Hydrogen Technologies

Lecture 8: Electrolysis IV

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Hochschule Kempten University of Applied Sciences

Fakultät Maschinenbau

Lecture Outline

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	Date	Place	Name	Content
1	07.10.2025	S0.13b	HYTECH 1	Hydrogen and Energy transition
1	07.10.2025	S0.13b	HYTECH 2	Hydrogen Production Overview
2	14.10.2025	S0.13b		
2	14.10.2025	S0.13b		
3	21.10.2025	S0.13b	HYTECH 3	Electrolysis - Electrochemistry and Thermodynamics
3	21.10.2025	S0.13b	HYTECH 4	Electrolysis - Kinetics, U-I-Curve
4	28.10.2025	S0.13b	HYTECH 5	Tutorial Hydrogen Production
4	28.10.2025	S0.13b	HYTECH 6	Tutorial Hydrogen Production
5	04.11.2025	S0.13b	HYTECH 7	Electrolysis - Membrane Materials
5	04.11.2025	S0.13b	HYTECH 8	Electrolysis - Catalysis, Electrodes
6	11.11.2025	S0.13b	HYTECH 9	Hydrogen Storage - Compression, Liquefication
6	11.11.2025	S0.13b	HYTECH 10	Hydrogen Storage - Metal Hydrides, LOHCs, Ammonia
7	18.11.2025	S0.13b	HYTECH 11	Fuel Cells - Introduction
7	18.11.2025	S0.13b	HYTECH 12	Fuel Cells - Thermodynamics and Polarization
8	25.11.2025	S0.13b	HYTECH 13	Fuel Cells - Systems
8	25.11.2025	S0.13b	HYTECH 14	Fuel Cells - Materials
9	02.12.2025	S0.13b	HYTECH 15	Characterization Methods
9	02.12.2025	S0.13b	HYTECH 16	Characterization Methods
10	09.12.2025	S0.13b	HYTECH 17	Tutorial Fuel Cells
10	09.12.2025	S0.13b	HYTECH 18	Tutorial Fuel Cells
11	16.12.2025	S0.13b	HYTECH 19	Electrolysis and Fuel Cells: Material Level Degradation
11	16.12.2025	S0.13b	HYTECH 20	Electrolysis and Fuel Cells: System Level Degradatiion
12	23.12.2025	S0.13b	HYTECH 21	Lab-Tour
12	23.12.2025	S0.13b	HYTECH 22	Lab-Tour
12	13.01.2026	S0.13b	HYTECH 23	Power to Liquid
12	13.01.2026	S0.13b	HYTECH 24	Power to Liquid
13	20.01.2026	S0.13b	HYTECH 27	Repetition und exam preparation
13	20.01.2026	S0.13b	HYTECH 28	Repetition und exam preparation

Last time…

- **There are several kind of water electrolyzers**
- **The different types are defined by the used electrolyte**
- **The different electrolyte lead to**
    - different Redox-Reactions
    - different half cell potentials
    - different pH
- **Ion conduction relies on Grotthus mechanism („Ion-hopping“)**
- **Membranes suffer gas cross-over, which decreases efficiency and limits operation window**

Today…

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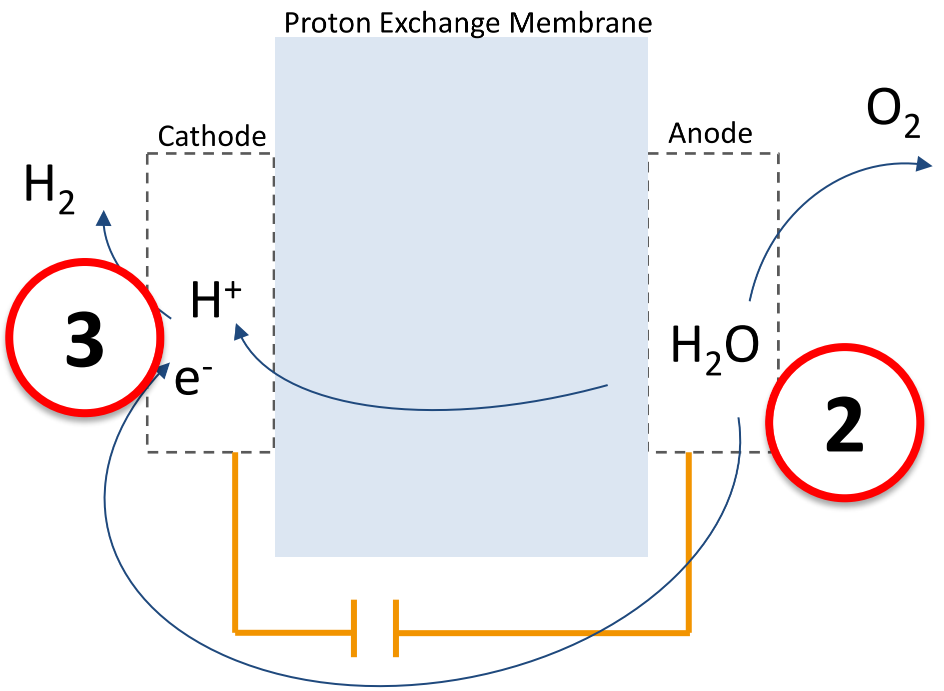
- Heterogeneous Catalysis
- Materials for electrodes

Materials for PEMWE

- 1) Proton Exchange Membrane
- 2) Anode Electrode
- 3) Cathode Electrode



PEMWE Electrodes

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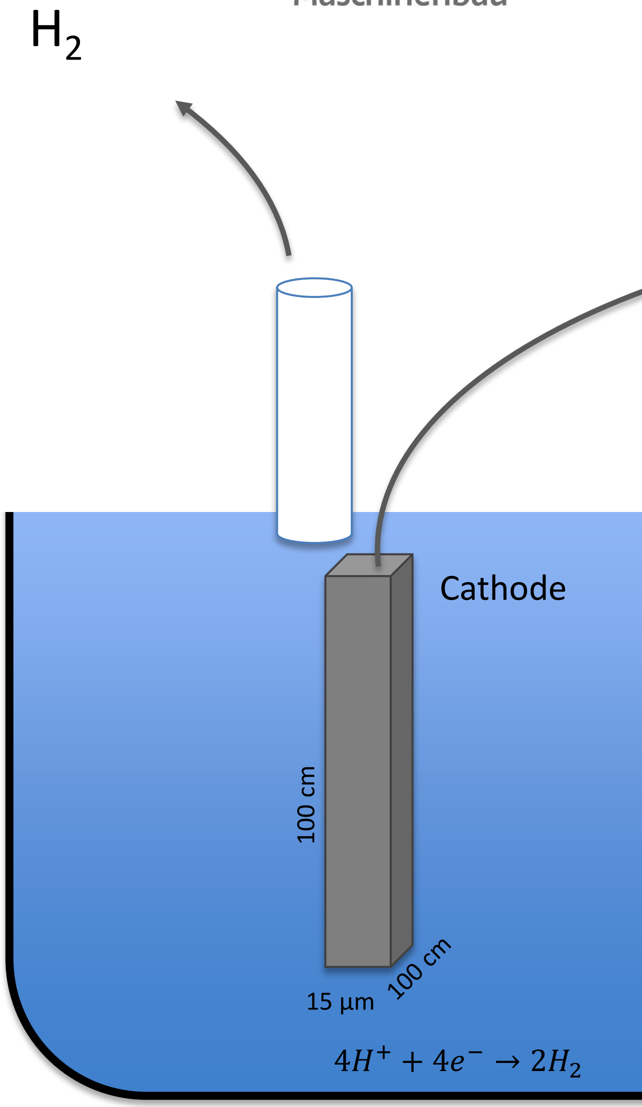
- **What‘s the job of an electrode?**
  - 1) Provide surface area (Remember: „Electrochemistry can only happen at Electrode/Electrolyte interfaces“!)
  - 2) Catalyze the half cell reactions

Surface Area of Electrodes

- **Assume a 100 * 100 cm cell area.**
  - Simple case: Pt foil (15 µm x 100 cm x 100 cm)
  - Volume: 15 cm³
  - Weight: 21.45 * 15 g = 321.75 g
  - Surface: 2 * 1 m² + 4 * 0.15 cm² = 2.00006 m²
  - „Specific Surface Area“: 2.00006 m² / 321.75 g = **0,0062 m² / g**



Surface Area of Electrodes

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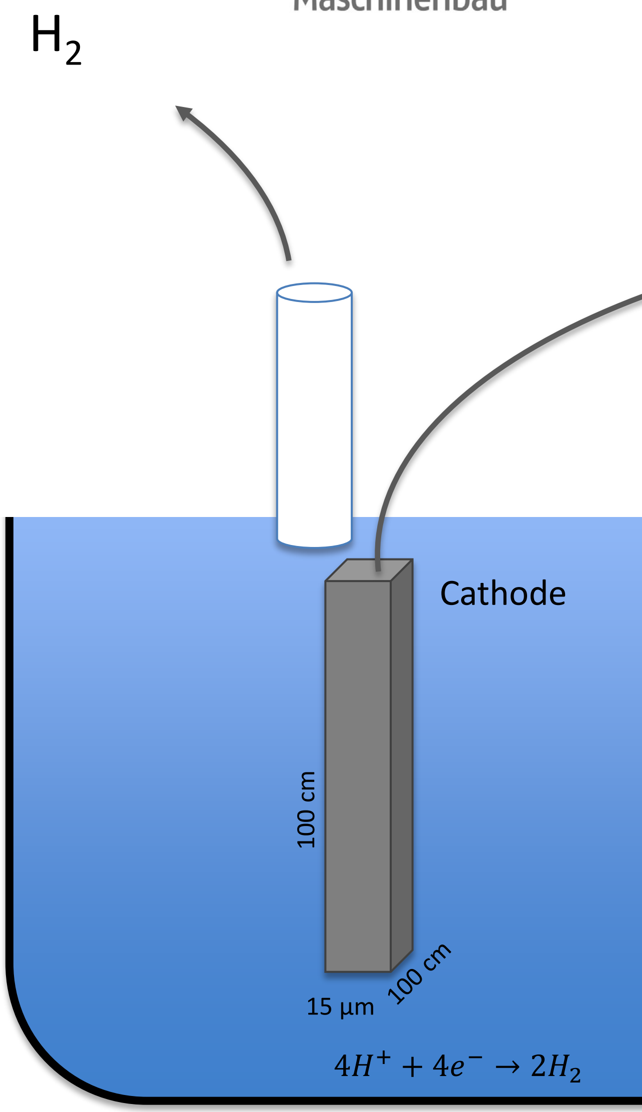
  - Surface: 2 * 1 m² + 4 * 0.15 cm² = 2.00006 m²
  - „Specific Surface Area“: 2.00006 m² / 321.75 g = **0,0062 m² / g**

- **What could you do to increase the specific surface area?**



Quiz: Surface Area of Electrodes

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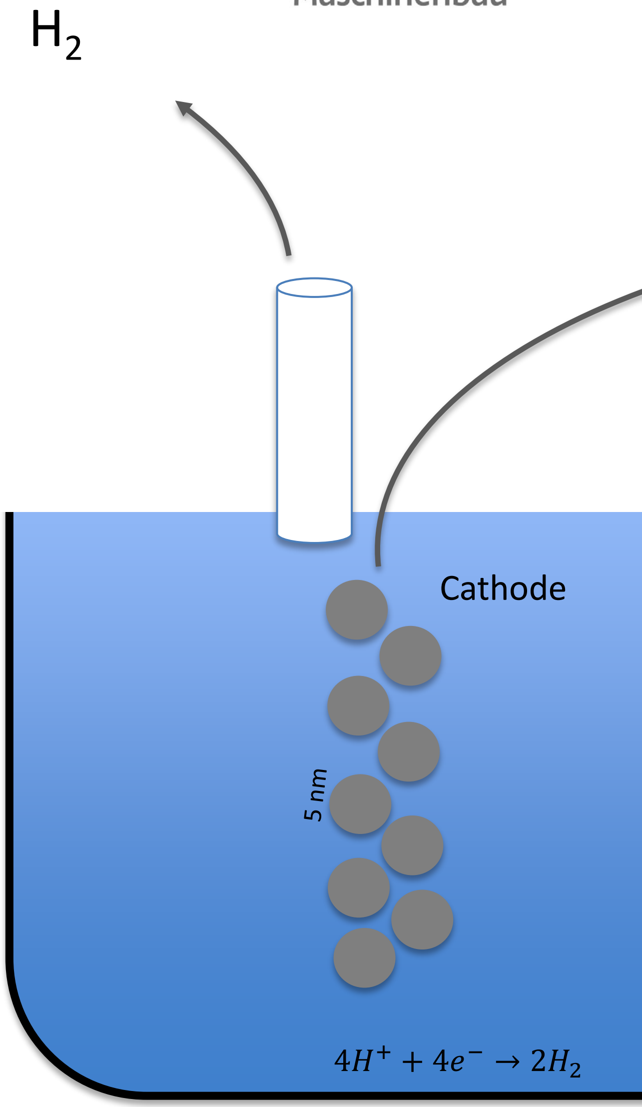
- **Nano-particles provide highes surface area at given material input!**
- **Assume a 100 * 100 cm cell area.**
  - Simple case: Pt foil (15 µm x 100 cm x 100 cm)
  - Volume: 15 cm³
  - Weight: 21.45 * 15 g = 321,75 g
  - Surface: 2 * 1 m² + 4 * 0.15 cm² = 2.00006 m²
  - „Specific Surface Area“: 2.00006 m² / 321.75 g = **0,0062 m² / g**
- **Imagine you invest the same mass of Pt (321.75 g) in nano-particles with 5 nm diameter. What Specific Surface Area can you get?**

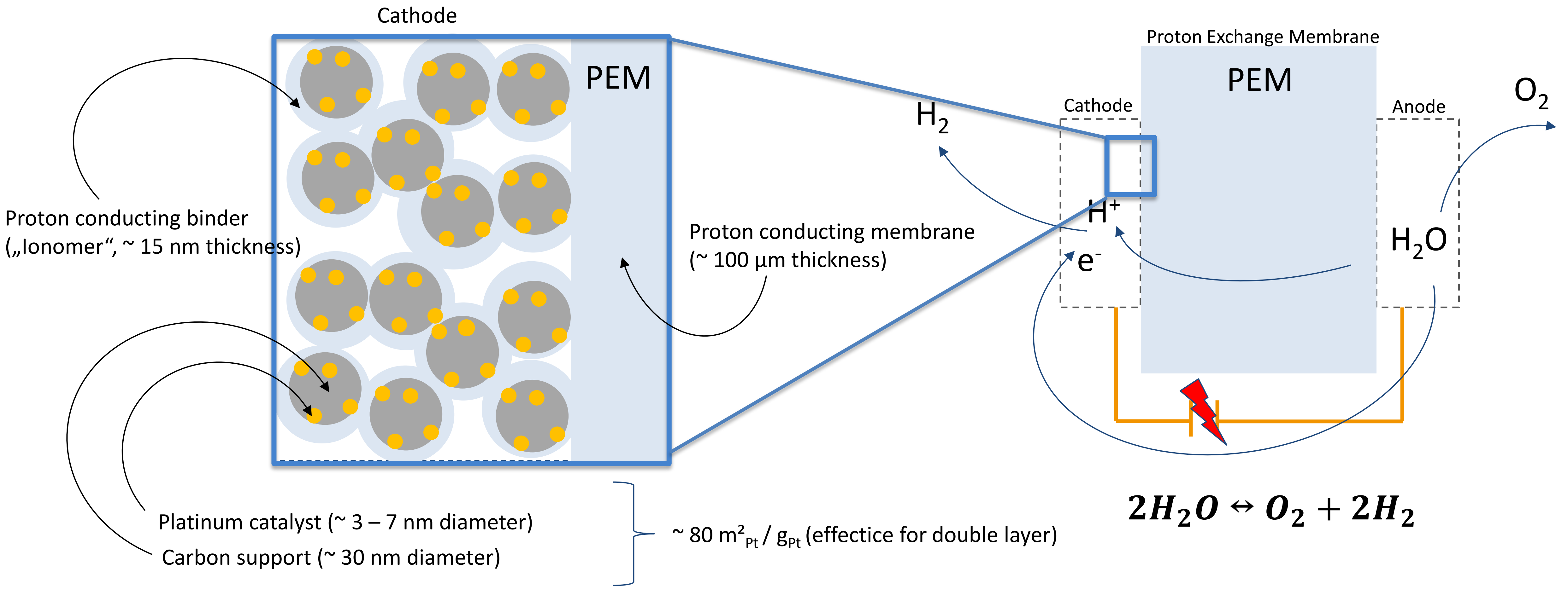
$$\boxed{V = 4/3 \cdot \pi \cdot r^3 \qquad O = 4 \cdot \pi \cdot r^2}$$

Volume „V“ and surface „O“ of spheres

$\boxed{55.81\ m^2/g}$

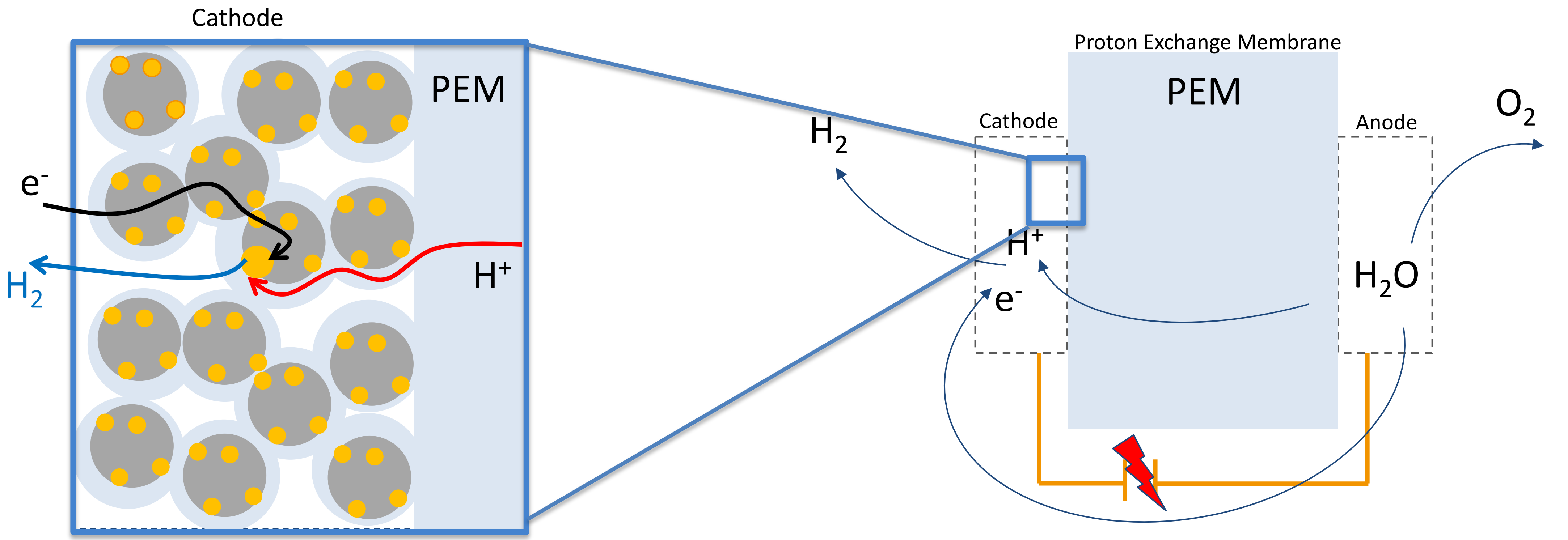


PEMWE Cathode Electrode Morphology



$$2H_2O \leftrightarrow O_2 + 2H_2$$

PEMWE Cathode Electrode Morphology



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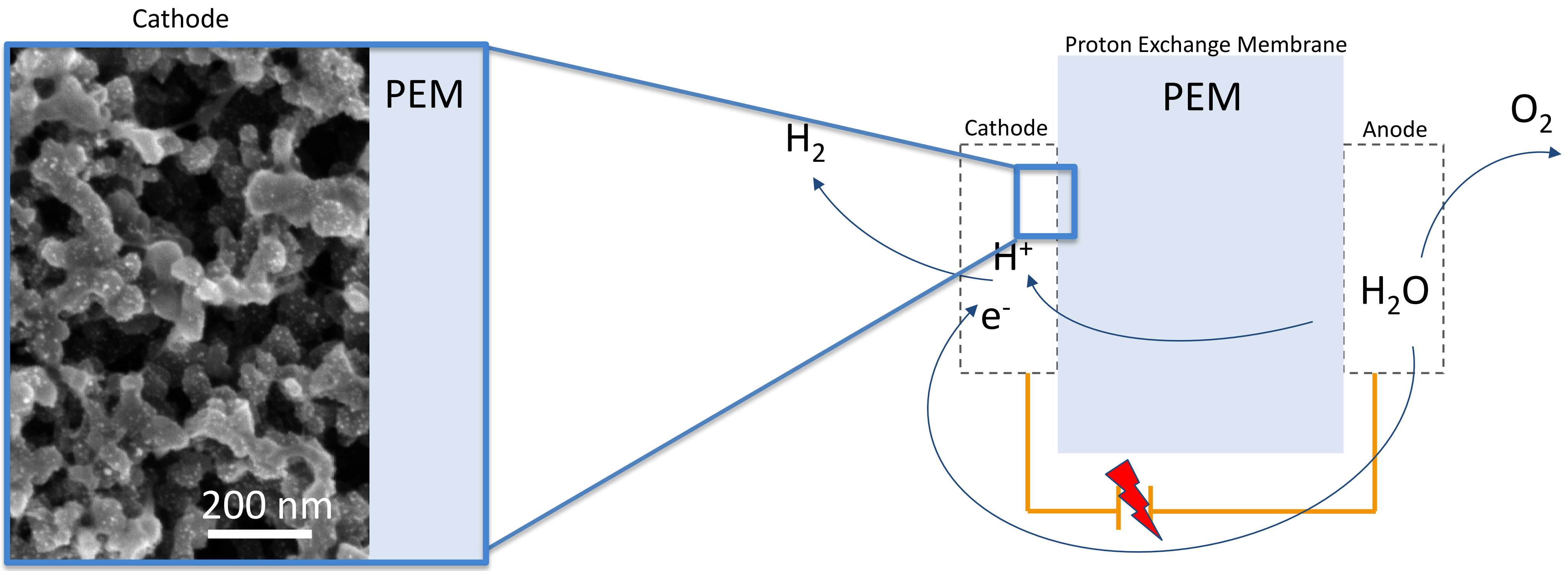
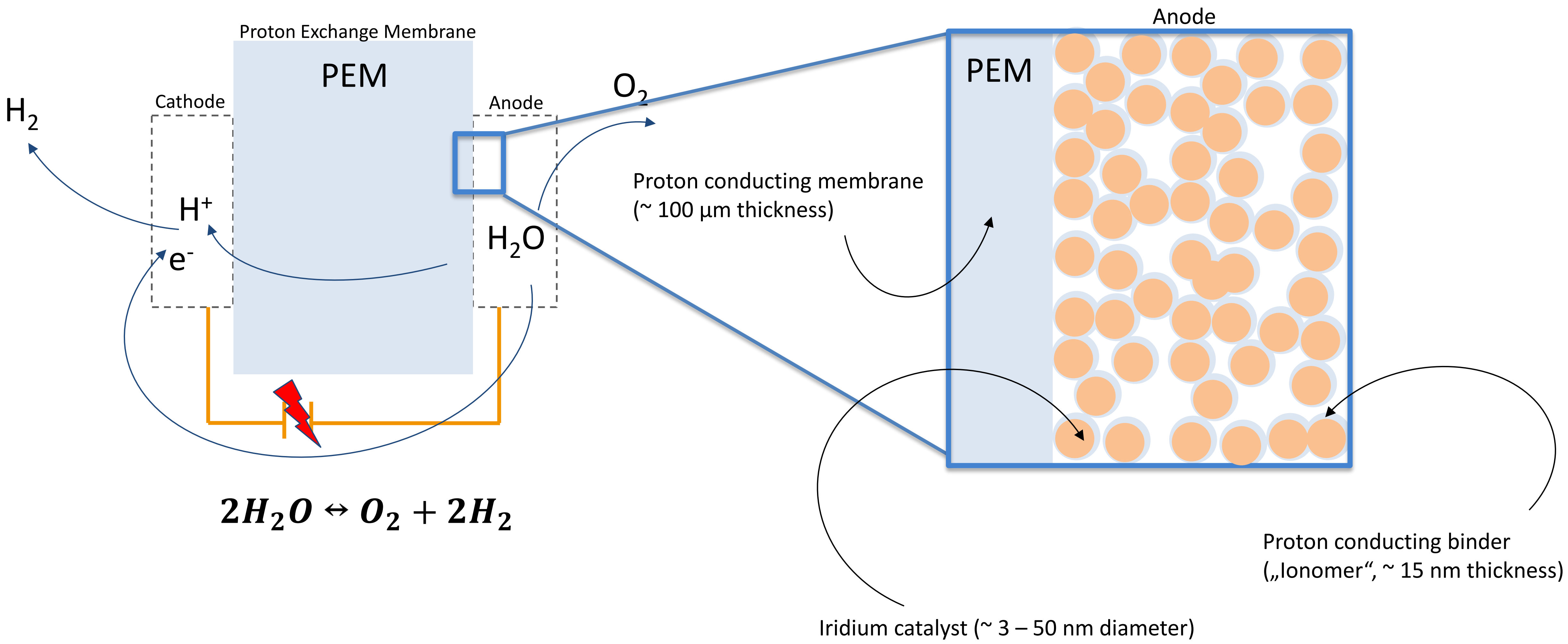
PEMWE Cathode Electrode Morphology



$$2H_2O \leftrightarrow O_2 + 2H_2$$

PEMWE Anode Morphology (Unsupported Catalyst)



$$2H_2O \leftrightarrow O_2 + 2H_2$$

PEMWE Anode Morphology

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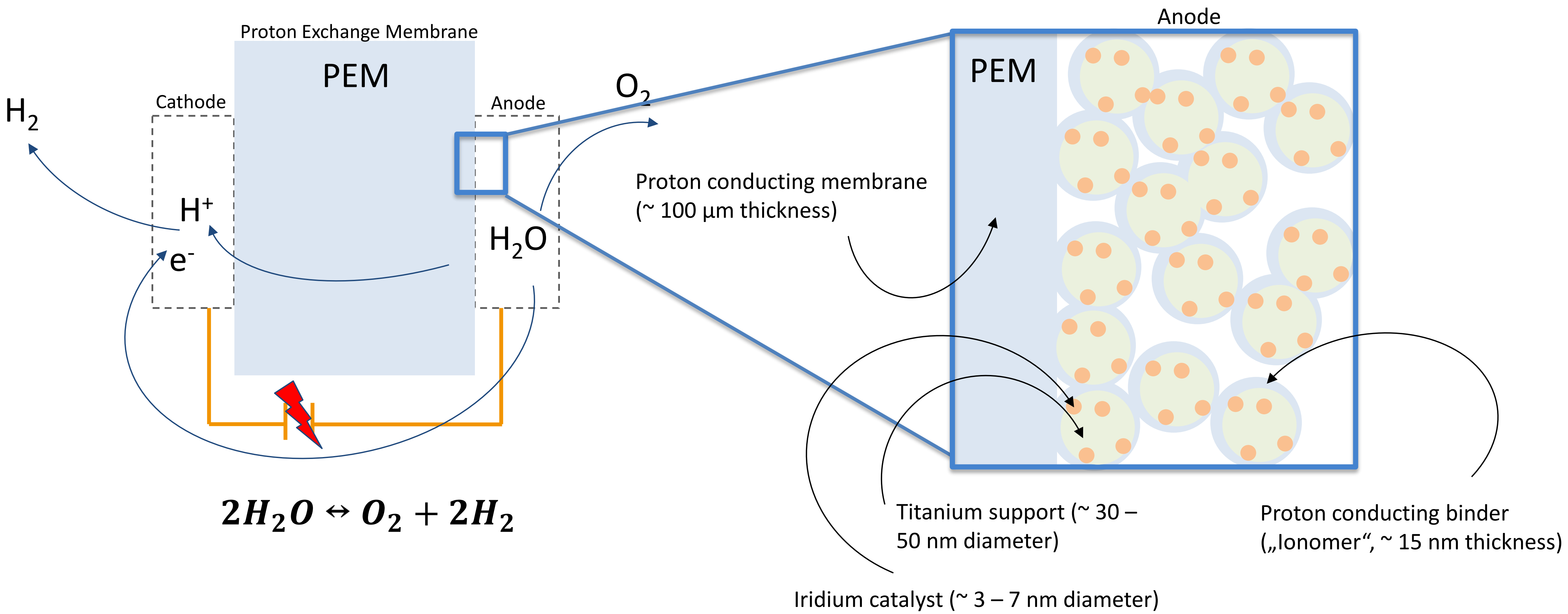

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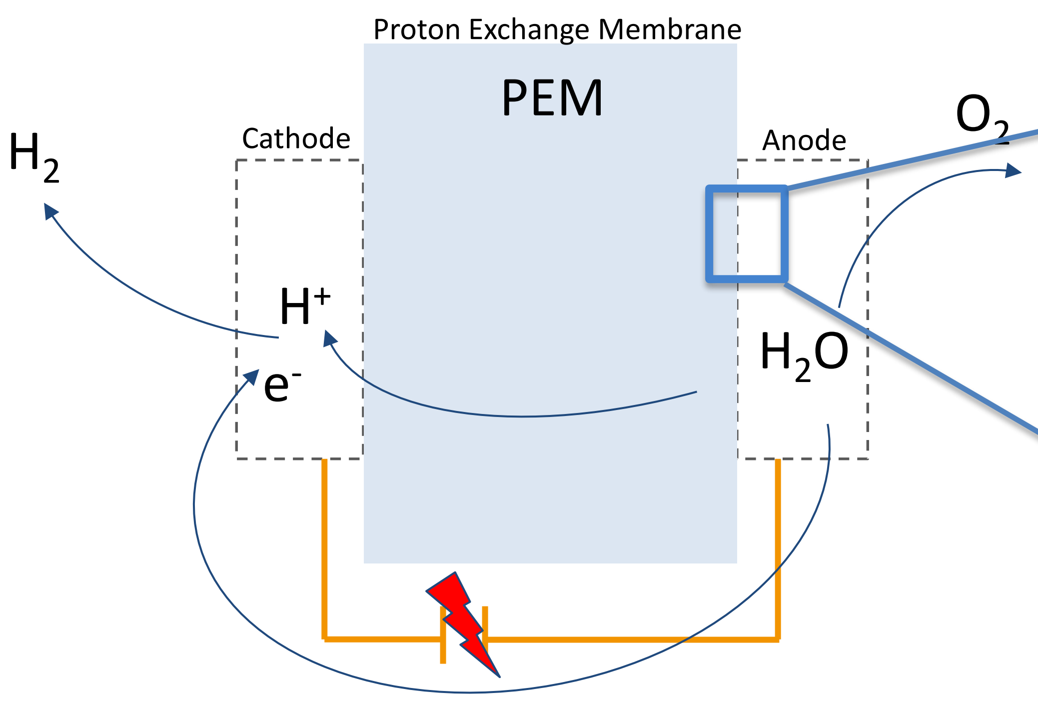
PEMWE Anode Morphology



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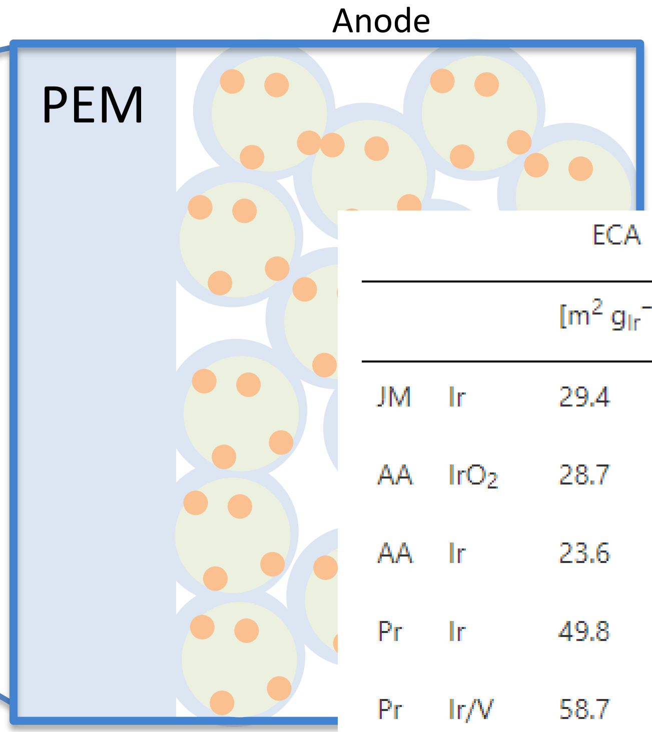

		ECA
		[$m^2\,g_{Ir}^{-1}$]
JM	Ir	29.4
AA	IrO_2	28.7
AA	Ir	23.6
Pr	Ir	49.8
Pr	Ir/V	58.7
Um	Ir	17.1
Um	Ir/TiO_2	15.8

Research needed!

PEMWE Anode Morphology

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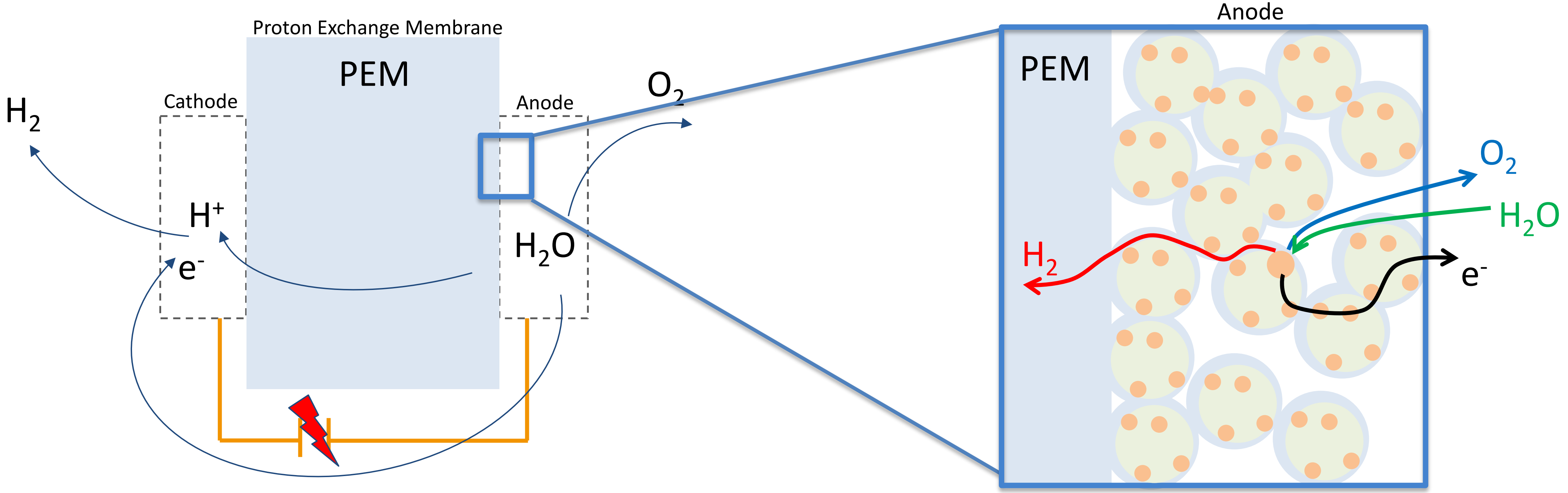

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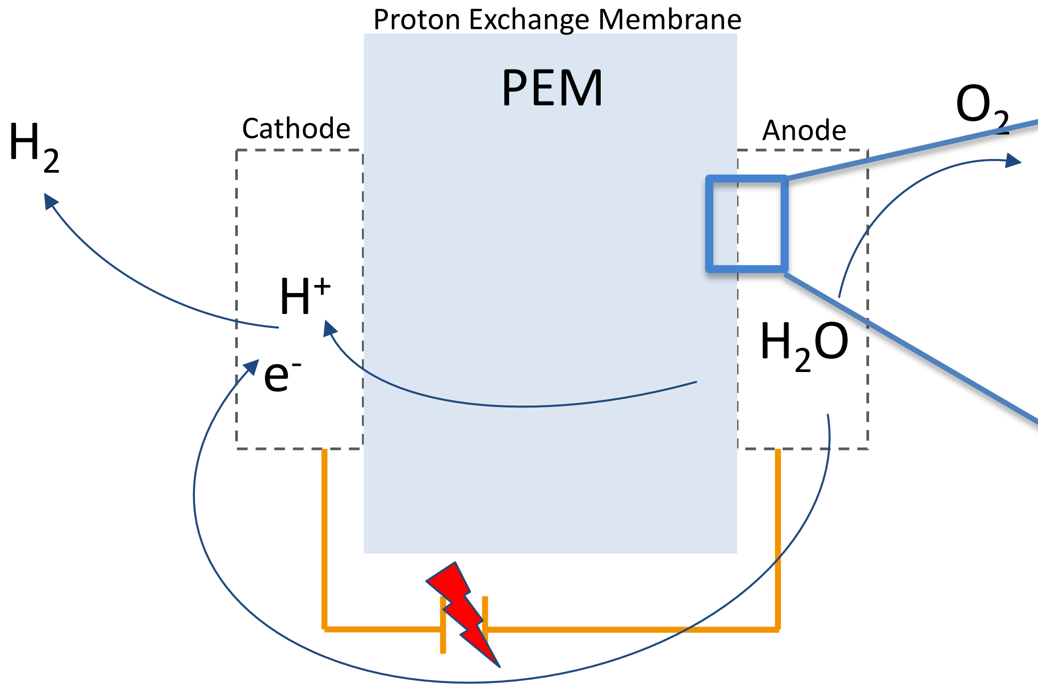
PEMWE Anode Morphology



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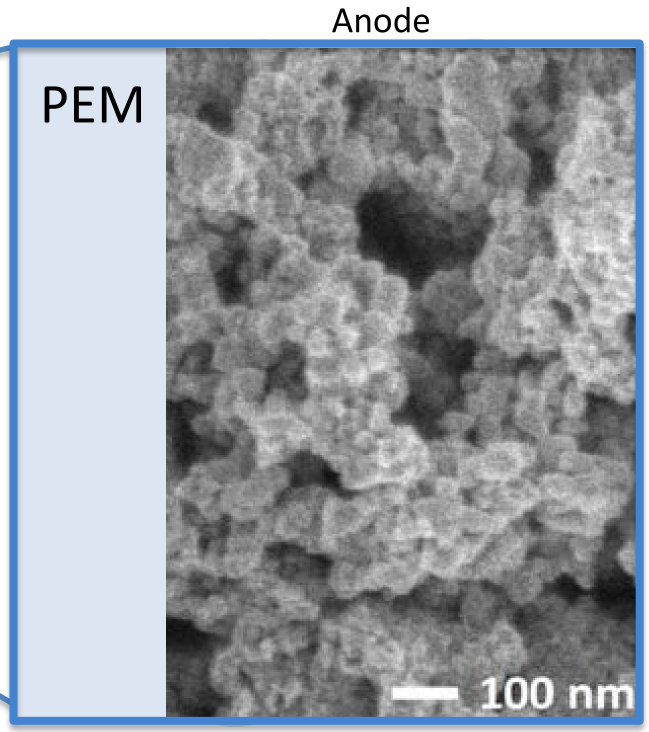

Bernt, Maximilian, and Hubert A. Gasteiger. "Influence of ionomer content in IrO2/TiO2 electrodes on PEM water electrolyzer performance." *Journal of The Electrochemical Society* 163.11 (2016): F3179-F3189.

PEMWE Catalyst Coated Membrane (CCM)

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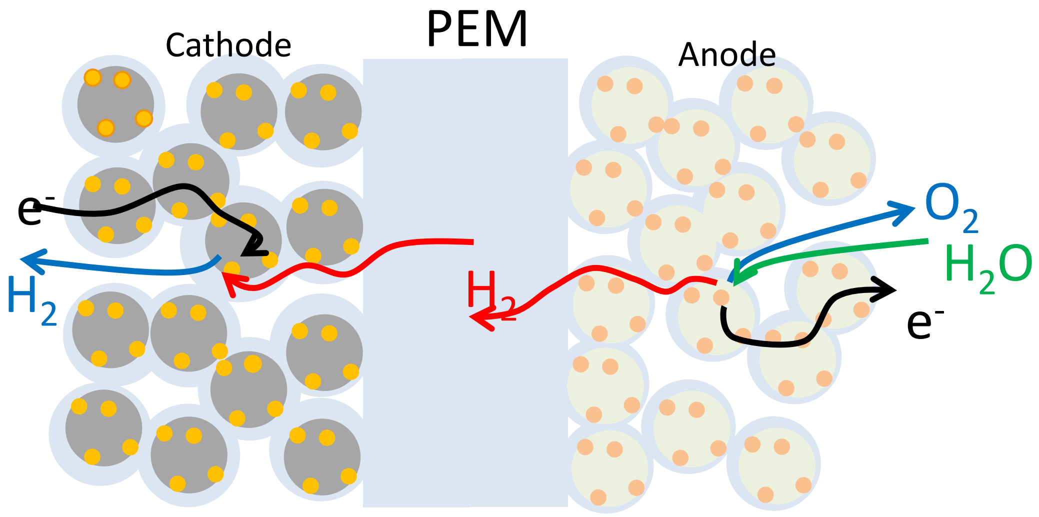
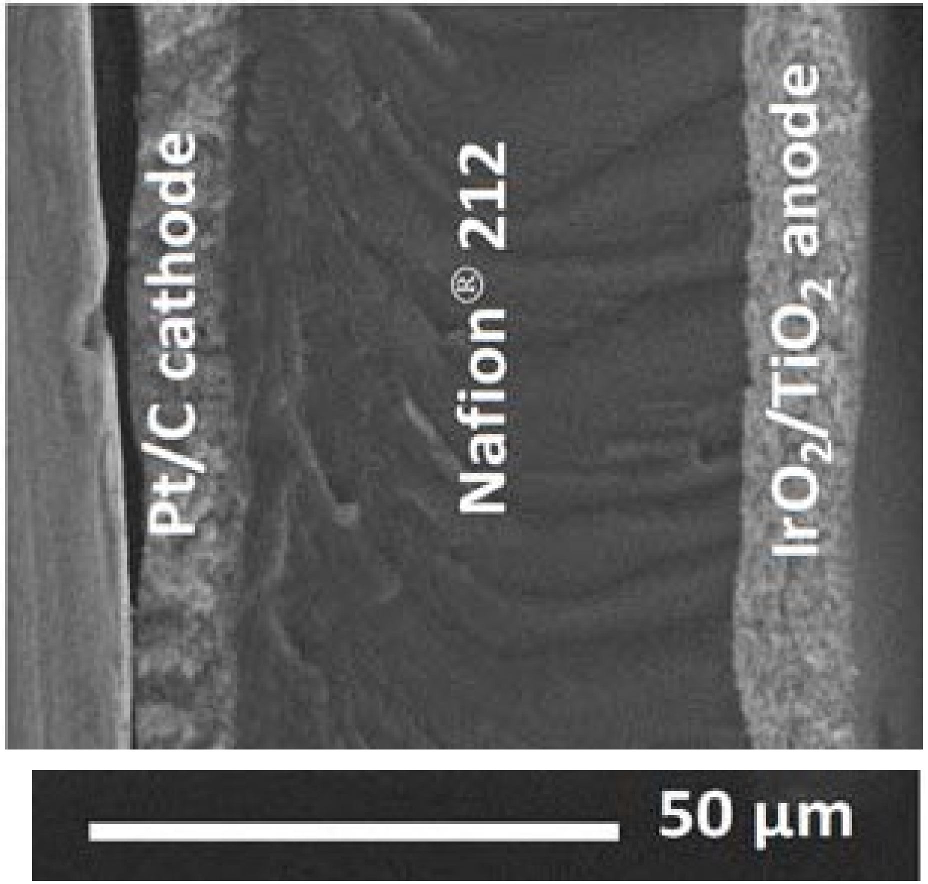
- Often also referred to as „Membrane Electrode Assembly“ (MEA)





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PEMWE Electrodes

- **What‘s the job of an electrode?**
  - 1) Provide surface area (Remember: „Electrochemistry can only happen at Electrode/Electrolyte interfaces“!)
  - **2) Catalyze the half cell reactions**

Introduction: Heterogeneous Catalysis

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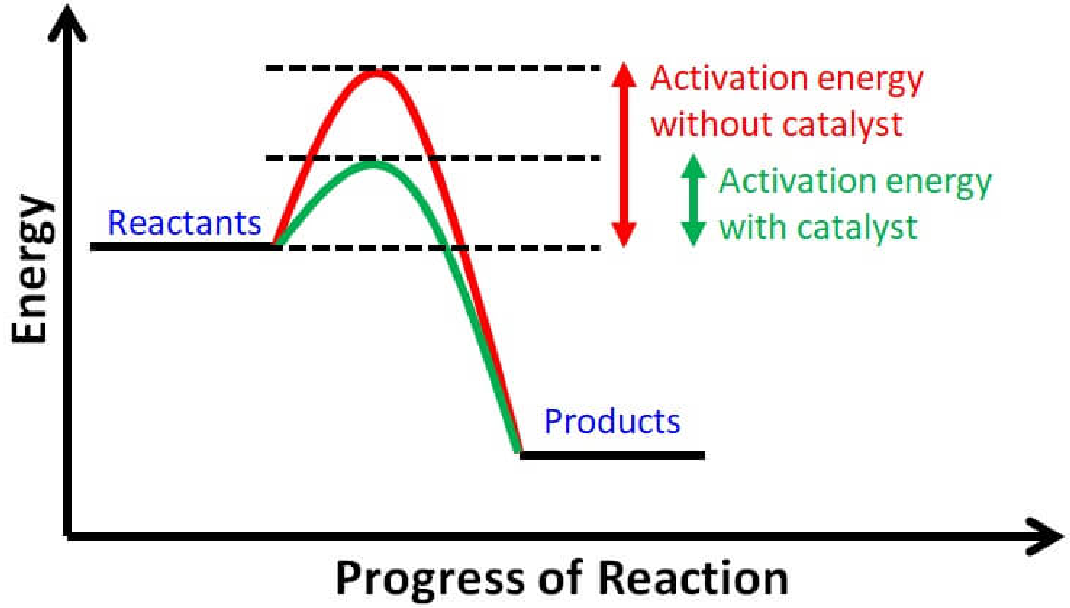
- Heterogeneous catalysts lower the reaction barrier of redox reactions



www.fuelcellstore.com/fuel-cell-components/catalyst

How?

Introduction: Heterogeneous Catalysis

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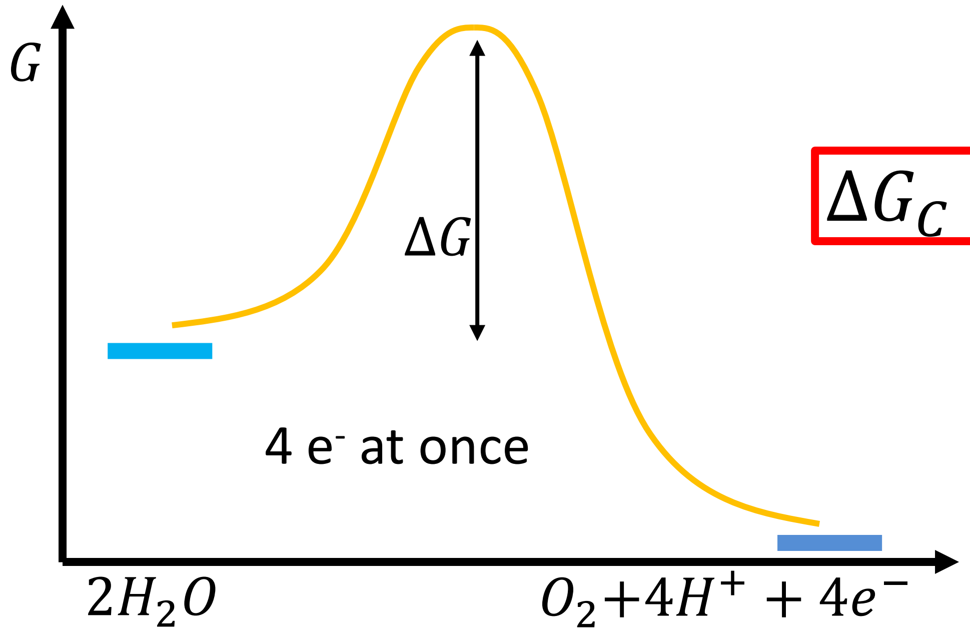
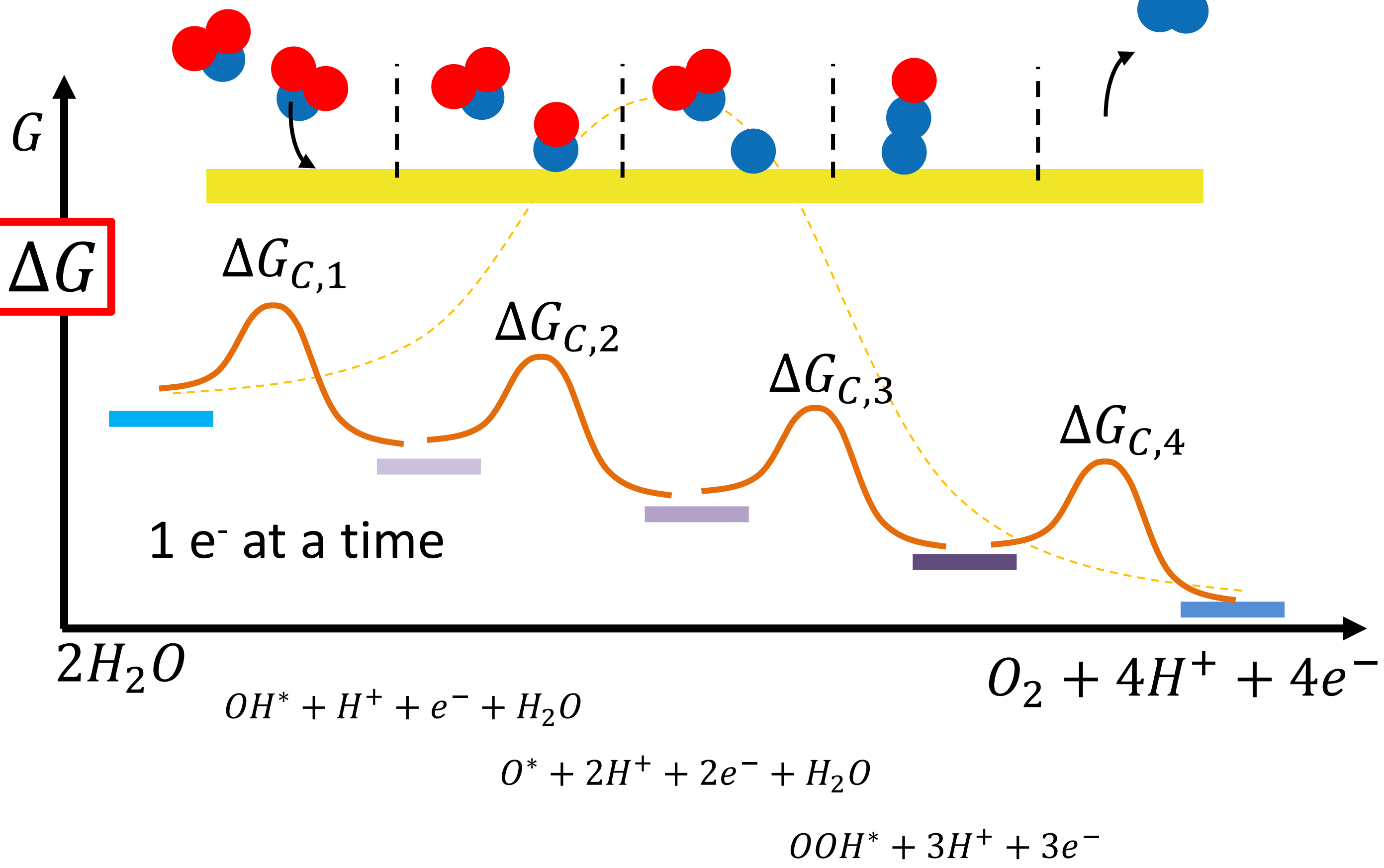
- **Heterogeneous catalysts lower the reaction barrier of redox reactions by allowing the reactant do adsorb and desorb to and from a metallic (electronically conductive) surface. This facilitates electron transfer!**

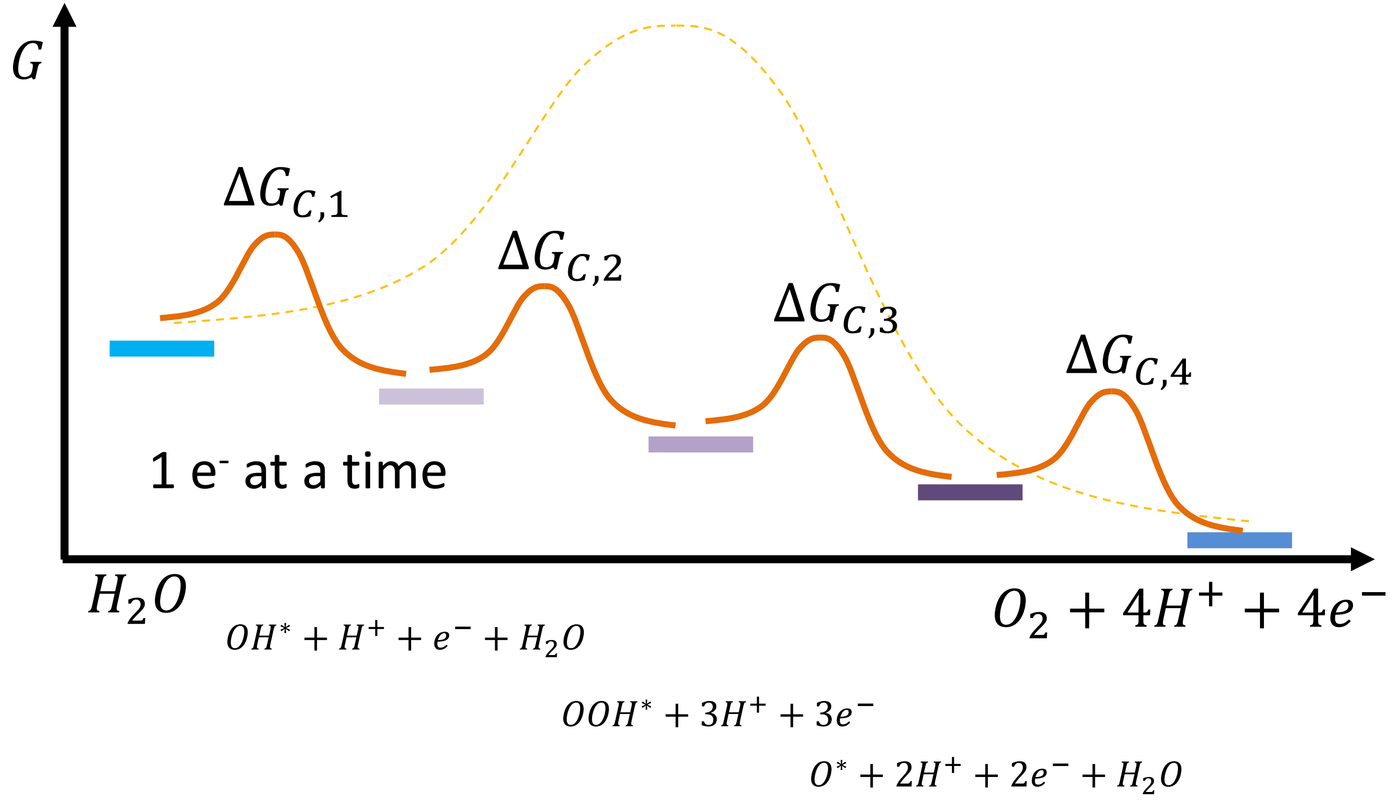


$\boxed{\Delta G_C \ll \Delta G}$



Introduction: Heterogeneous Catalysis

- Biggest ΔG_C is rate limiting!
- Ideal catalyst: $\Delta G_{C,1} = \Delta G_{C,2} = \Delta G_{C,3} = \Delta G_{C,4}$



Introduction: Heterogeneous Catalysis

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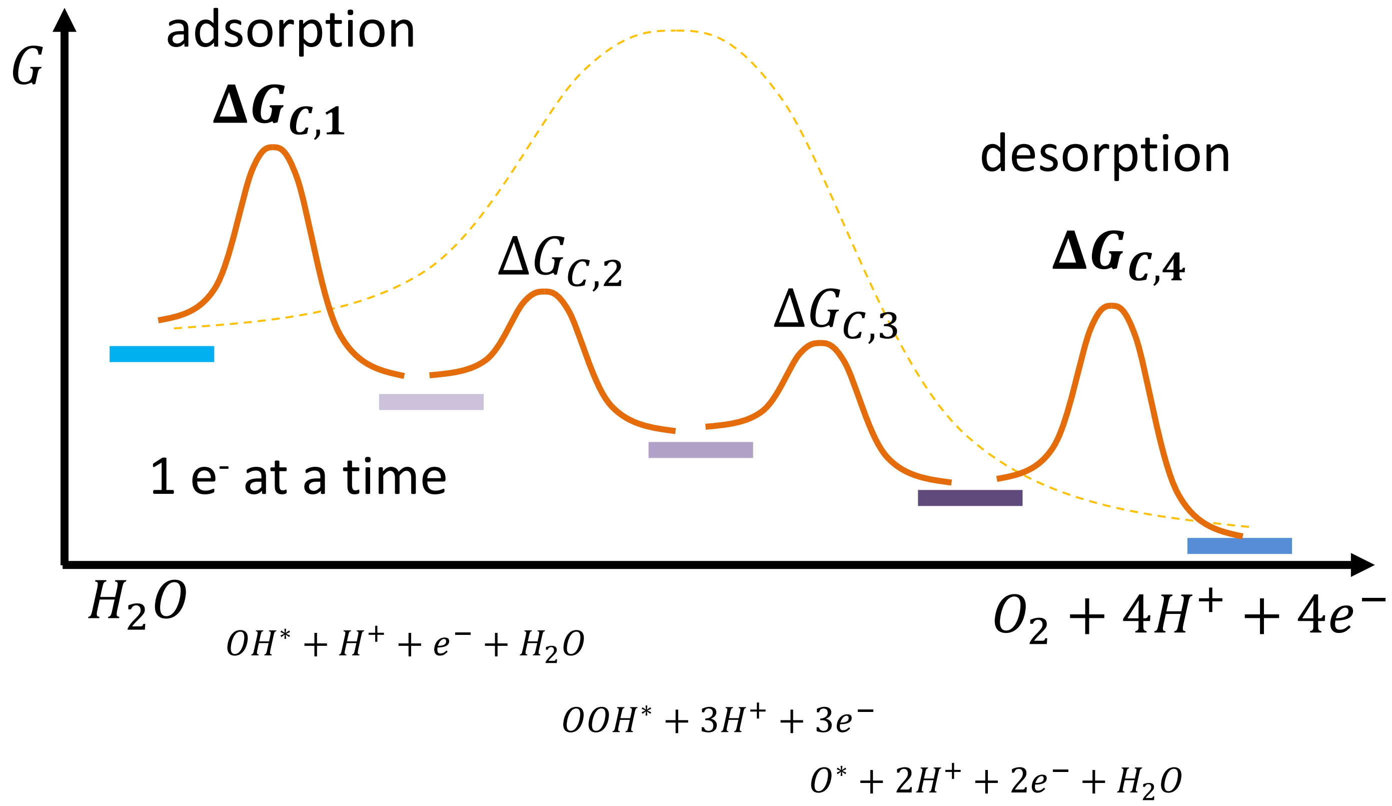
- Biggest ΔG_C is rate limiting!
- Real catalyst: $\Delta G_{C,1} \approx \Delta G_{C,4} > \Delta G_{C,3} \approx \Delta G_{C,4}$
- Adsorption and desorption are critical!
- „Good“ catalyst is defined by ist binding force to reactants and products



Introduction: Heterogeneous Catalysis

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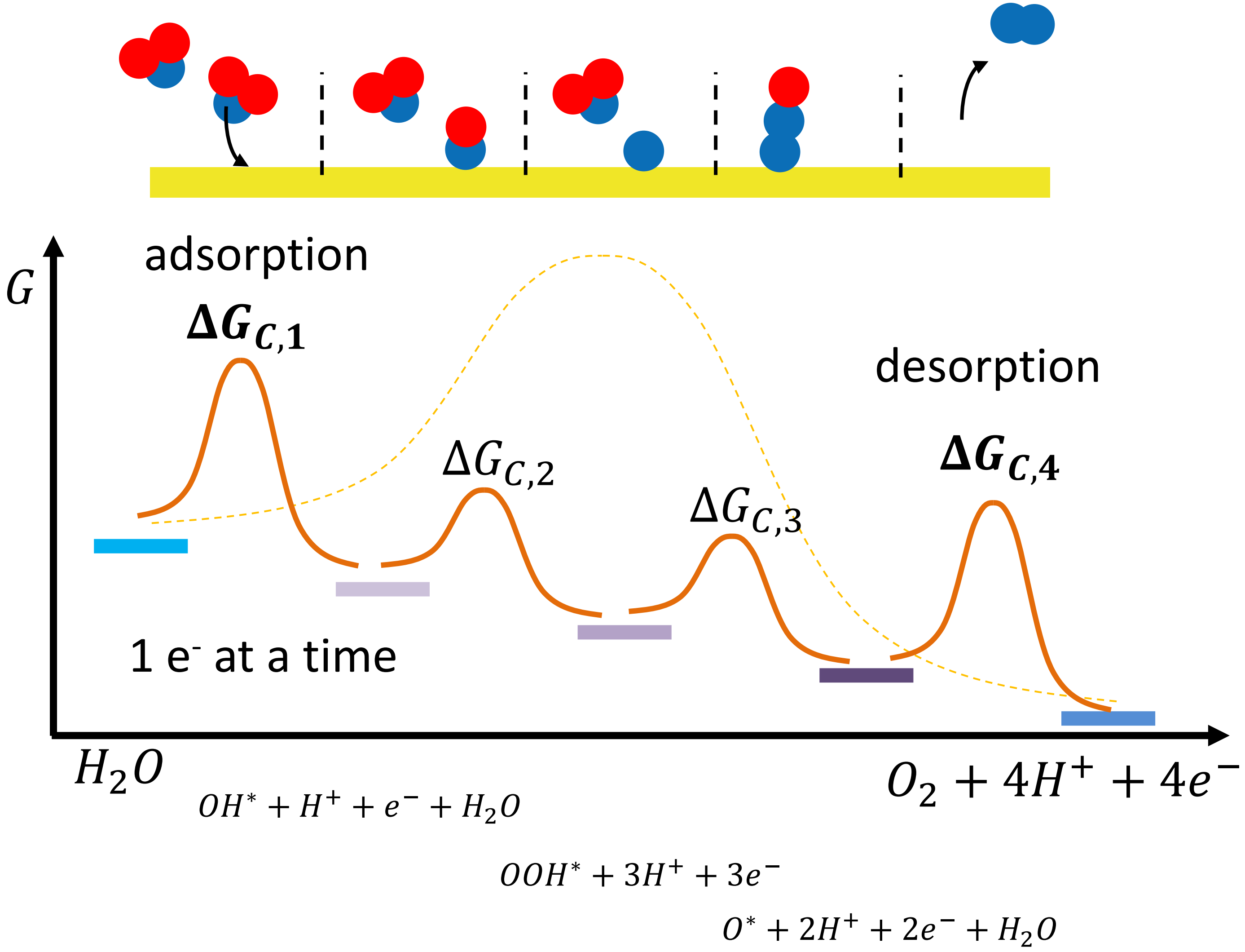
- Adsorption and desorption are critical!
- „Good" catalyst is defined by ist binding force to reactants and products
- Catalyt needs to compromise adsorption and desorption



Introduction: Heterogeneous Catalysis

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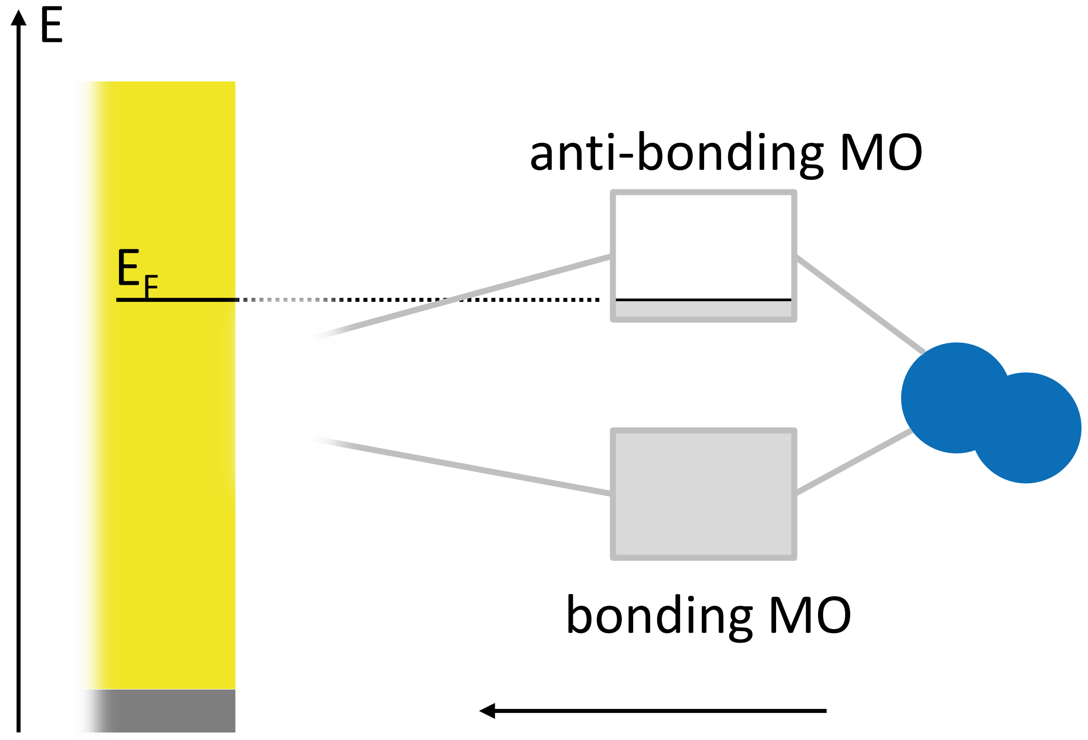
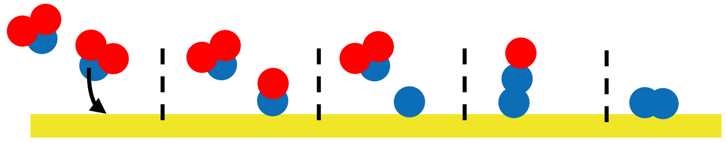
- **Fermi level of catalyst material defines binding force to oxygen by filling up molecular orbitals**



- Fermi level too low, bonding force too strong
- No desorption!
- Bad catalyst!



Source: Hammer and Norskov, *Why gold is the noblest of all the metals*, Nature (376) 1995

Introduction: Heterogeneous Catalysis

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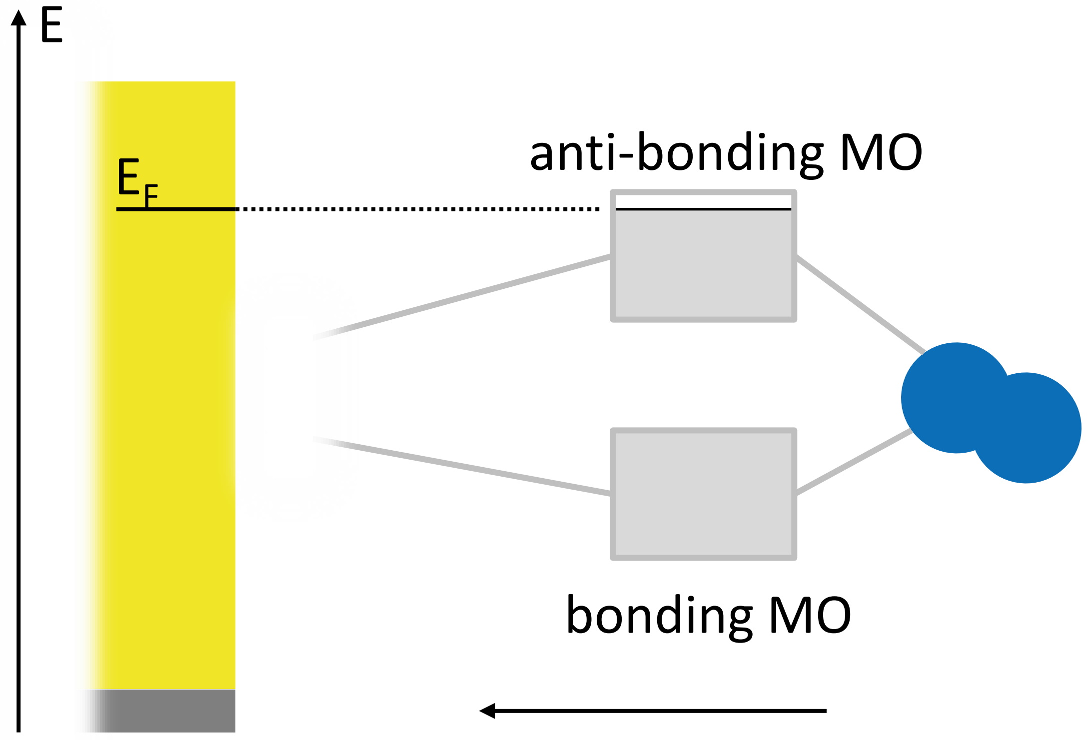
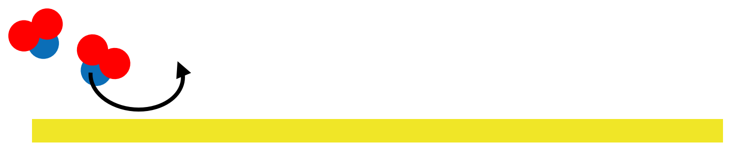


- Fermi level too high, bonding force too weak
- No adsorption!
- Bad catalyst!



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Introduction: Heterogeneous Catalysis

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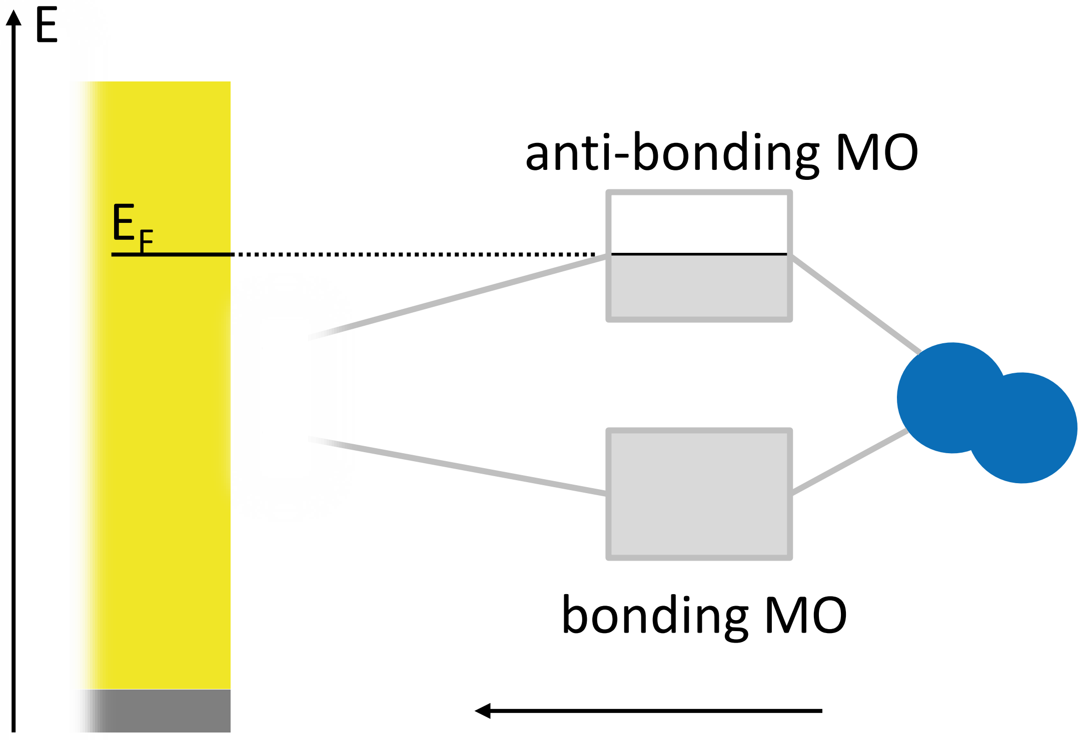
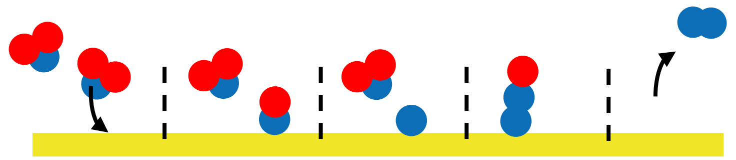


- Fermi level just right, bonding force just right
- Adsorption and desorption possible!
- Good catalyst!



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Introduction: Heterogeneous Catalysis

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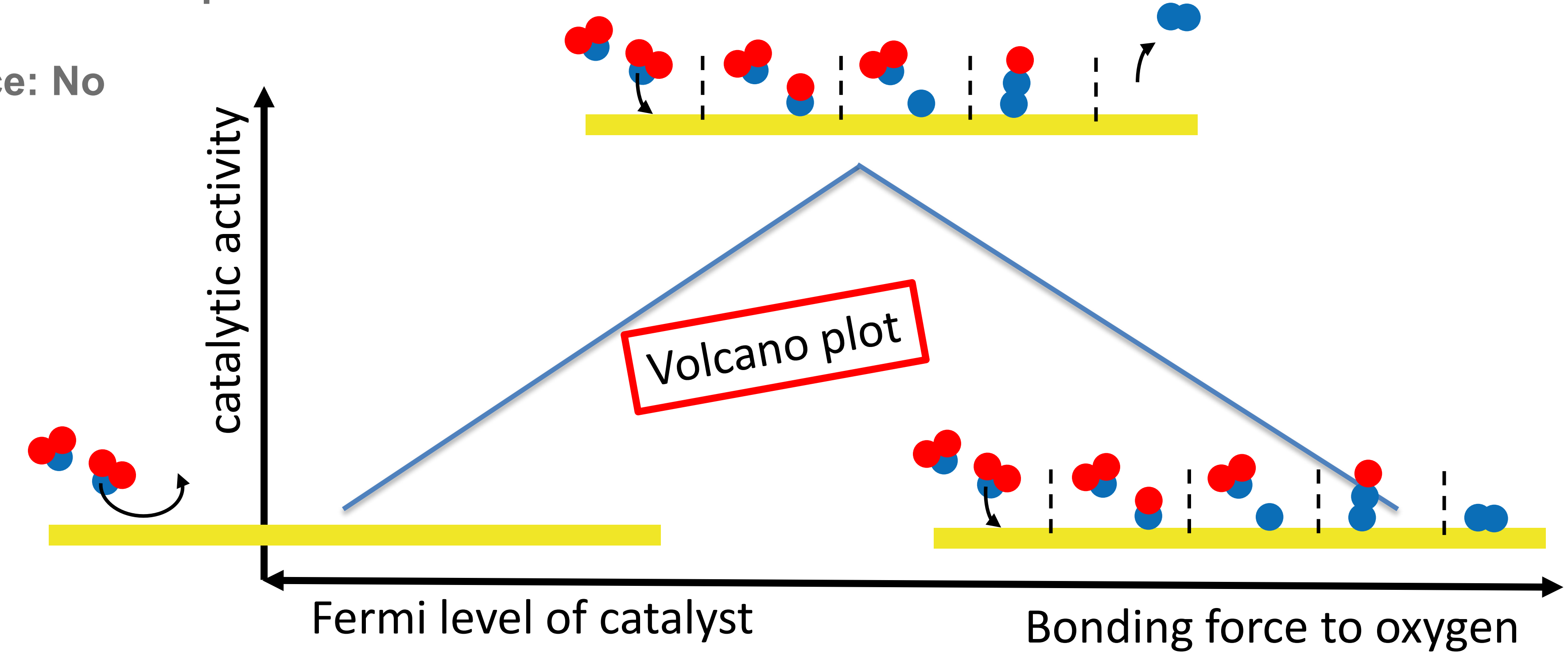
- Fermi level of catalyst defines bonding force to oxygen
- Too weak bonding force: No adsorption!
- Too strong bonding force: No desorption!



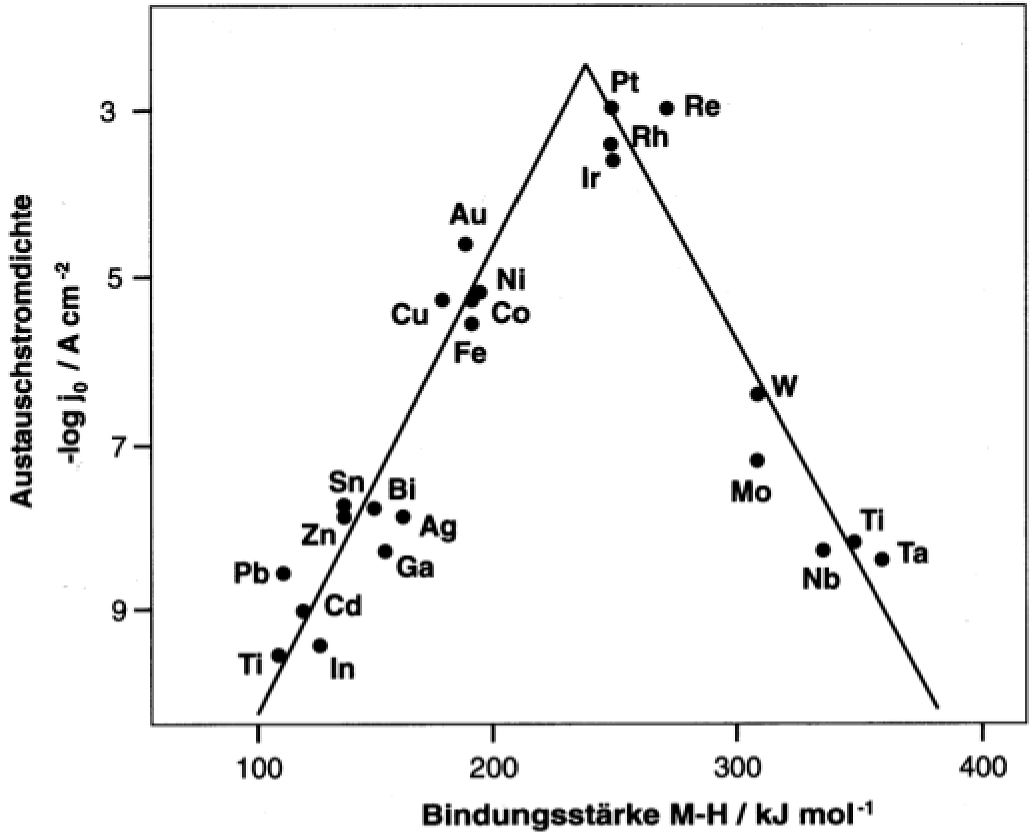
PEMWE Cathode Catalysis

- **Bonding force of catalyst to Hydrogen is determining the catalytic activity**

$$2\,H^+ + 2\,e^- \xrightarrow{\Delta G_1} H_{(ad)} + H^+ + e^-$$

$$H_{(ad)} + H^+ + e^- \xrightarrow{\Delta G_2} H_2$$

- **Platinum is best!**
- **Typical: 1 mg/cm²**



Schmidt, Volkmar M.: Elektrochemische Verfahrenstechnik: Grundlagen, Reaktionstechnik, Prozessoptimierung, Wiley-VCH, Weinheim, (2003).

https://www.technischechemie.tu-berlin.de/fileadmin/fg109/Publikationen/2010_The_Mechanism_of_Water_Oxidation__From_Electrolysis_via.pdf

PEMWE Cathode Catalysis

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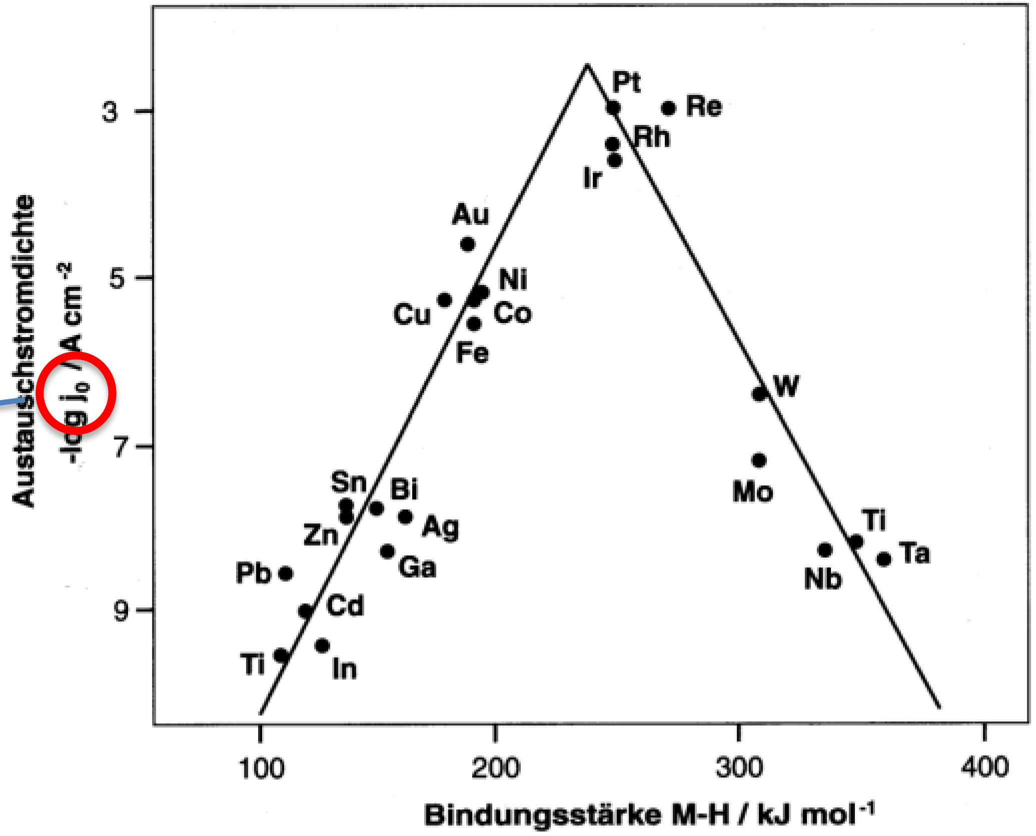
- **Remember Butler-Volmer: Catalyst enhance exchange current density and accelerate reaction kinetics!**

$$j_{eff}(\eta) = j_0 * e^{\frac{-\Delta G}{RT}} * \left(e^{\frac{\alpha\eta}{RT}} - e^{\frac{-(1-\alpha)\eta}{RT}}\right)$$



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PEMWE Anode Catalysis

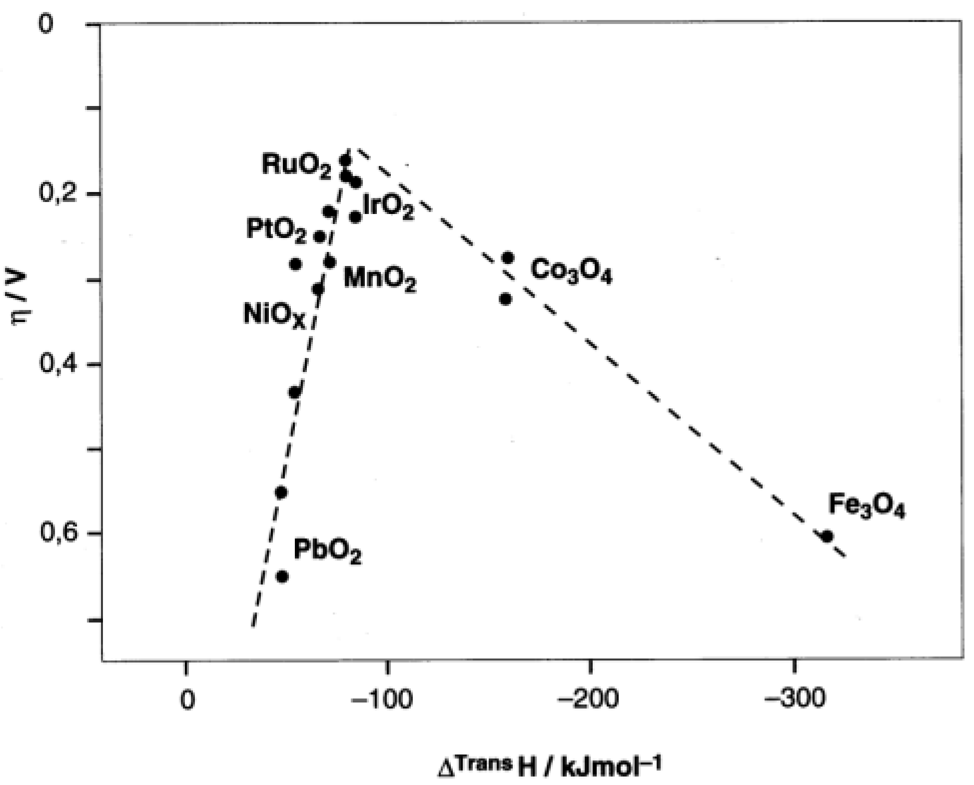
- **Bonding force of catalyst to Oxygen is determining the catalytic activity**

$$2\,H_2O \xrightarrow{\Delta G_1} OH_{(ad)} + H^+ + e^- + H_2O$$

$$OH_{(ad)} + H^+ + e^- + H_2O \xrightarrow{\Delta G_2} O_{(ad)} + 2\,H^+ + 2e^- + H_2O$$

$$O_{(ad)} + 2\,H^+ + 2e^- + H_2O \xrightarrow{\Delta G_3} OOH_{(ad)} + 3\,H^+ + 3e^-$$

$$OOH_{(ad)} + 3\,H^+ + 3e^- \xrightarrow{\Delta G_4} O_2 + 4\,H^+ + 4\,e^-$$



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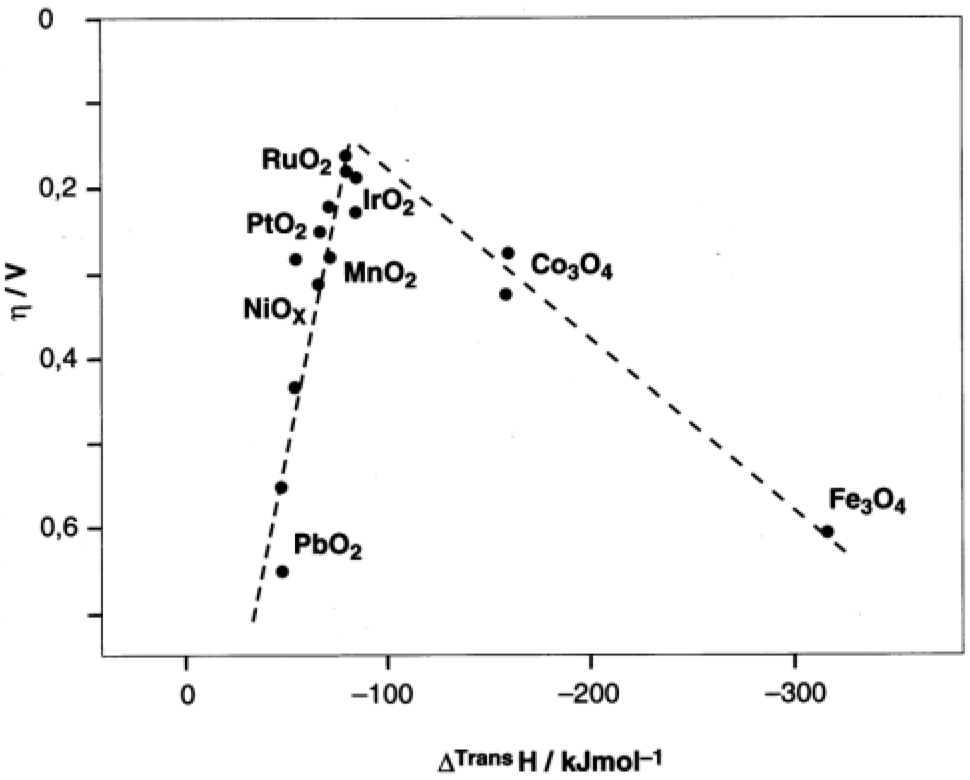
PEMWE Anode Catalysis

- Bonding force of catalyst to Oxygen is determining the catalytic activity
- Why are we using Iridium? Ruthenium seems better!
- Why are there only oxides listet?

Stability!



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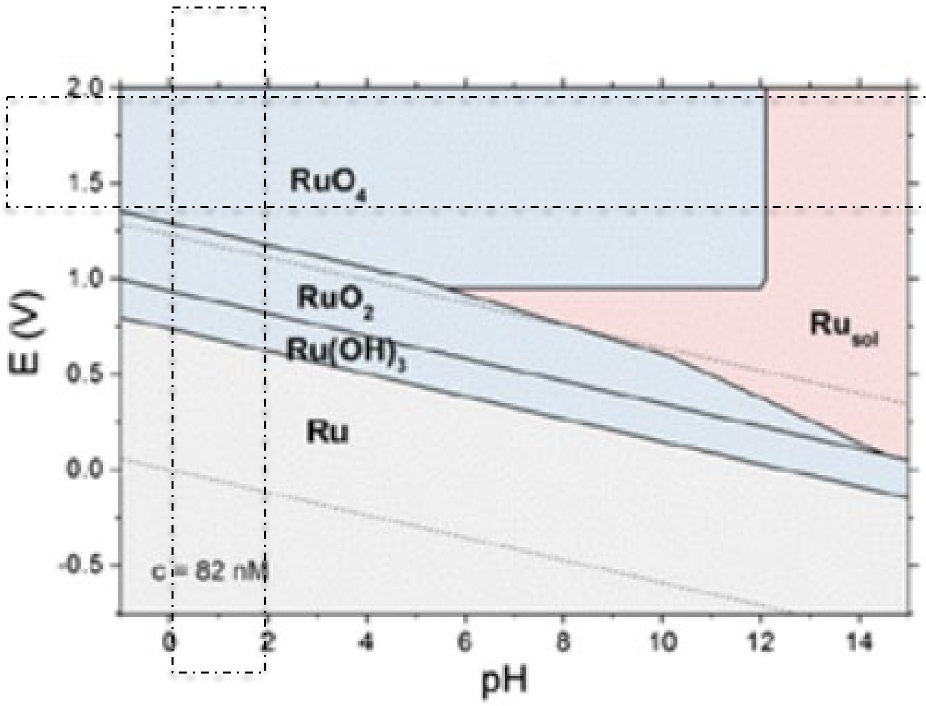
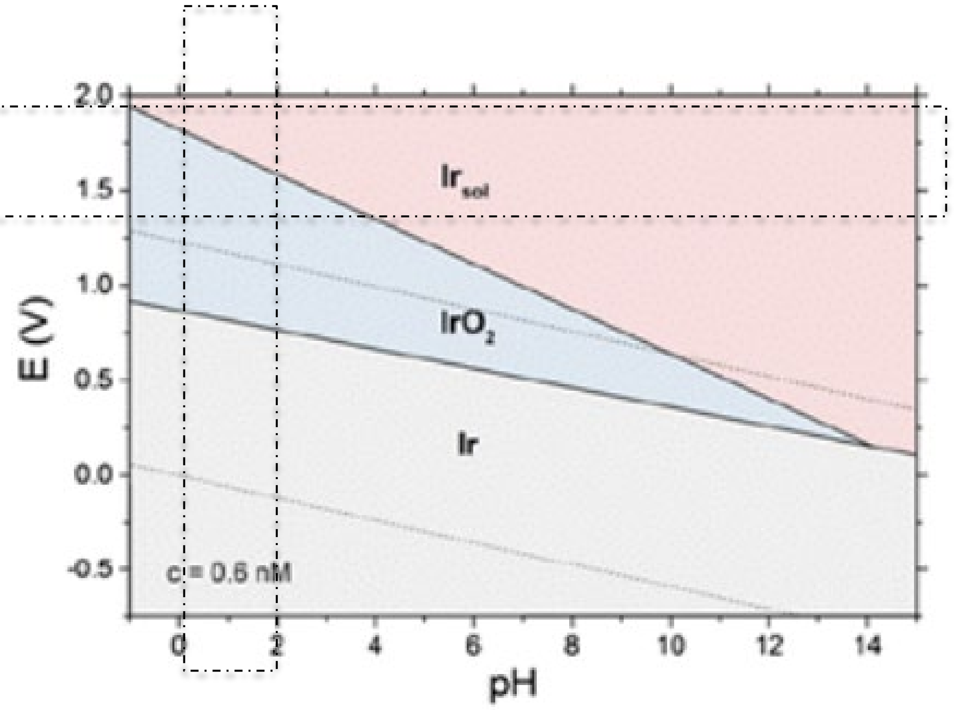
PEMWE Anode Catalysis

- Combination of potential > 1.4 V and low pH-value make most materials unstable!
- IrO_2: Compromising catalytic activity and stability! (typical 2 mg/cm²)



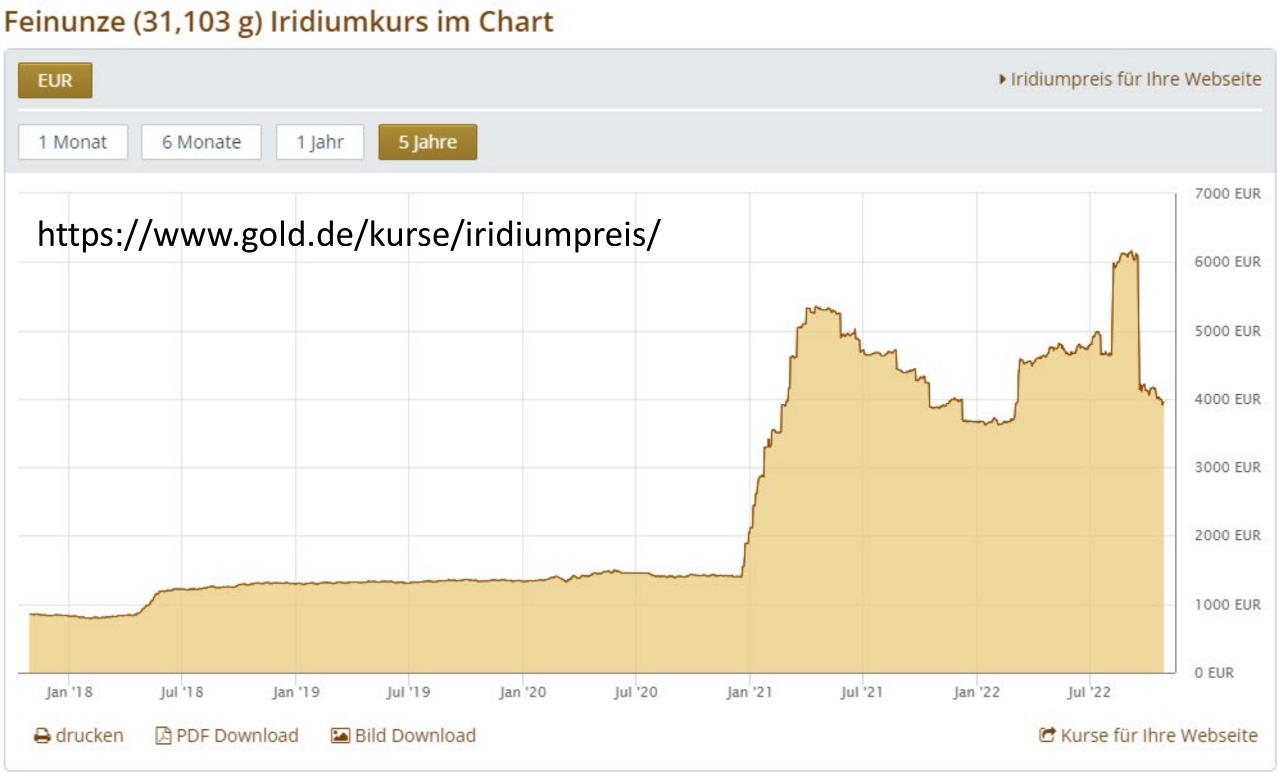


Ru unstable!
RuO_2 unstable!

Ir unstable!
IrO_2 stable!

Iridium is big problem!

Iridium is incredibly expensive!



https://www.gold.de/kurse/platinpreis/

Iridium is big problem!

Iridium is very scarce!

- **Required catalyst amount for PEM electrolysis: 1-2.5 g_{Ir}/kW**
- **Global iridium production 7.5 t/year**
- **How much electrolyzer capacity could be max. installed in the next year/decade?**
  - Max. 7.5 GW/year

Iridium is big problem!

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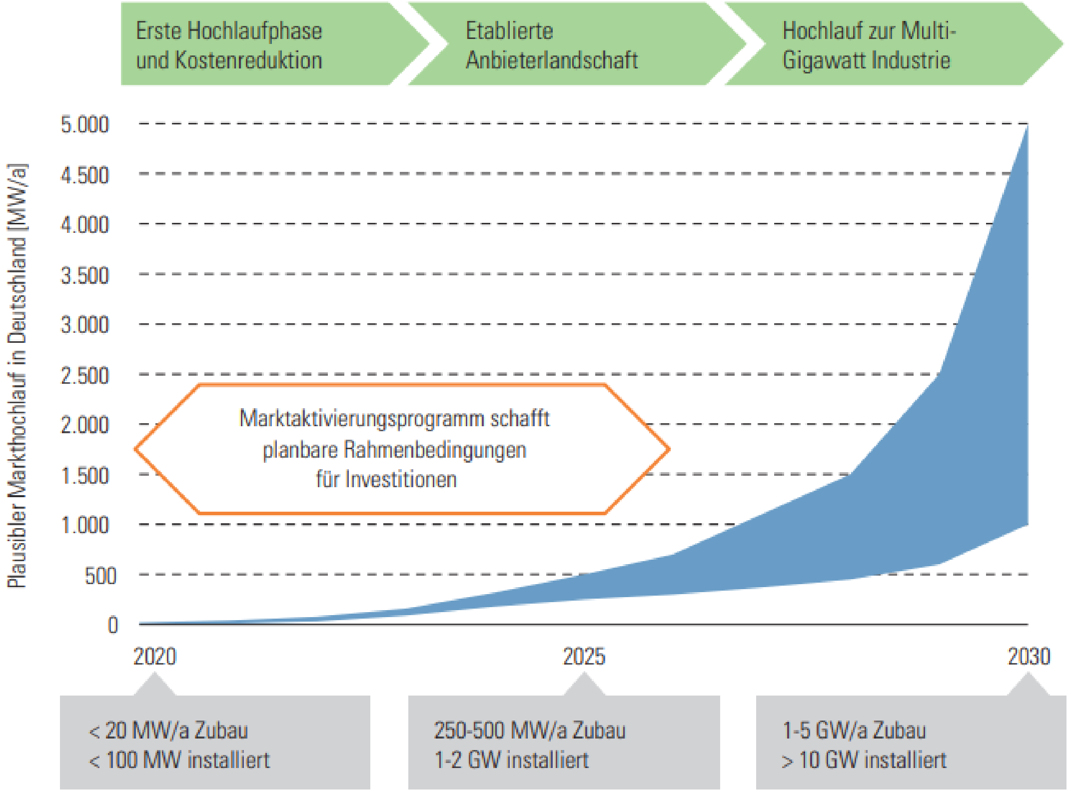
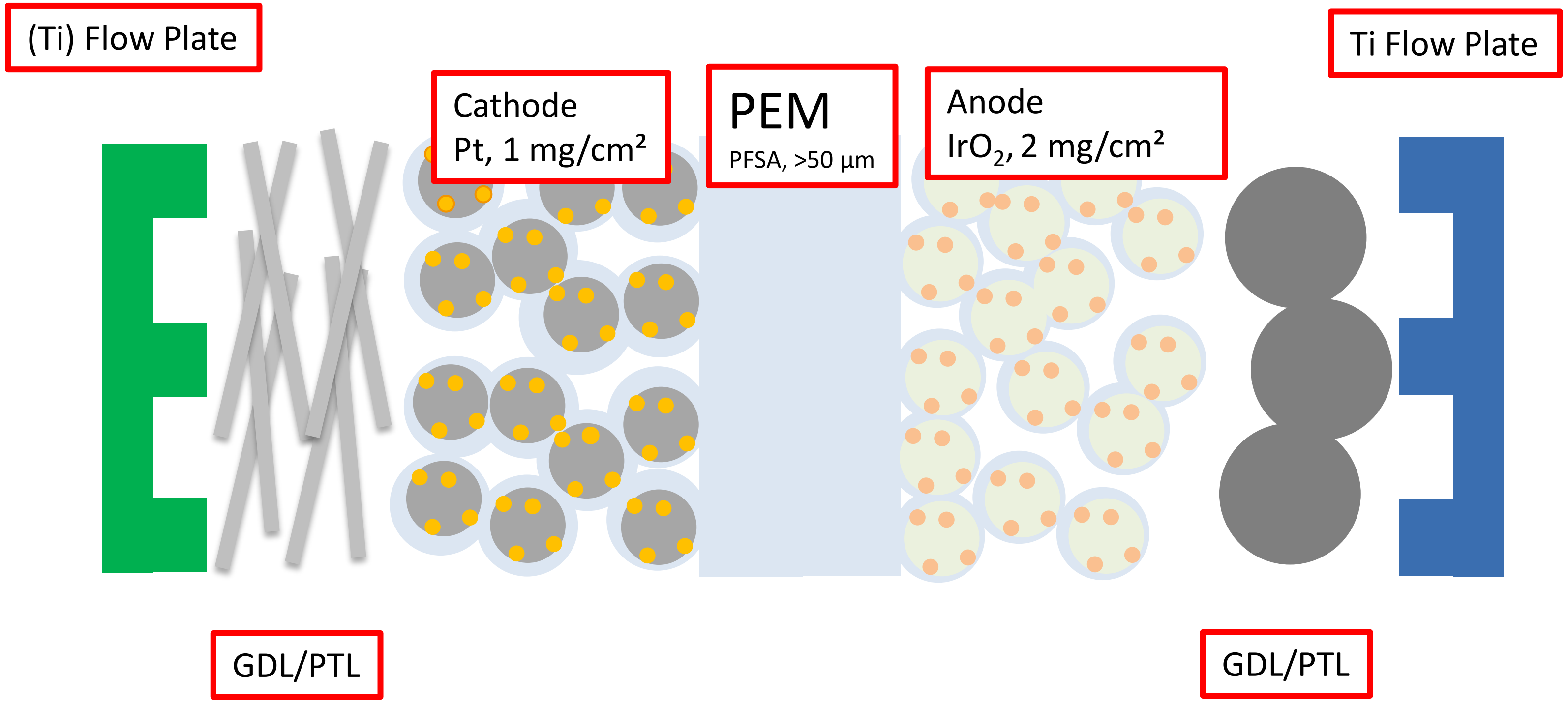
- **Required catalyst amount for PEM electrolysis: 1-2.5 g_{Ir}/kW**
- **Global iridium production 7.5 t/year**
- **How much electrolyzer capacity could be max. installed in the next year/decade?**
  - Max. 7.5 GW/year
  - German-Demand: ~ 1-5 GW/year

Research necessary!



https://www.now-gmbh.de/wp-content/uploads/2020/09/181127_bro_a4_indwede-studie_kurzfassung_de_v03.pdf

Gas diffusion media and porous transport layers



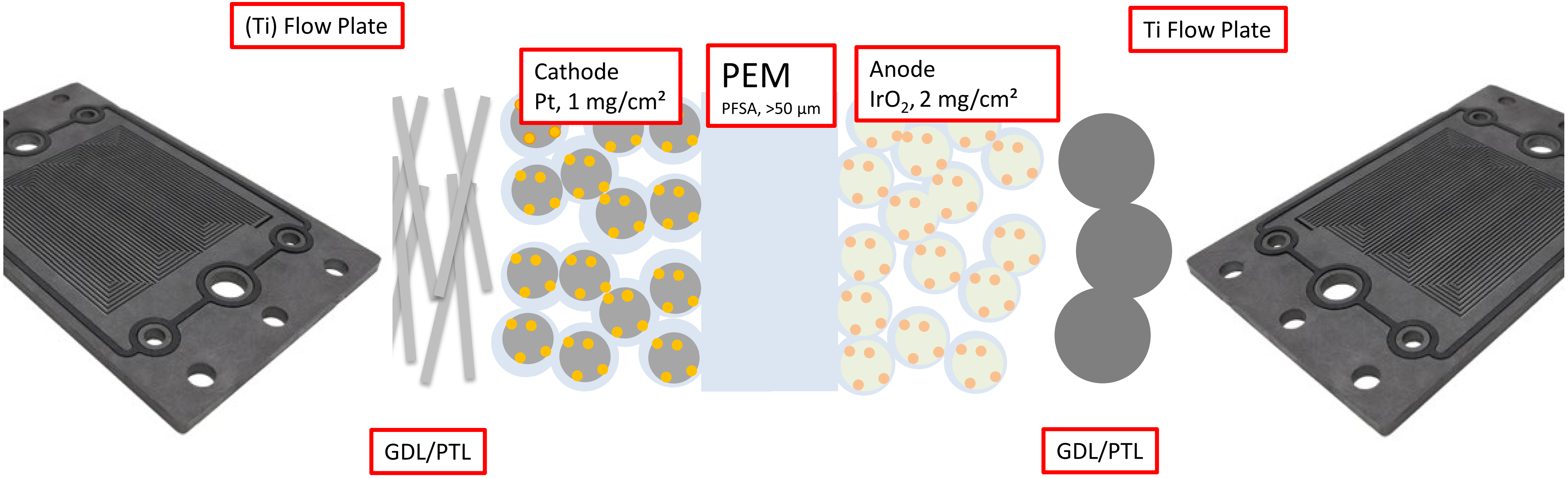
Gas Diffusion Layer
Porous Transport Layer

Gas Diffusion Layer
Porous Transport Layer

Gas diffusion media and porous transport layers

Hochschule Kempten
University of Applied Sciences

Fakultät
Maschinenbau

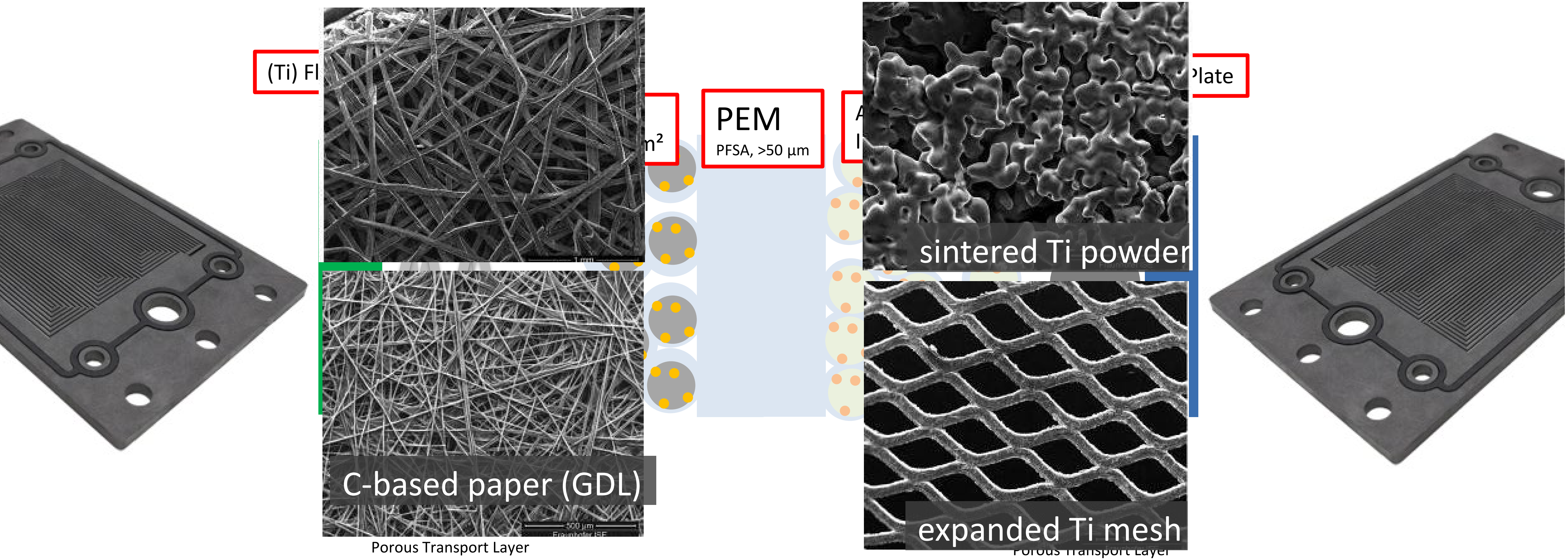


Gas Diffusion Layer
Porous Transport Layer

Gas Diffusion Layer
Porous Transport Layer

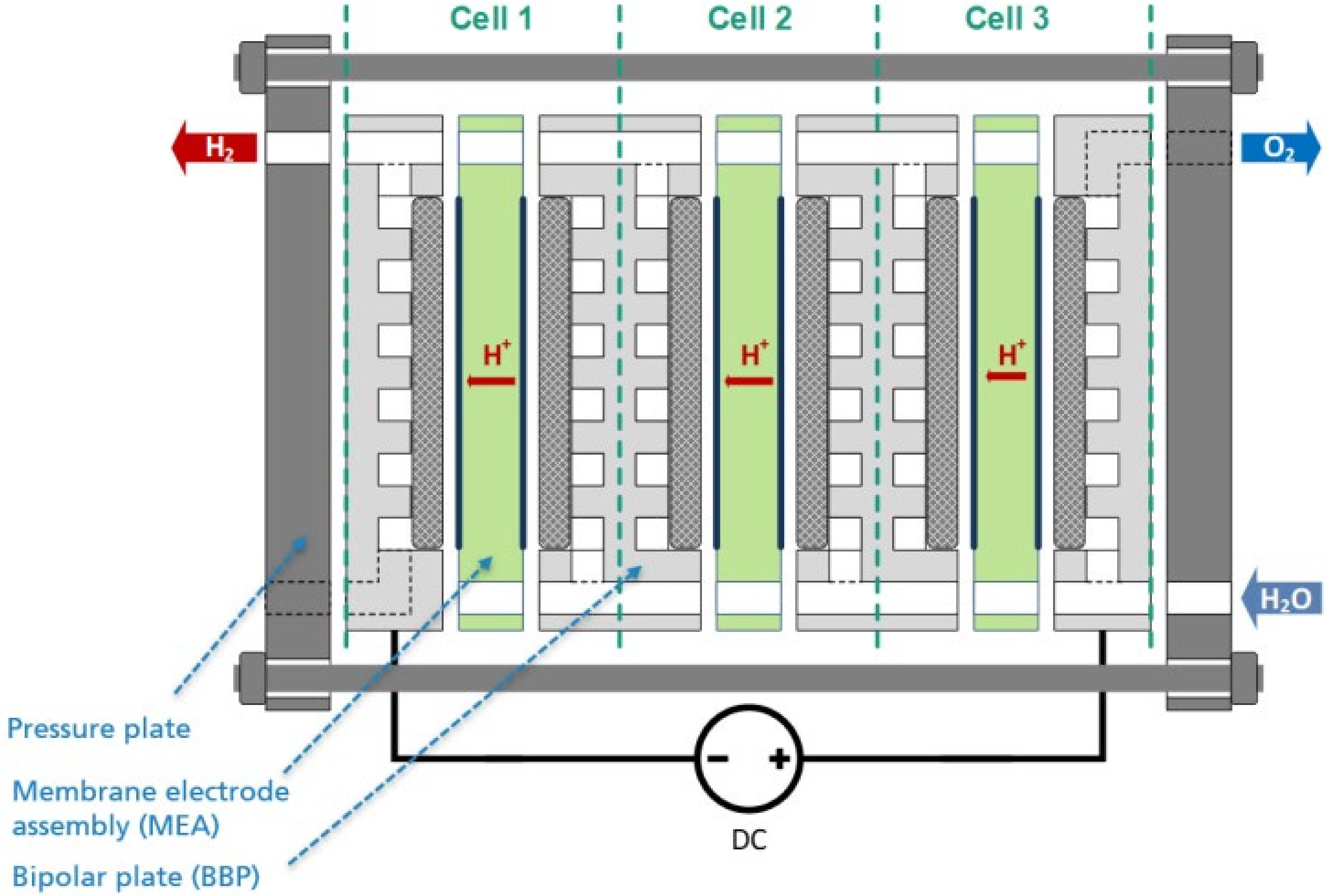
https://www.fuelcellstore.com/blog-section/pressure-distribution-in-bipolar-plate-flow-channels

Gas diffusion media and porous transport layers



PEMWE Stack Design

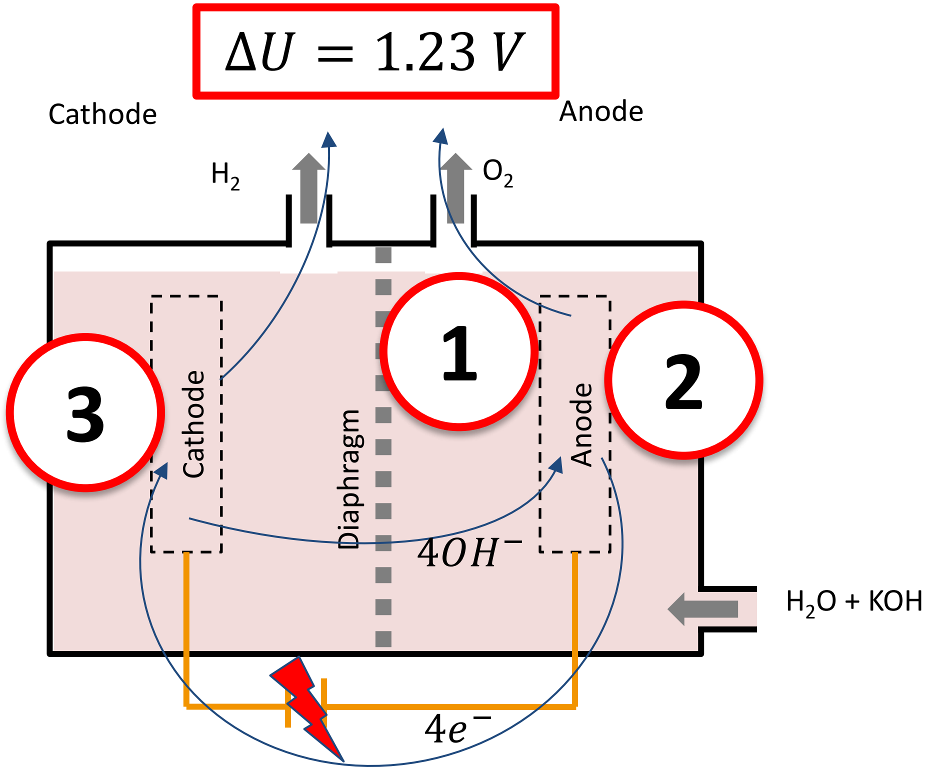
Hochschule Kempten University of Applied Sciences
Fakultät Maschinenbau



Bilder: Siemens „Sylizer 300“

Materials for AWE

- 1) Liquid Electrolyte
- 2) Anode Electrode
- 3) Cathode Electrode



$$2H_2O \leftrightarrow O_2 + 2H_2$$

Alkaline Electrolyte

- Autoprotolysis of water

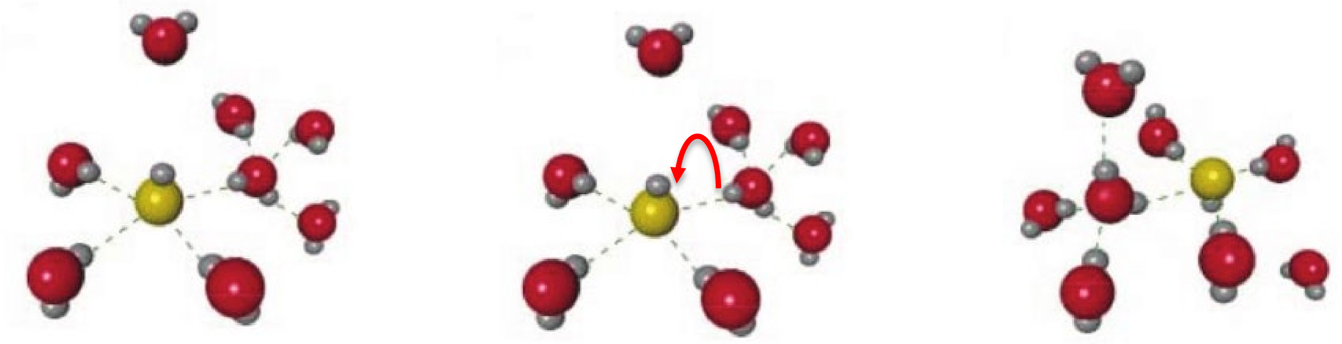
$$2\,H_2O \rightleftharpoons H_3O^+ + OH^-$$

- In alkaline water electrolyis, we need a surplus of OH^-

$$KOH + H_2O \rightarrow K^+ + OH^-$$

- Conduction of OH^- via Grotthus mechanism

- Typically 20 – 30 wt% KOH in H_2O



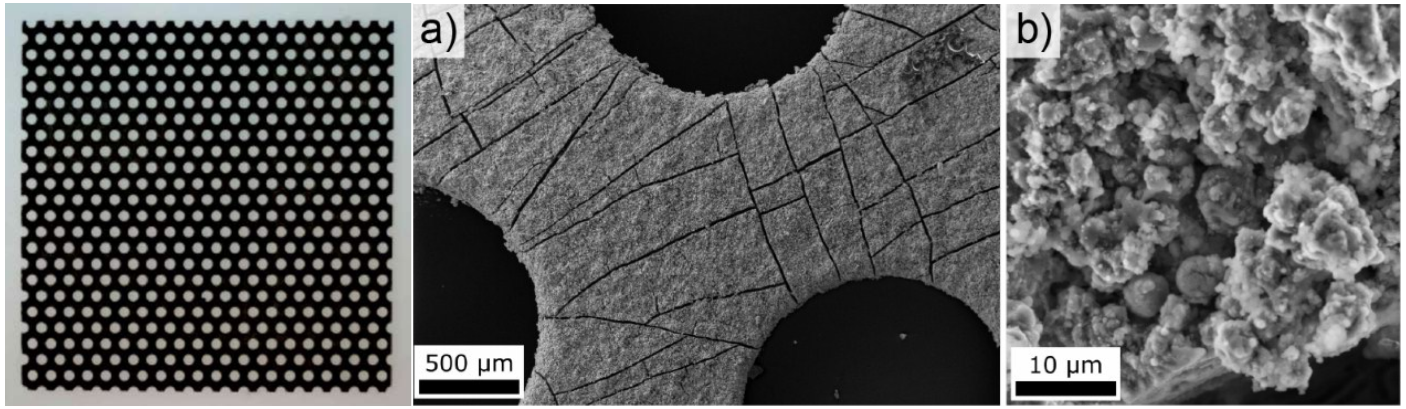
DOI:10.5772/intechopen.77148

AWE Anode Electrode

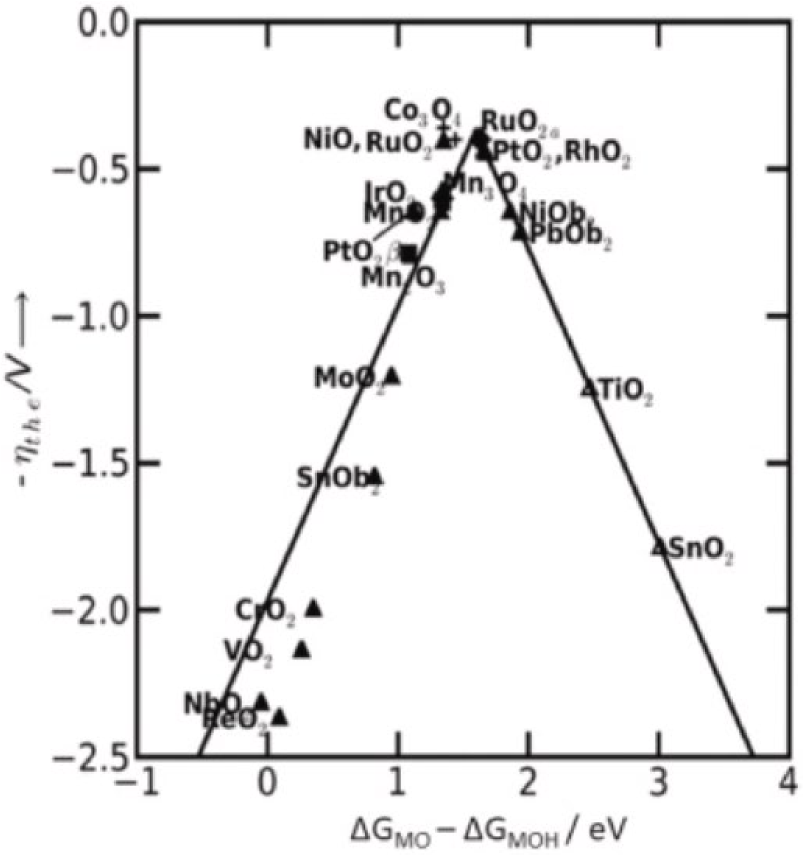
- **OH-bonds are critical on the anode!**

$$4OH^{-} \rightarrow O_2 + 2H_2O + 4e^{-}$$

- **Raney-Nickel coated steel plates**



Kraglund, M. R., Carmo, M., Schiller, G., Ansar, S. A., Aili, D., Christensen, E., & Jensen, J. O. (2019). Ion-solvating membranes as a new approach towards high rate alkaline electrolyzers. *Energy & Environmental Science*, *12*(11), 3313-3318.

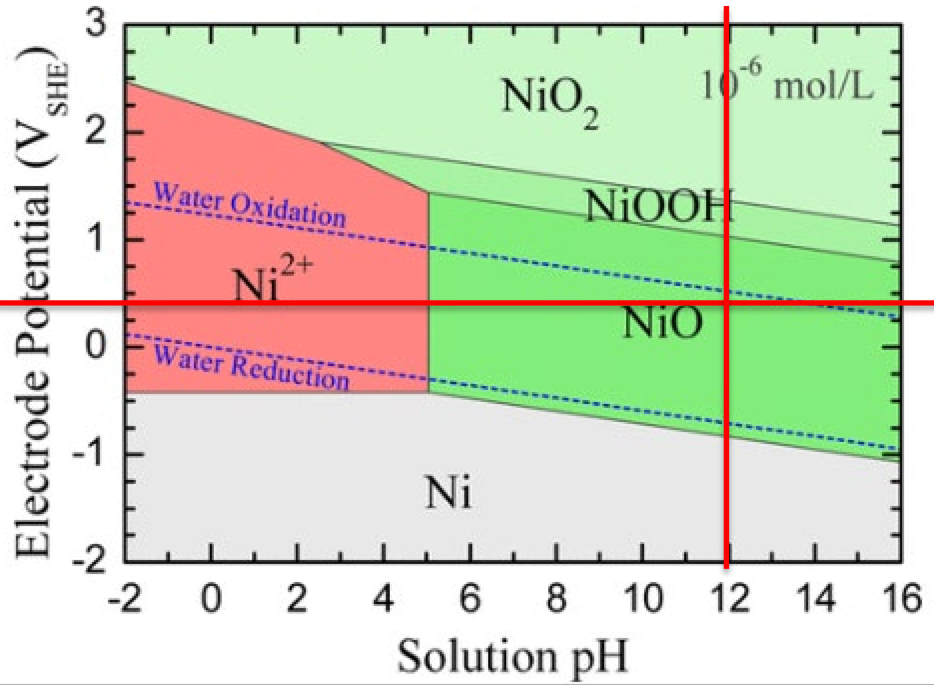


https://www.sciencedirect.com/science/article/pii/S0378775321005966

AWE Anode Electrode

- Nickel is stable at high pH

$$U_{RHE,A} = 0.4\,V$$



https://pubs.acs.org/doi/abs/10.1021/acs.jpcc.7b02771

AWE Cathode Electrode

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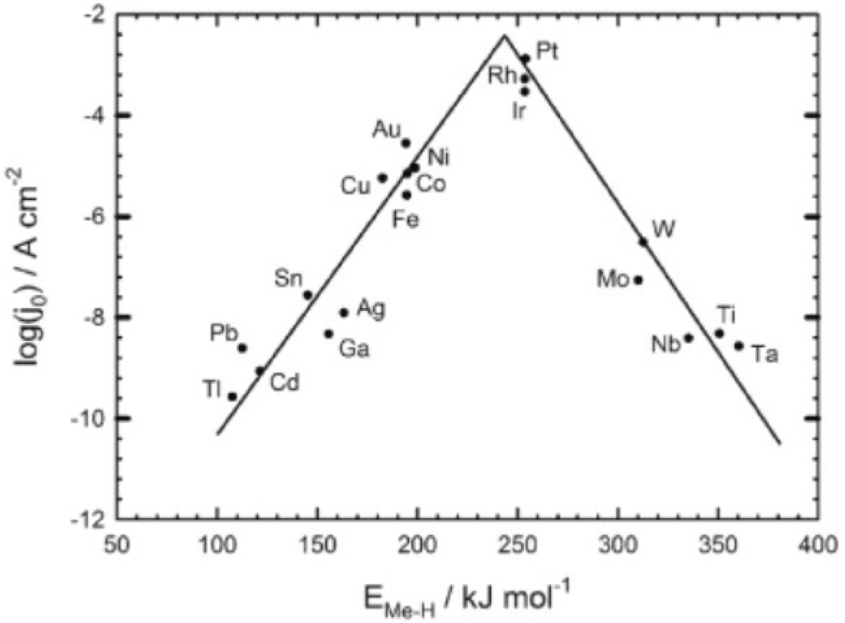
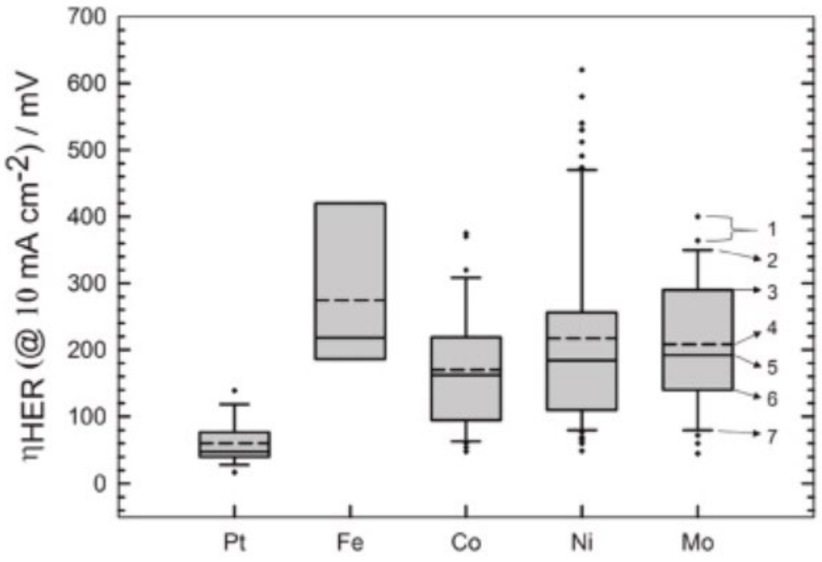
- **H-bonds are critical on the cathode!**

$$4H_2O + 4e^- \rightarrow 2H_2 + 4OH^-$$

https://www.sciencedirect.com/science/article/pii/S0378775321002494



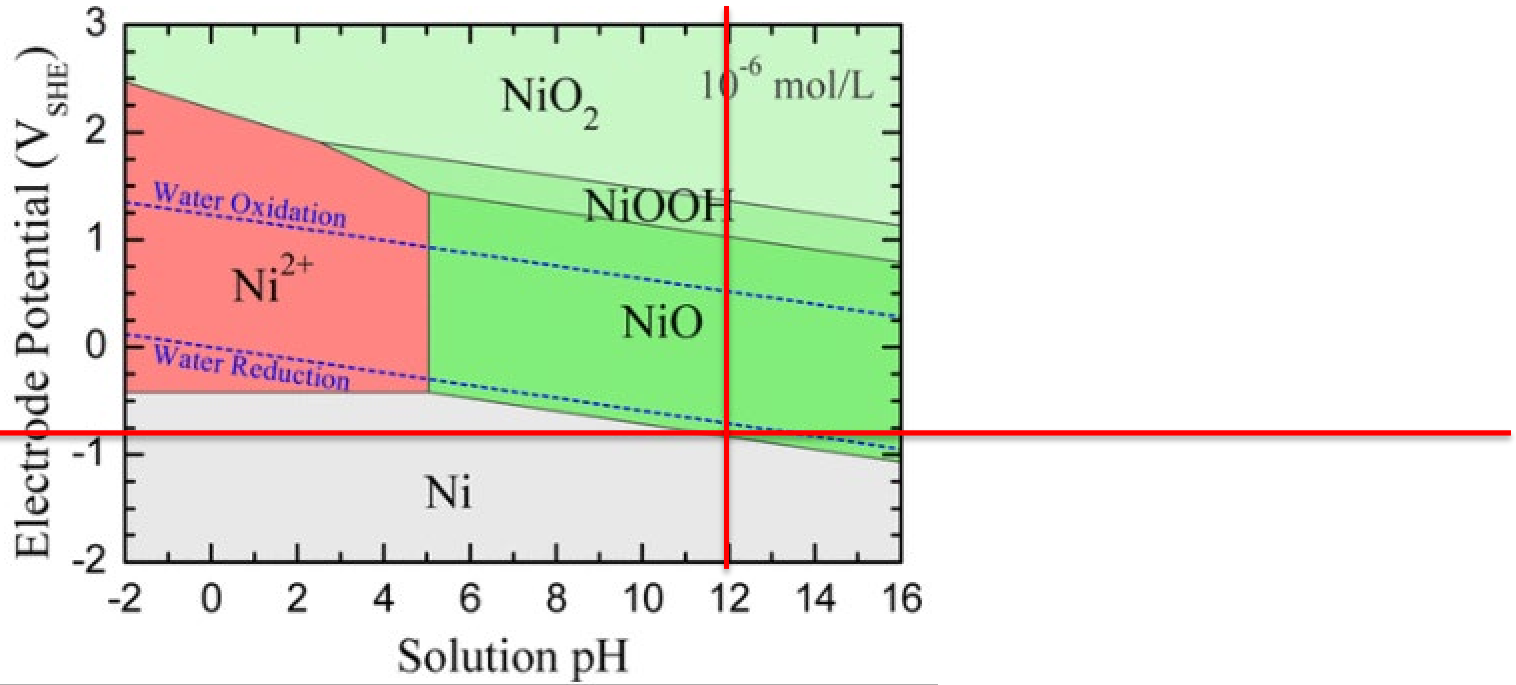


- **Raney-Nickel coated steel plates**

AWE Cathode Electrode

- Nickel is stable at high pH

$$U_{RHE,C} = -0.83\ V$$



https://pubs.acs.org/doi/abs/10.1021/acs.jpcc.7b02771

AWE Cathode Electrode

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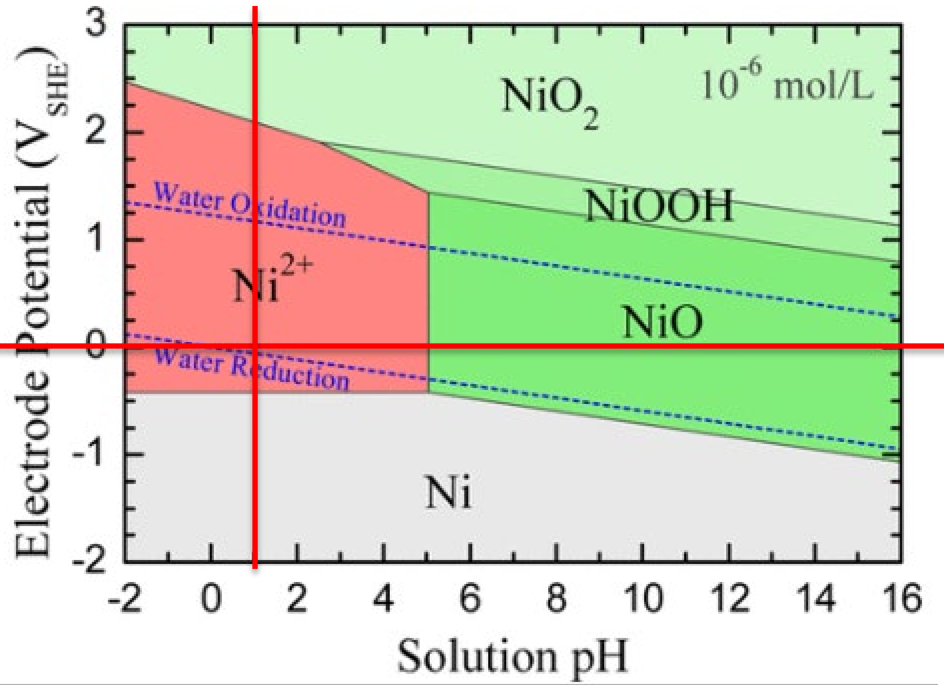
- **Reminder: Nickel would not be stable in PEM electrolysis**

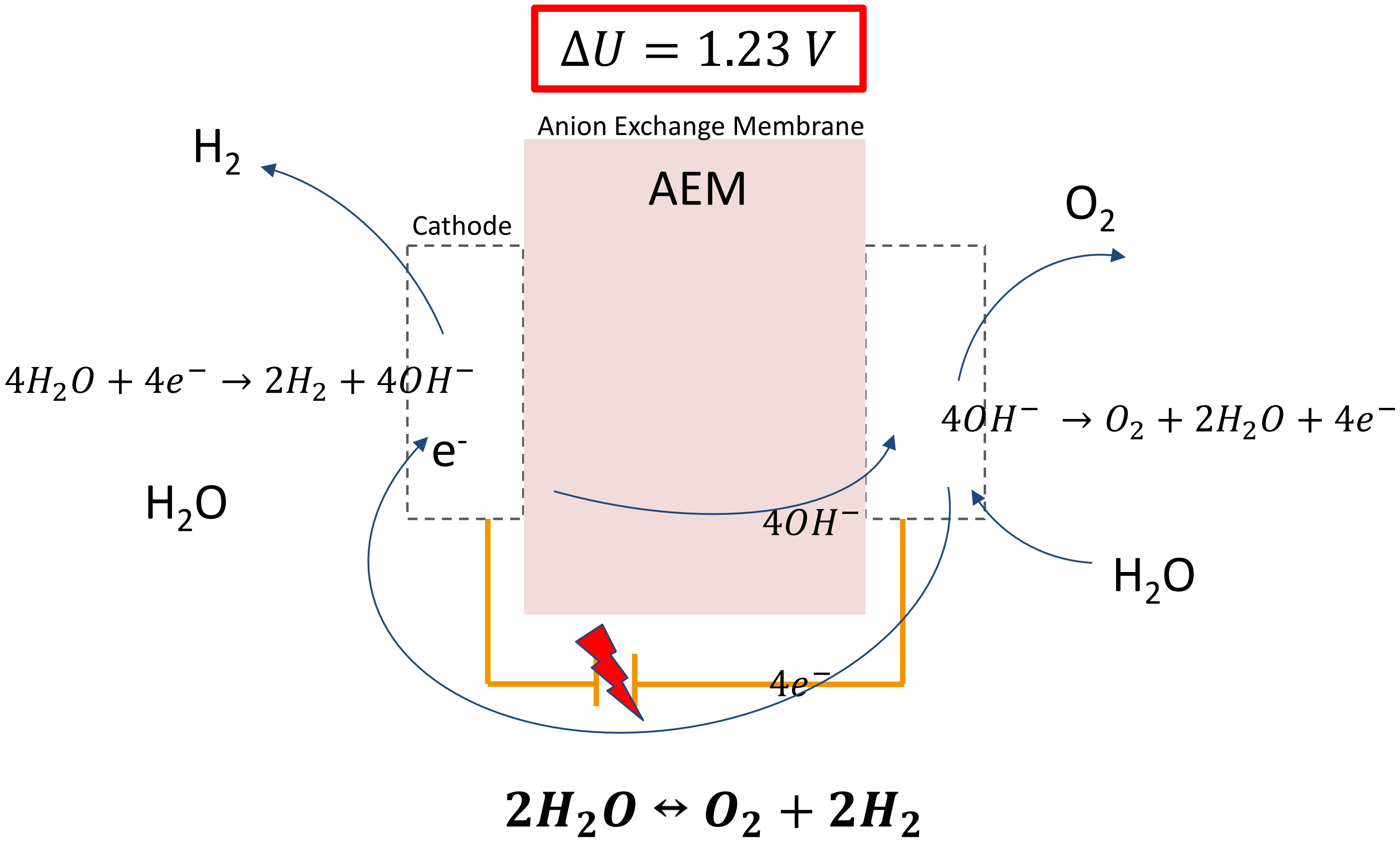
$$U_{RHE,C} = 0\ V$$



https://pubs.acs.org/doi/abs/10.1021/acs.jpcc.7b02771

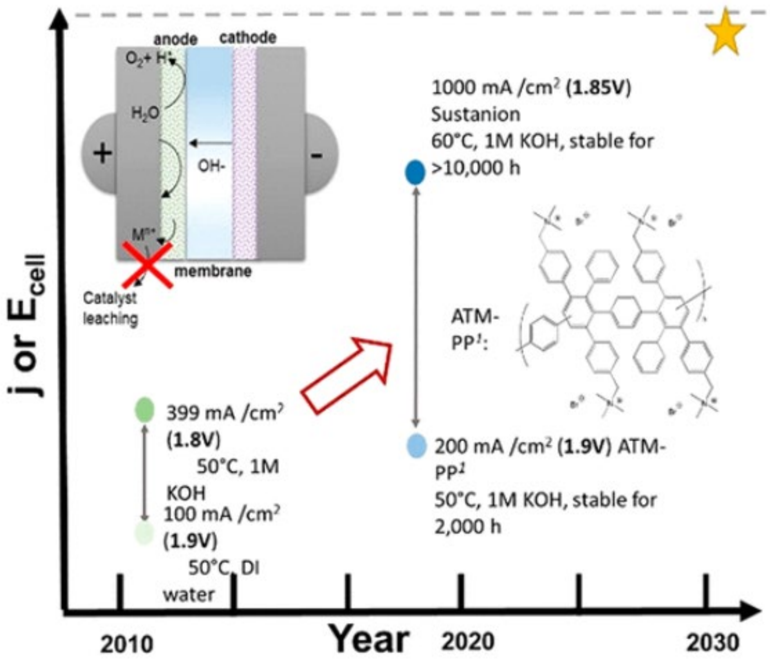
Materials for AEMWE

- 1) Anion Exchange Membrane
- 2) Anode Electrode
- 3) Cathode Electrode

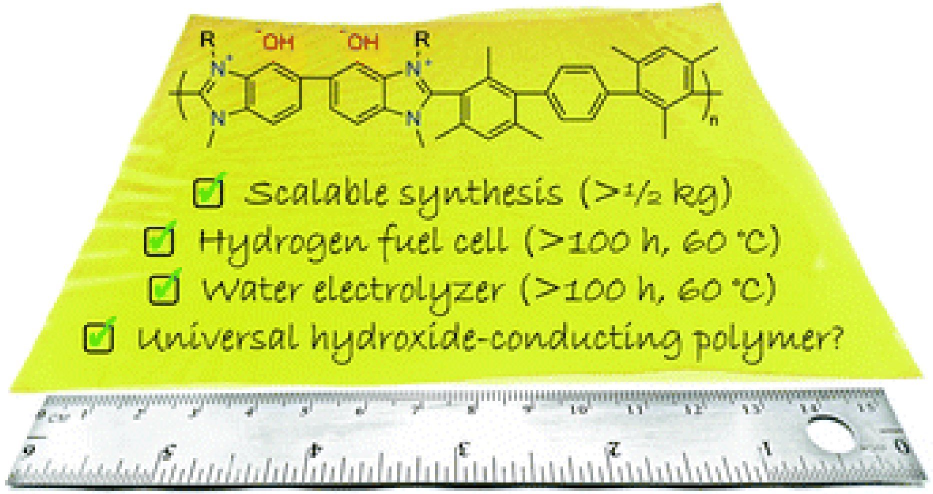


Anion Exchange Membrane

- First stable commercially available membrane material for OH^- conduction presented in 2017
- Often based on polyaromates with quarternary ammonium groups



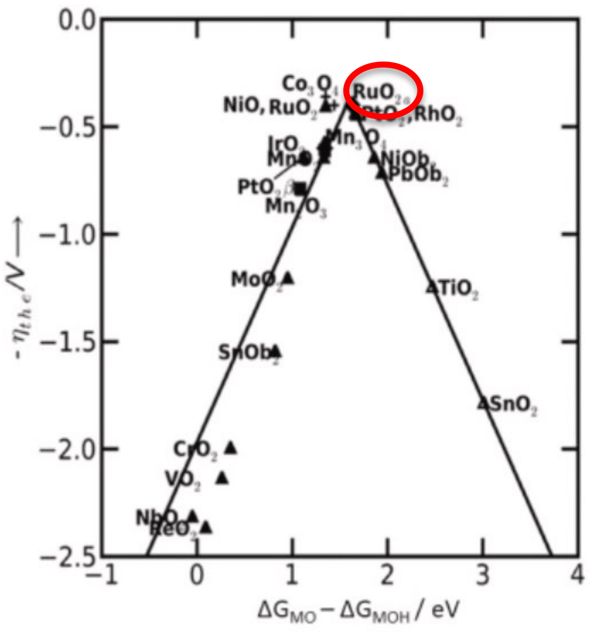
https://pubs.acs.org/doi/full/10.1021/acs.chemrev.1c00854

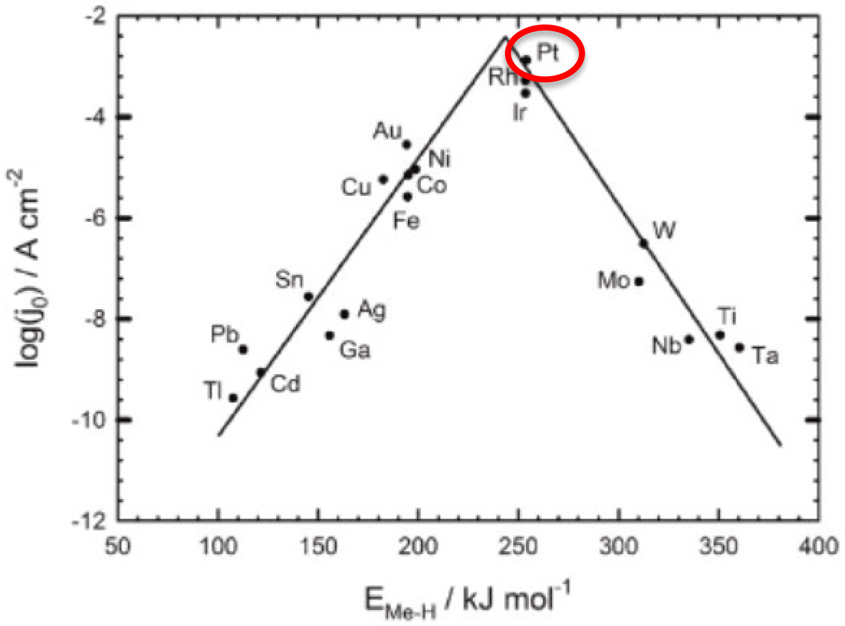


Wright, Andrew G., et al. "Hexamethyl-p-terphenyl poly (benzimidazolium): a universal hydroxide-conducting polymer for energy conversion devices." *Energy & Environmental Science* 9.6 (2016): 2130-2142.

AEMWE Anode and Cathode Electrodes

- **Catyltic requirements similar to AWE, but highly dispersed materials needed!**
  - No highly dispersed Ni available!
  - Therefore: Ruthenium (Anode) and Platinum (Cathode). Both is available in highly dispersed state.





PEMWE vs. AWE

	PEMWE	AWE
H_2 Crossover	Low	high
Max. Current Density	High	Low
Dynamic	Yes	No
Investment Costs	710 €/kW	670 €/kW
Volumetric Power Density	high	medium

Dynamic vs. Cheap

AEMWE!!!

Summary

- **Electrodes in electrolyzers provide very high specific surface area by beeing nano-particles!**

- **Electrode materials need to show good catalytic activity!**
  - Binding-characteristics of reactant to surface is crucial.

- **Electrode materials need to be stable under respective potentials ans pH-values.**

- **PEMWE:**
  - Anode: IrO_2 nanoparticles
  - Cathode: Pt nanoparticles

- **AWE:**
  - Anode: Nickel
  - Cathode: Nickel

