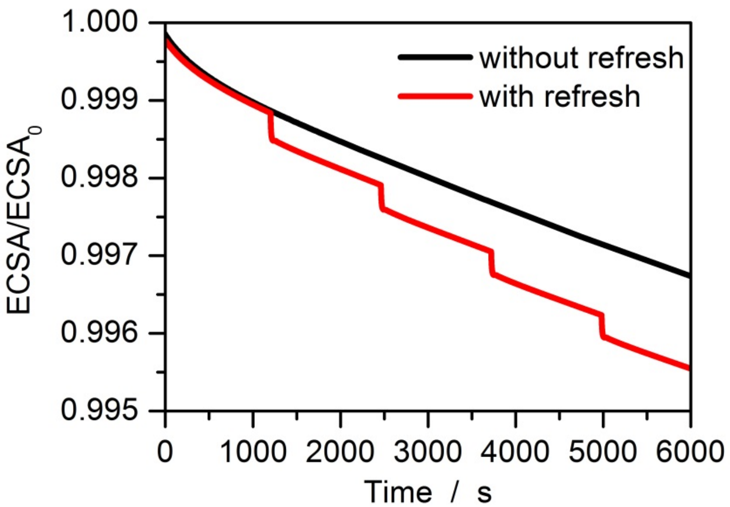


Catalyst degradation: Modeling the refresh procedure

- Refresh leads to a reduction of the oxides → recovery of reversible degradation
- But accelerated irreversible degradation due to
  - reduction of protective layer
  - enhanced place exchange rate

→Trade-off between performance optimization and irreversible degradation





PART II – Membrane degradation in PEMFC

Membrane degradation

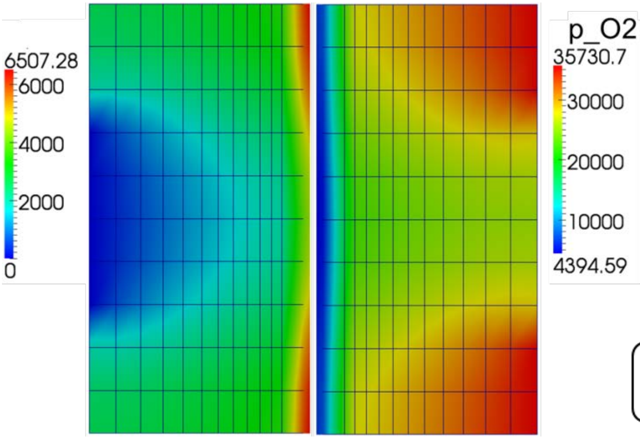
Membrane degradation can occurs in terms of

- Membrane thinning
- Pin-hole formation
- Loss of conductivity

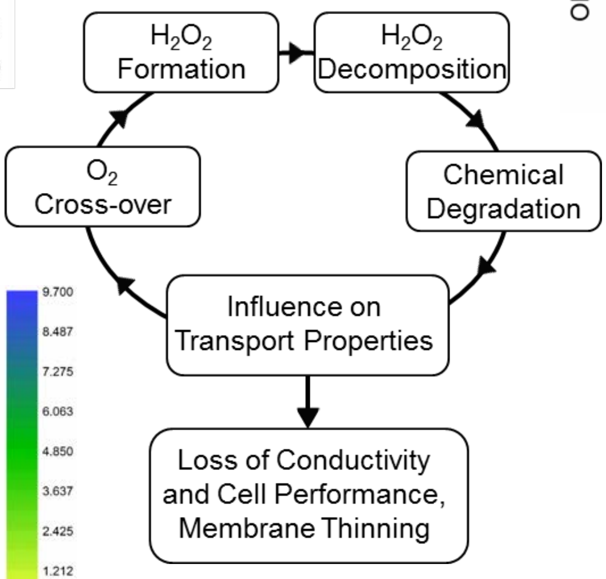
Questions:

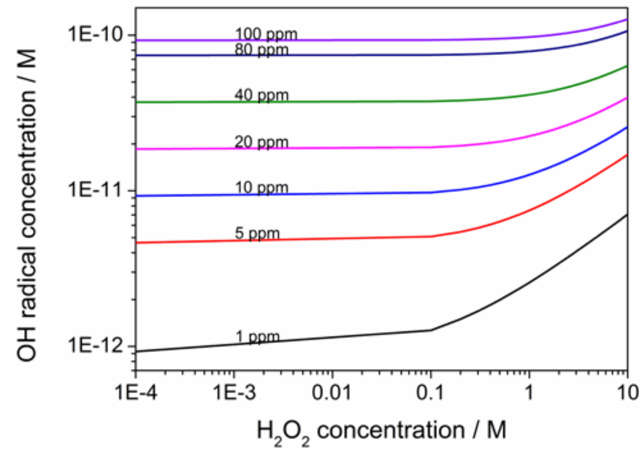
- Which mechanisms lead to membrane degradation?
- How can we describe these mechanisms by a physical model?
- How can we avoid/reduce membrane degradation?

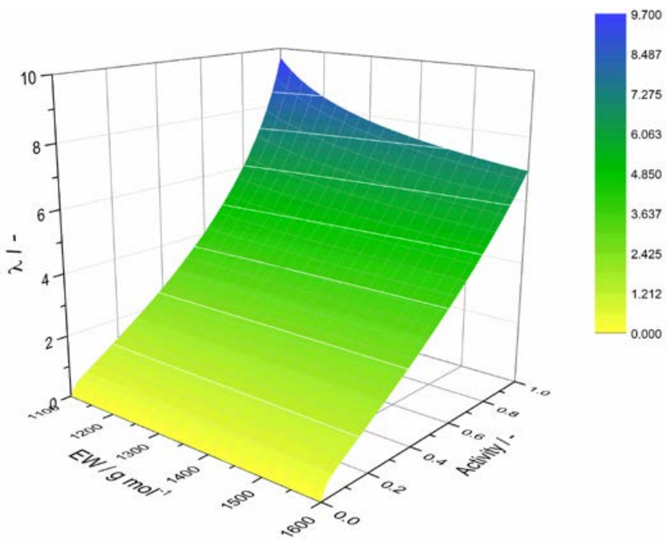
Membrane Degradation: Overview

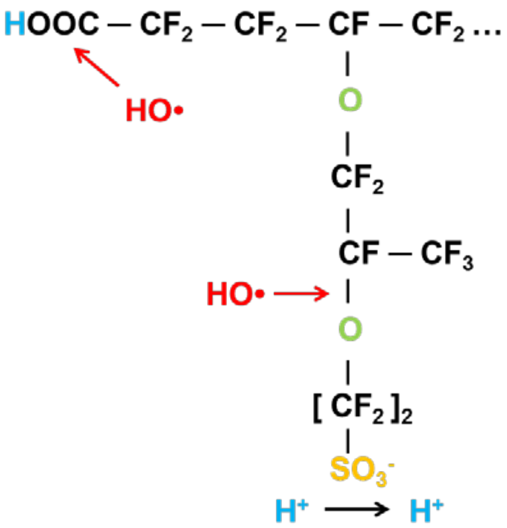


$$O_2 + 2H^+ + 2e^- \rightarrow H_2O_2$$







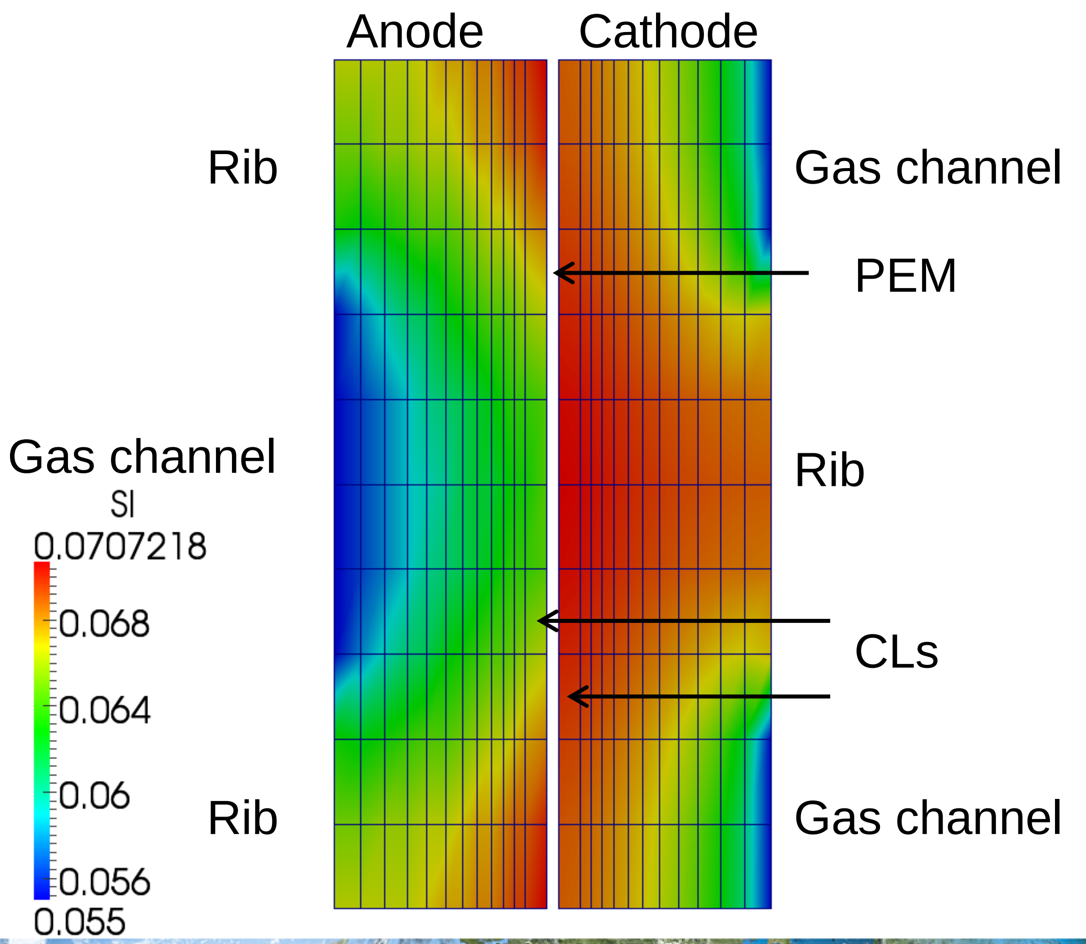


Membrane degradation: Coupling with cell model

Membrane degradation strongly depends on the local conditions

- Water content in the membrane
- Anode oxygen concentration due to crossover
- Anode and cathode potential
- Iron ion concentrations

→ The degradation model has to be imbedded in a complete cell model



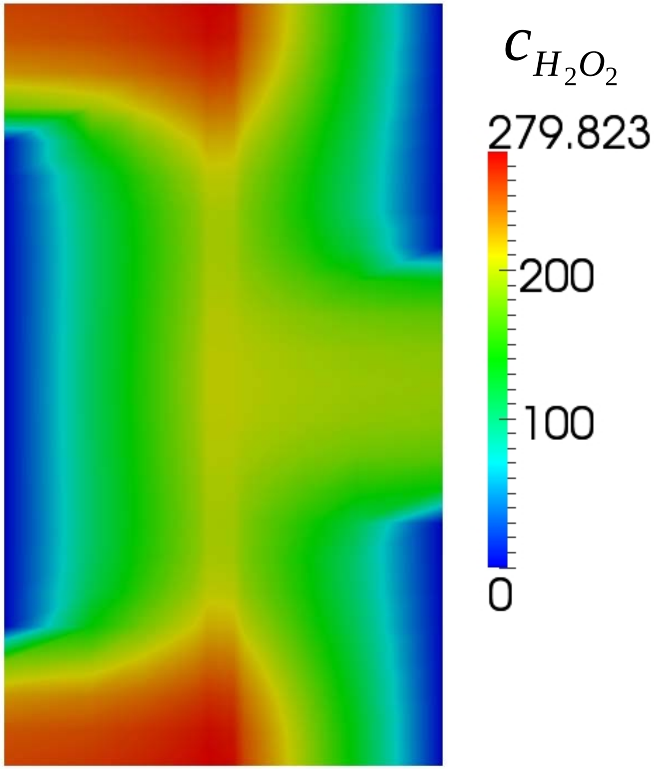
Membrane degradation: Hydrogen peroxide formation

- Two electron transfer:
  $O_2 + 2H^+ + 2e^- \rightarrow H_2O_2$
- Equilibrium potential E_0=0.695V
- Reaction rate

$$r = k_{H_2O_2} c_{O_2} c_{H^+}^2$$

$$k_{H_2O_2} = k^0 \exp\left(-\frac{E_a}{RT}\right) \exp\left(-\frac{\alpha F}{RT} \eta_{2e^-}\right)$$

- Reaction favored by the low potential at anode
- Reaction rate depends on the oxygen crossover

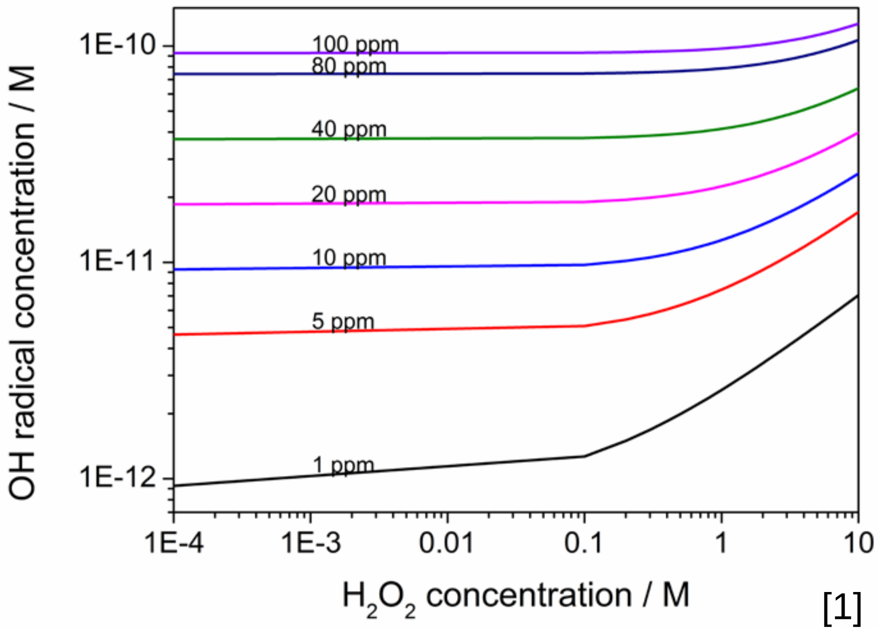


Membrane degradation: Radical formation

Radical formation due to H_2O_2 decomposition

Nr.	Reaction
1	$Fe^{2+} + H_2O_2 + H^+ \rightarrow Fe^{3+} + HO\bullet + H_2O$
2	$Fe^{3+} + H_2O_2 \rightarrow Fe^{2+} + HOO\bullet + H^+$
3	$Fe^{2+} + HOO\bullet + H^+ \rightarrow Fe^{3+} + H_2O_2$
4	$Fe^{3+} + HOO\bullet \rightarrow Fe^{2+} + O_2 + H^+$
5	$HO\bullet + H_2O_2 \rightarrow HOO\bullet + H_2O$
6	$HOO\bullet + H_2O_2 \rightarrow HO\bullet + H_2O + O_2$
7	$2HOO\bullet \rightarrow H_2O_2 + O_2$

[1]

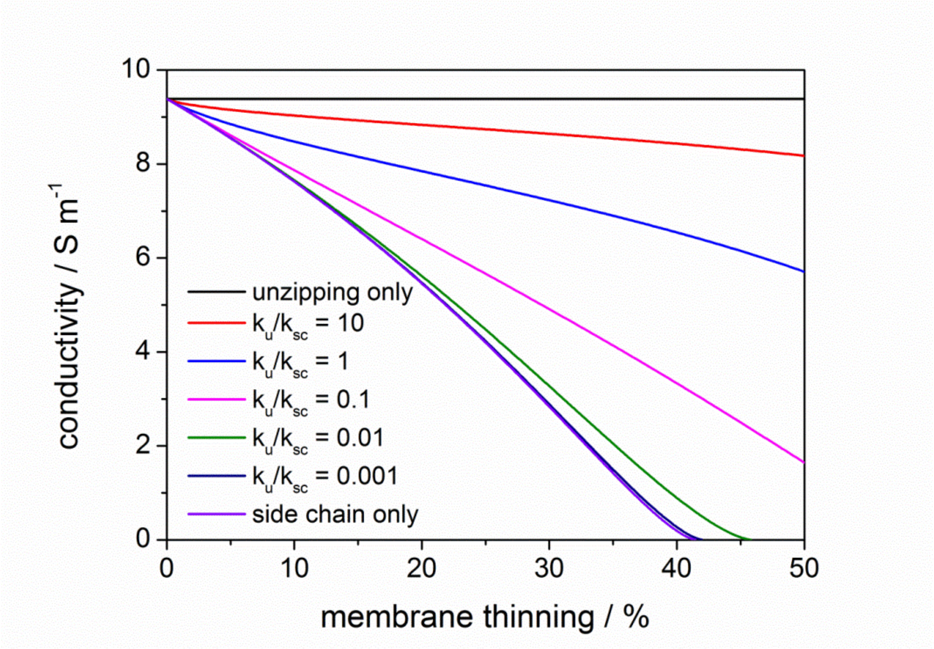


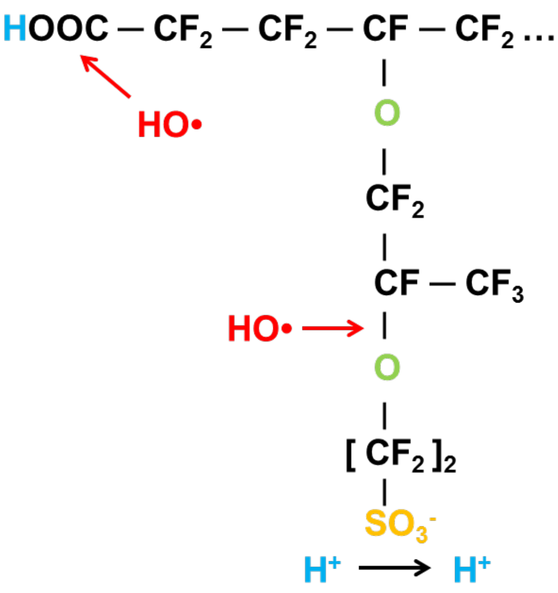
[1]

[1]: Ghelichi et al., *J. Phys. Chem. B,* 2014.

Membrane degradation: Radical attack

- Two radical attack mechanisms can occur [1]:
  - Unzipping of the back bones
  - Attack on the side chains
- Only side chain scission affects the conductivity





[1]: Ghelichi et al., *J. Phys. Chem. B,* 2014.

Summary

- The development of predictive fuel cell models is challenging:
  - Catalyst and membrane degradation are complex multi-step processes
  - The degradation strongly depends on the local conditions inside the cell

- DMFC show reversible and irreversible performance degradation
  - Irreversible degradation, related to a reduction of the electrochemical active surface area, can be described by a particle growth model
  - Reversible degradation is caused by platinum oxide formation
  - Both mechanisms are strongly coupled

- Chemical degradation of the membrane in PEMFC proceeds in several steps: Oxygen crossover from cathode to anode → Hydrogen peroxide formation →Radical formation → Radical attack of the membrane

- Specific in situ and ex situ experiments are required to identify and quantify certain mechanisms

"It can scarcely be denied that the supreme goal of all theory is to make the irreducible basic elements as simple and as few as possible without having to surrender the adequate representation of a single datum of experience“

Albert Einstein

Thank you for your attention

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