Hochschule Kempten
University of Applied Sciences

Fakultät Maschinenbau

Hydrogen Technologies

Lecture 4: Water Electrolysis II

Prof. Matthias Klingele

Last lecture…

- **Electrolyzer is an electrochemical energy converter**
  - Converts electrical energy (electrical work) into chemical energy
  - Uses voltage to drive an endothermic reaction

- **Water splitting reaction is in equilibrium at 1.23 V (standard conditions)**

U=1.23 V

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

U>1.23 V

$$2H_2O \rightarrow 2H_2 + O_2$$

Goal of this lecture

- How much Hydrogen is produced if we increase from 1.23 V to e.g. 2.0 V?

U=2 V

$$2H_2O \rightarrow 2H_2 + O_2$$

???

- Important, because it yields the efficiency of an electrolyzer

Lecture Outline

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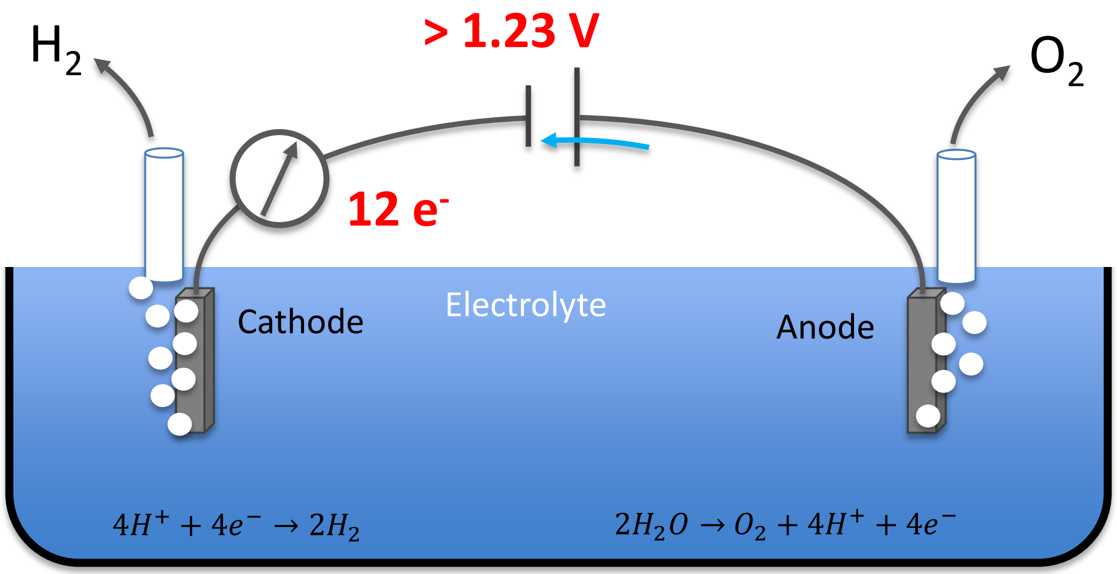
	Date	Place	Name	Content
1	07.10.2025	S0.13b	HYTECH 1	Hydrogen and Energy transition
1	07.10.2025	S0.13b	HYTECH 2	Hydrogen Production Overview
2	14.10.2025	S0.13b		
2	14.10.2025	S0.13b		
3	21.10.2025	S0.13b	HYTECH 3	Electrolysis - Electrochemistry and Thermodynamics
3	21.10.2025	S0.13b	HYTECH 4	Electrolysis - 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

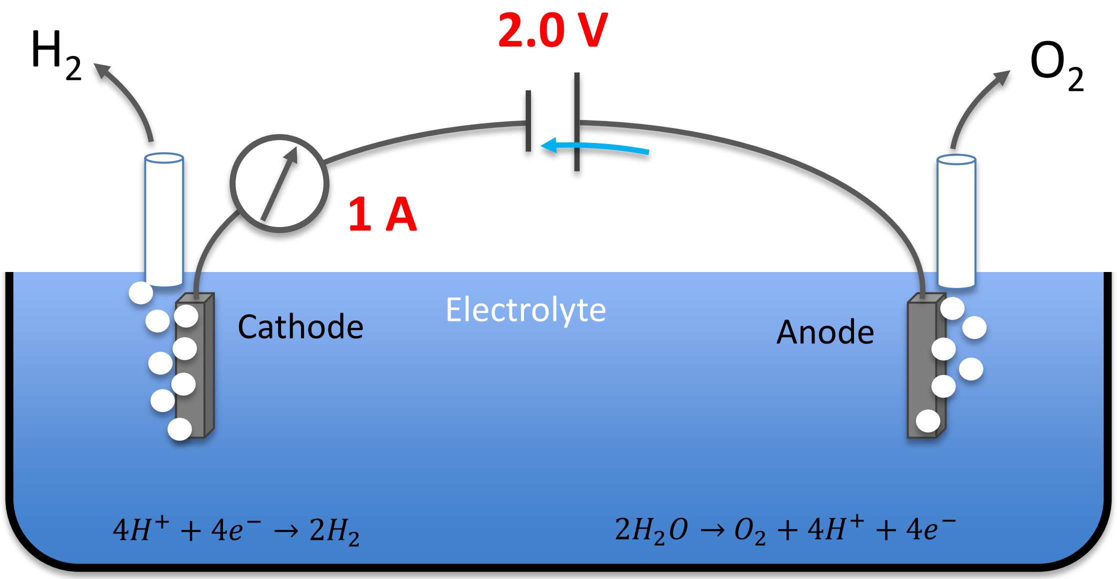
Hydrogen Production correlates directly to Electron Transfer

- How many H_2 molecules per second are produced if we meaure 12 electrons per second?



Hydrogen Production correlates directly to Electron Transfer

- How many H_2 molecules per second are produced if we measure a current of 1 A?



1 Coulomb is the charge of ~ $6.24 \cdot 10^{18}$ electrons

Hydrogen Production correlates directly to Electron Transfer

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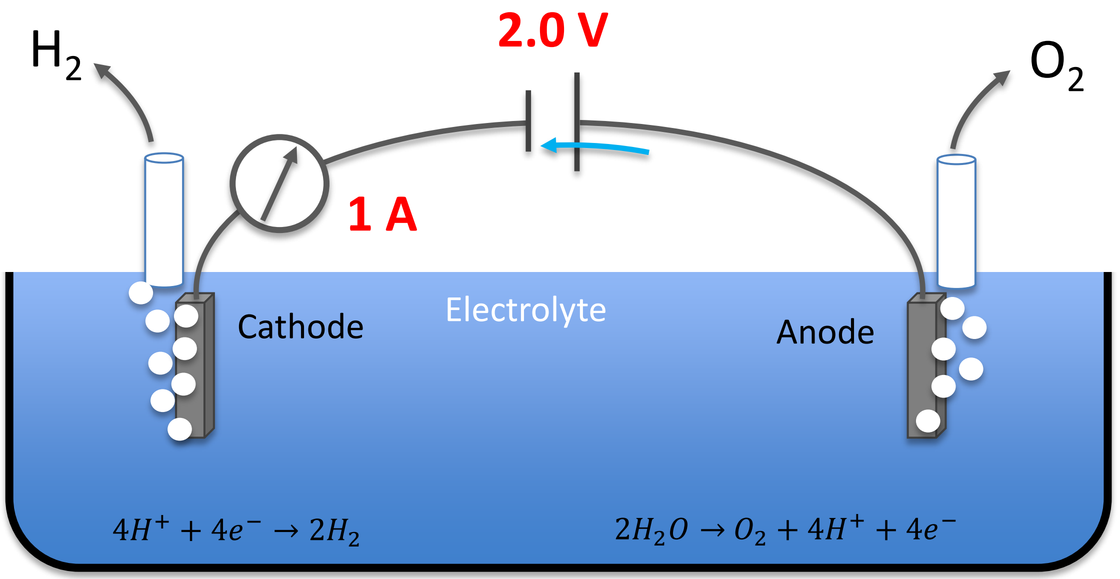
- How many H_2 molecules per second are produced if we measure a current of 1 A?

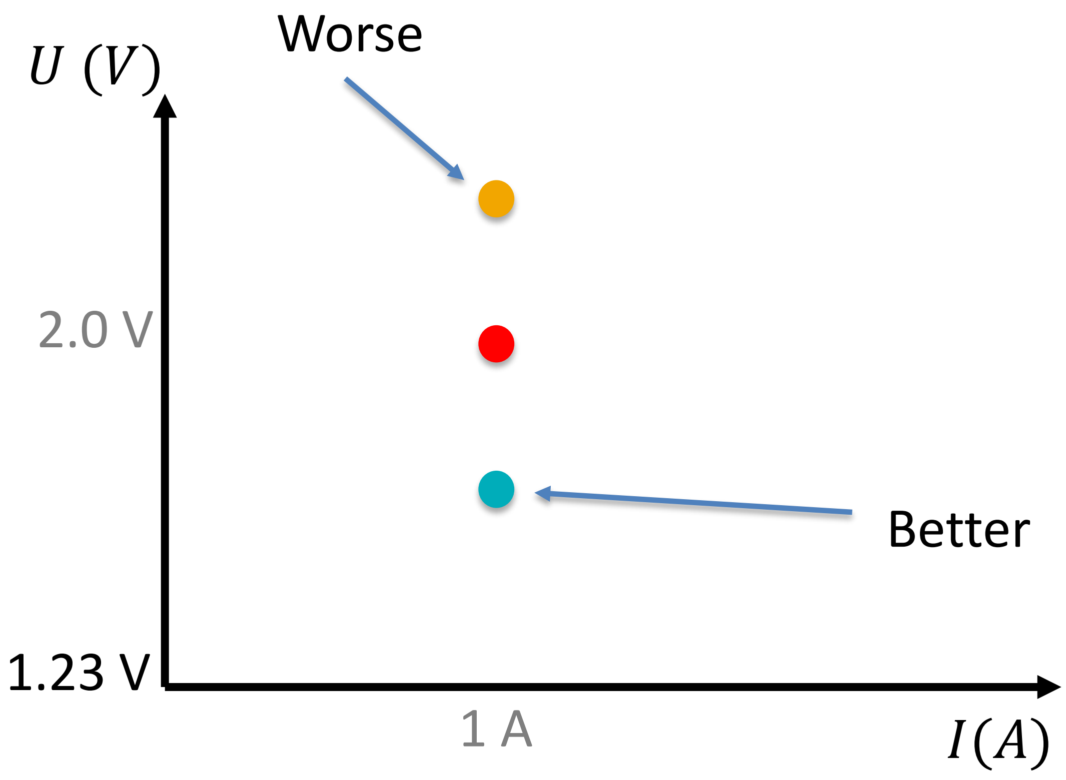


1 Coulomb is the charge of ~ $6.24*10^{18}$ electrons

Ratio of U and I define efficiency!

Hydrogen Production correlates directly to Electron Transfer

- **Correlation of input electrical energy and output Hydrogen is characterized by „Polarization Curve"**
  - Plot voltage over current density



Electrolyzers are Planar Structures

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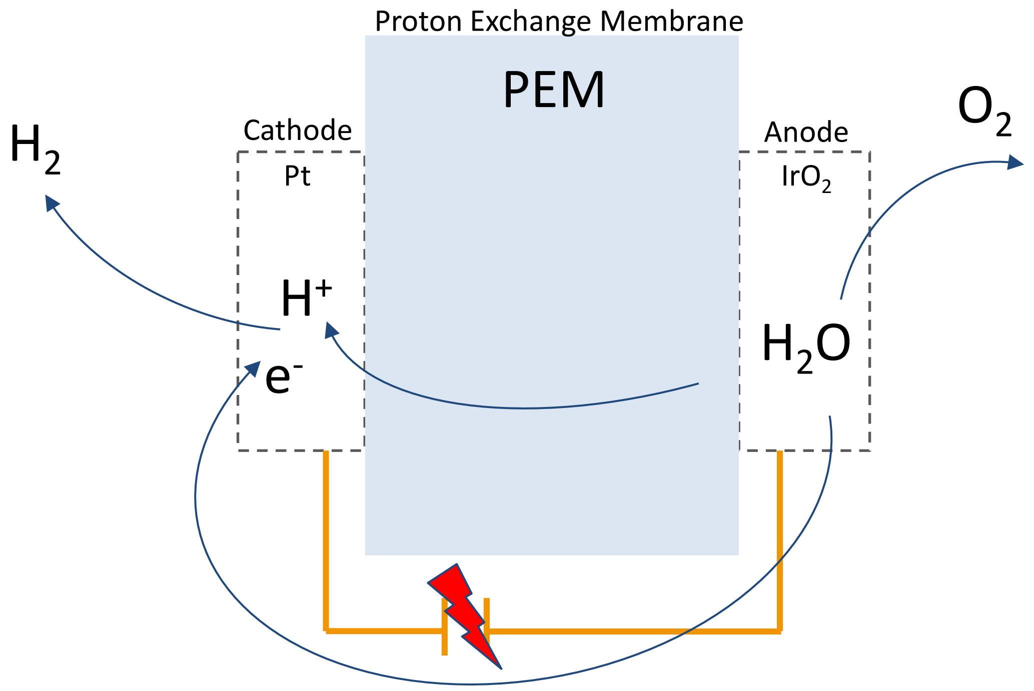
- **Example PEM („Proton Exchange Membrane“) Electrolyzer**

$$4H^+ + 4e^- \rightarrow 2H_2$$



$$2H_2O \rightarrow O_2 + 4H^+ + 4e^-$$

$$2H_2O \rightarrow O_2 + 2H_2$$

Hydrogen Production correlates directly to Electron Transfer

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- **Correlation of input electrical energy and output Hydrogen is characterized by „Polarization Curve“**
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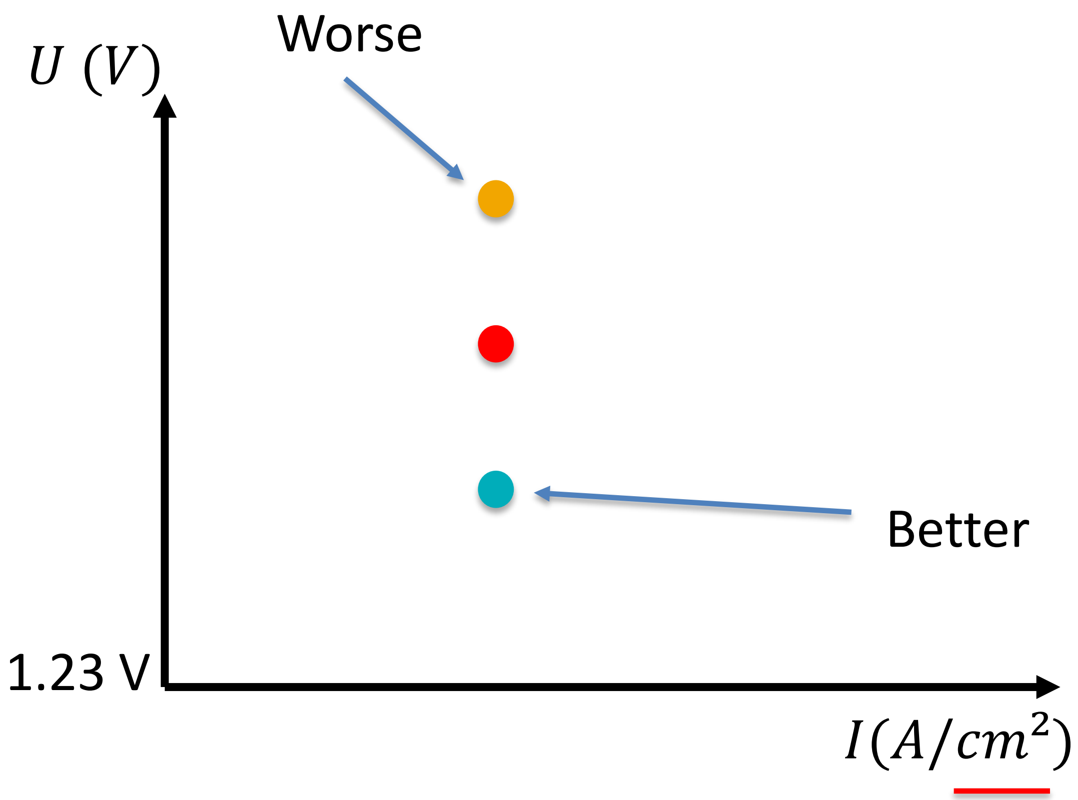

Hydrogen Production correlates directly to Electron Transfer

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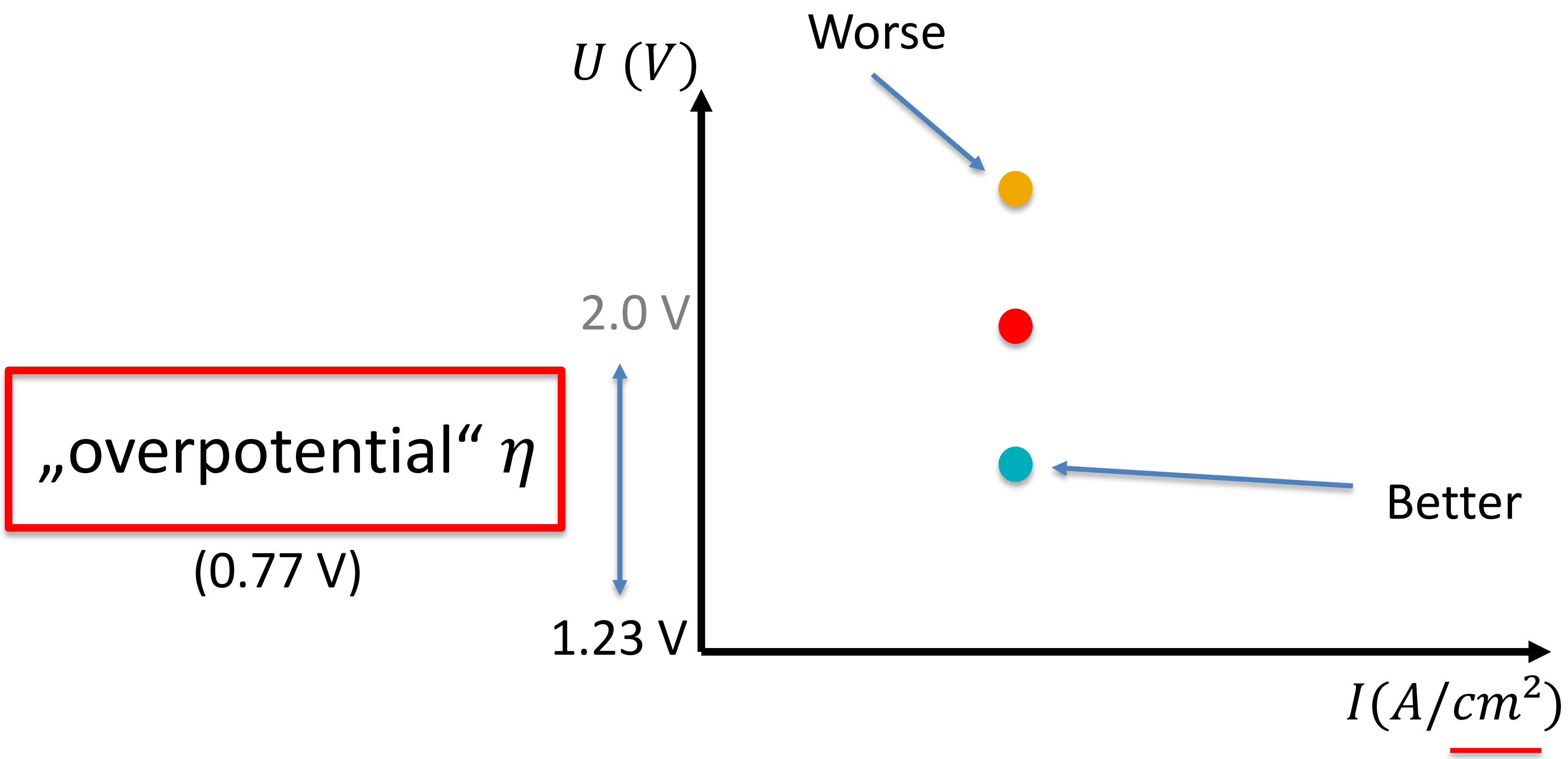

Hydrogen Production correlates directly to Electron Transfer

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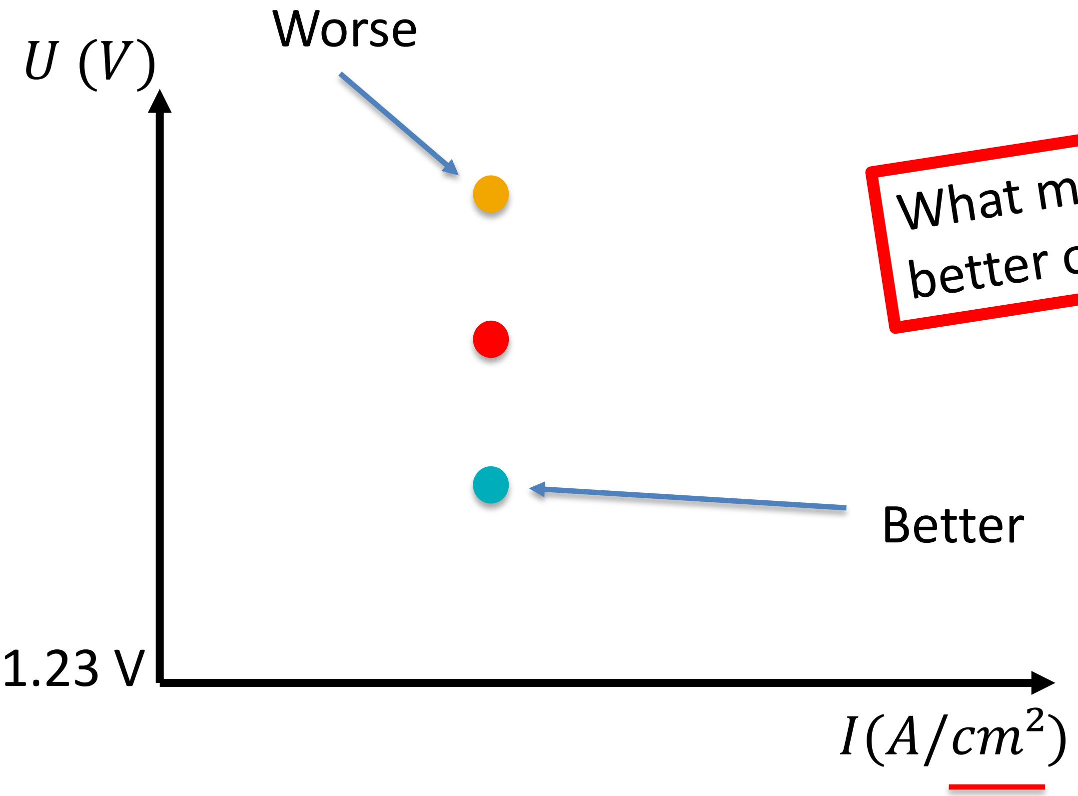

What makes an Electrolyzer better or worse?

Loss Mechanisms of Electrolyzers: Kinetics

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- Chemical reactions happen with a finite reaction rate (reaction rate is aka „kinetics“)

Happens with reaction **finite** reaction rate k $[\frac{1}{s}]$

$$2H_2O \rightarrow 2H_2 + O_2$$

- Overall reaction only as fast as the slower half-cell reaction

slow

$$2H_2O \rightarrow O_2 + 4H^+ + 4e^-$$

Limiting!

fast

$$4H^+ + 4e^- \rightarrow 2H_2$$

- If no other losses: Measured current is proportional to reaction rate!

Why is the Reaction Rate of Chemicals Finite?

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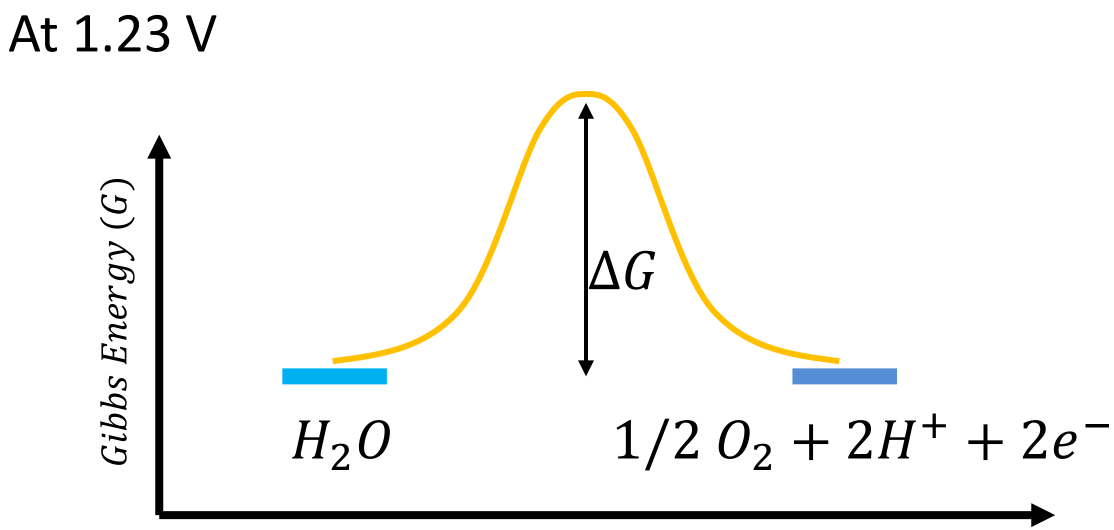
- Chemical reactions need to overcome a reaction barrier (Arrhenius)
- Example water oxidation in Electrolysis:



Svante Arrhenius

(also first to predict climate change in 1896!)

Why is the Reaction Rate of Chemicals Finite?

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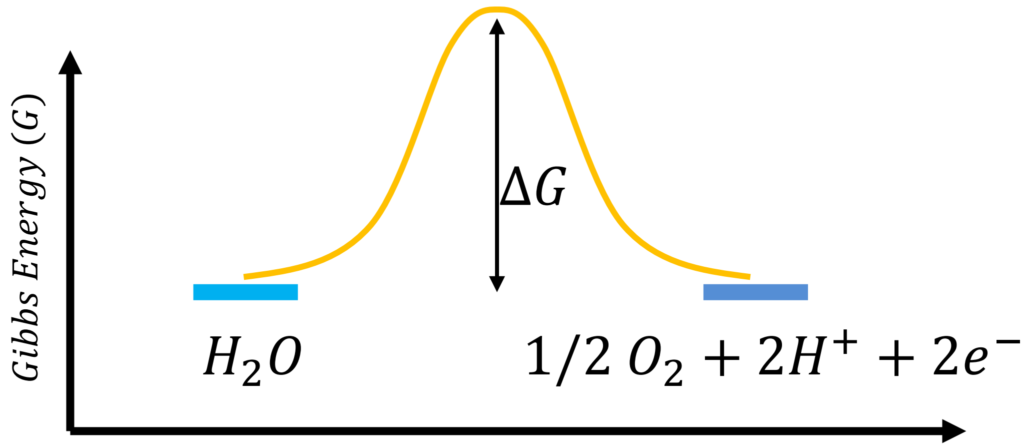
- Chemical reactions need to overcome a reaction barrier
- Example water oxidation in Electrolysis:

At 1.23 V



Reaction rate forward: $\vec{k} \sim e^{\frac{-\Delta G}{RT}}$

Reaction rate backward: $\overleftarrow{k} \sim e^{\frac{-\Delta G}{RT}}$

Current density: $\vec{j} = j_0 * e^{\frac{-\Delta G}{RT}} = \overleftarrow{j}$

Why is the Reaction Rate of Chemicals Finite?

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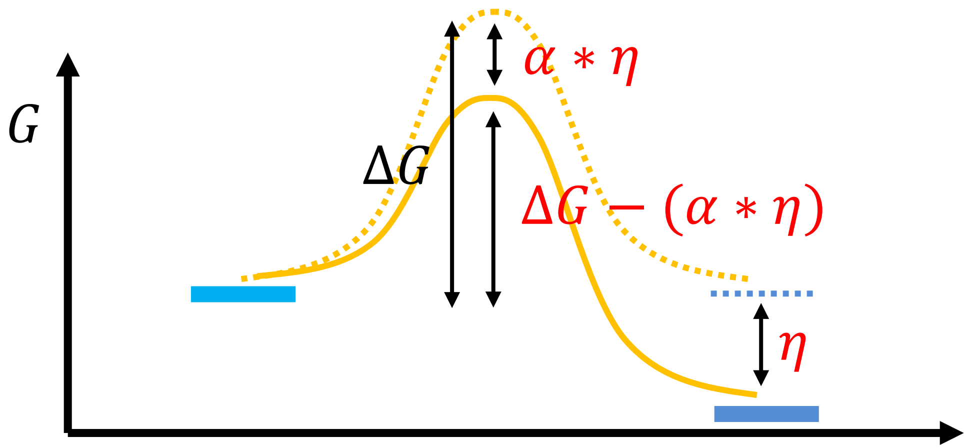
- Chemical reactions need to overcome a reaction barrier
- Example water oxidation in Electrolysis:

At $(1.23 + \eta)$ V



Symmetry coefficient: $0 < \alpha < 1$

(fraction of η which can be used for lowering ΔG)

Reaction rate forward: $\vec{j} = j_0 * e^{\frac{-(\Delta G - (\alpha * \eta))}{RT}}$

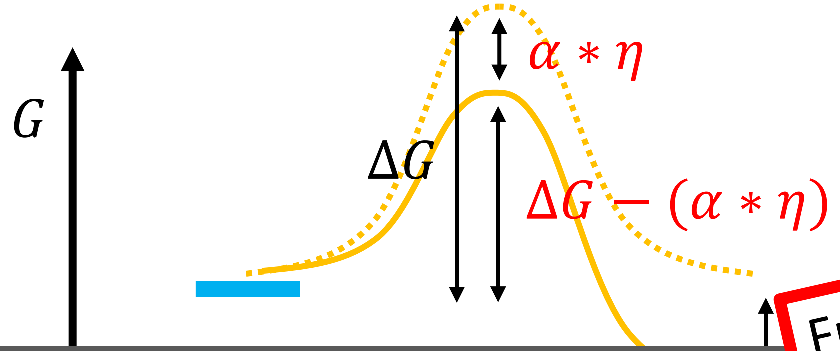
Reaction rate backward: $\overleftarrow{j} = j_0 * e^{\frac{-(\eta + \Delta G - (\alpha * \eta))}{RT}}$

Current density: $\vec{j} > \overleftarrow{j}$ $\quad j_{eff} = \vec{j} - \overleftarrow{j}$

Why is the Reaction Rate of Chemicals Finite?

- **Chemical reactions need to overcome a reaction barrier**
- **Example water oxidation in Electrolysis:**

At $(1.23 + \eta)$ V



Reaction rate forward: $\vec{j} = j_0 * e^{\frac{-(\Delta G - (\alpha * \eta))}{RT}}$

Reaction rate backward: $\overleftarrow{j} = j_0 * e^{\frac{-(\eta + \Delta G - (\alpha * \eta))}{RT}}$

From Wikipedia

Batteries and fuel cells [edit]

In operating batteries and fuel cells, charge transfer coefficient is the parameter that signifies the fraction of overpotential that affects the current density. This parameter has had a mysterious significance in electrochemical kinetics for over three quarters of the previous century[citation needed]. It can also be said that charge transfer coefficient is the heart of electrode kinetics.

Correlation of Kinetics with Overpotential: Butler-Volmer

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- **The Butler-Volmer Equation correlates reaction rate (kinetics) with overpotential in electrochemical cells**

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

Correlation of Kinetics with Overpotential: Butler-Volmer

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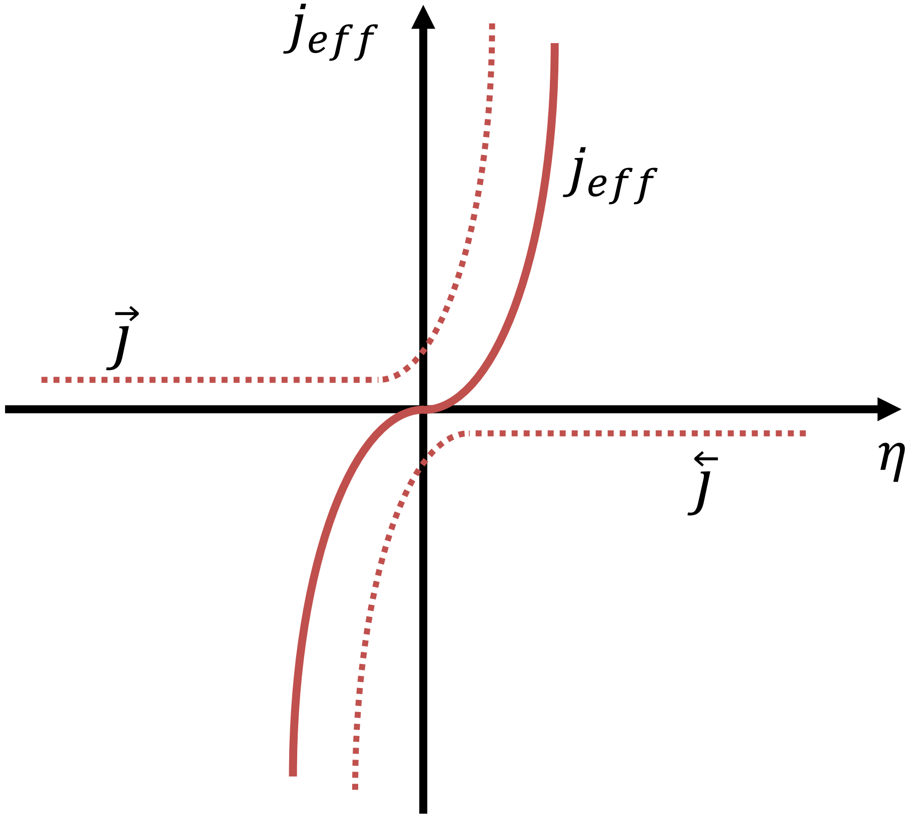


drawn for $\alpha = 0.5$

Correlation of Kinetics with Overpotential: Butler-Volmer

- **The Butler-Volmer Equation correlates reaction rate (kinetics) with overpotential in electrochemical cells**

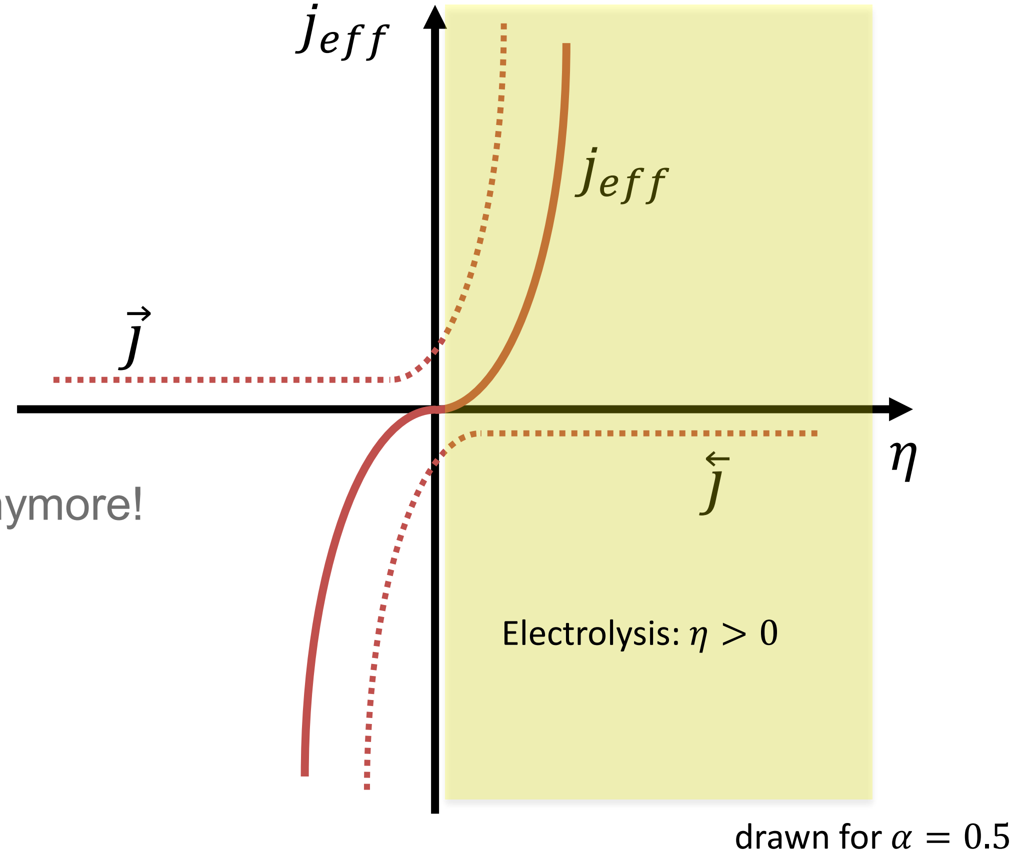
$$j_{eff}(\eta) = j_0 * e^{\frac{-\Delta G}{RT}} * \left(e^{\frac{\alpha\eta}{RT}} - e^{\frac{-(1-\alpha)\eta}{RT}}\right)$$

- **Meaning of Butler-Volmer:**
  - For low overpotentials, reaction rates are low!
  - For high overpotentials, reaction rates are not limiting anymore!

Slow for low η

$$2H_2O \rightarrow O_2 + 4H^+ + 4e^-$$

Fast for big η

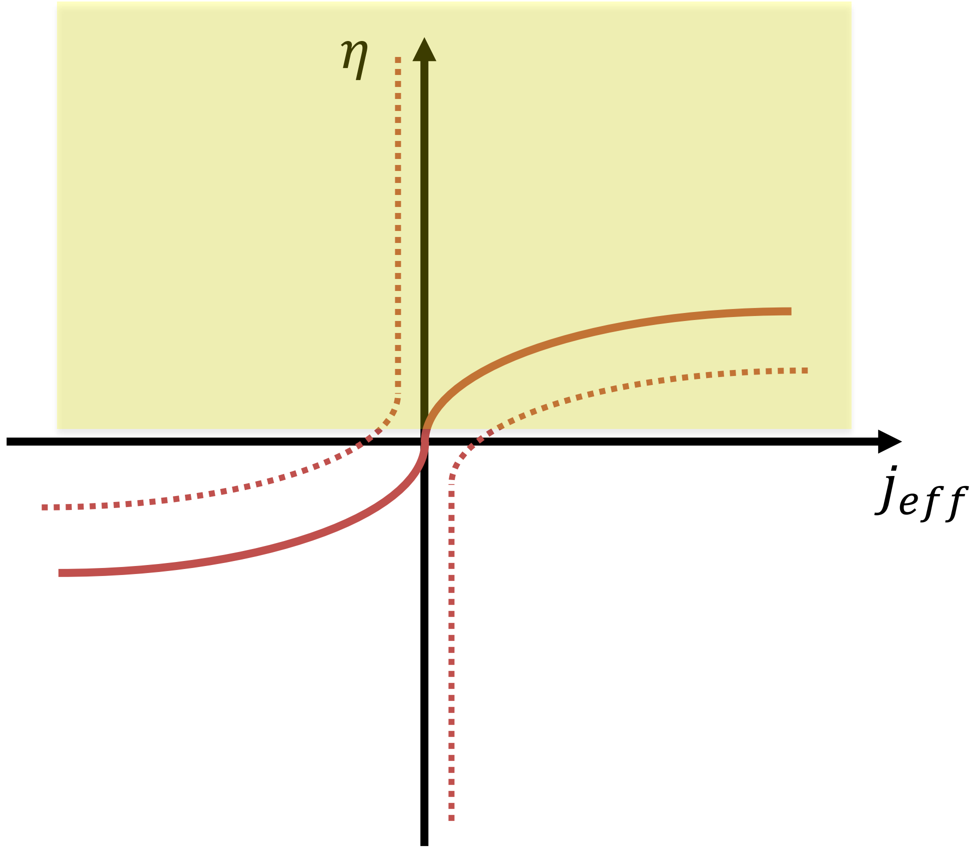


Implications of Reaction Kinetics on Polarization Curve

- **Low overpotentials and slow reaction kinetics lead to logarithmic losses in the Polarization curve**

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

$$\Rightarrow \quad \eta \sim \ln(j_{eff})$$



Implications of Reaction Kinetics on Polarization Curve

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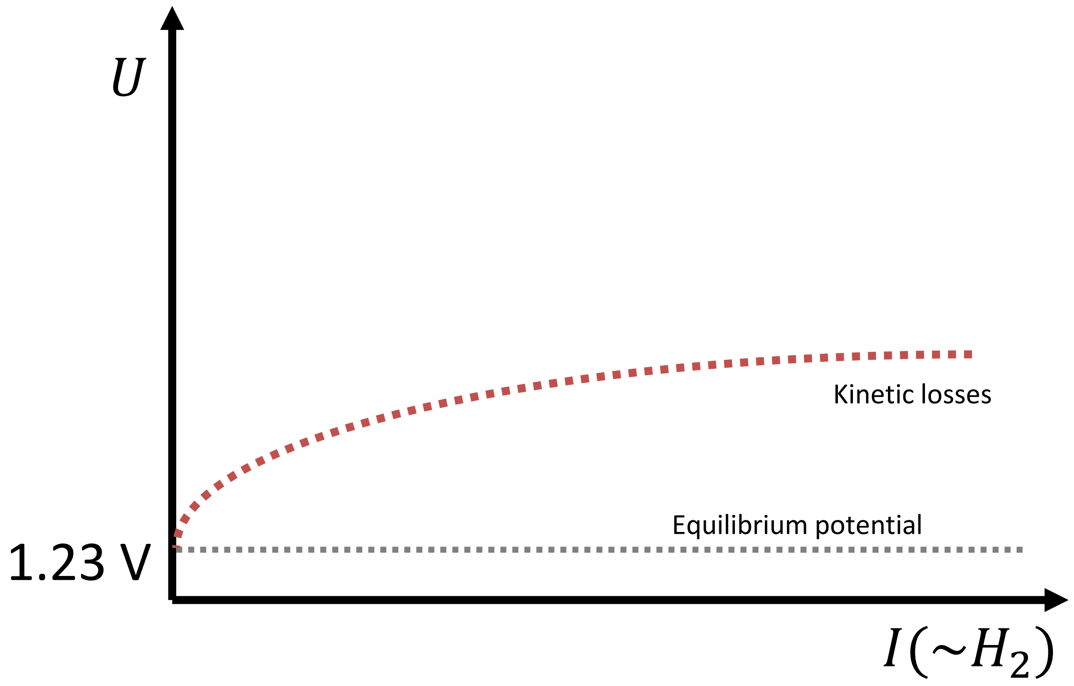
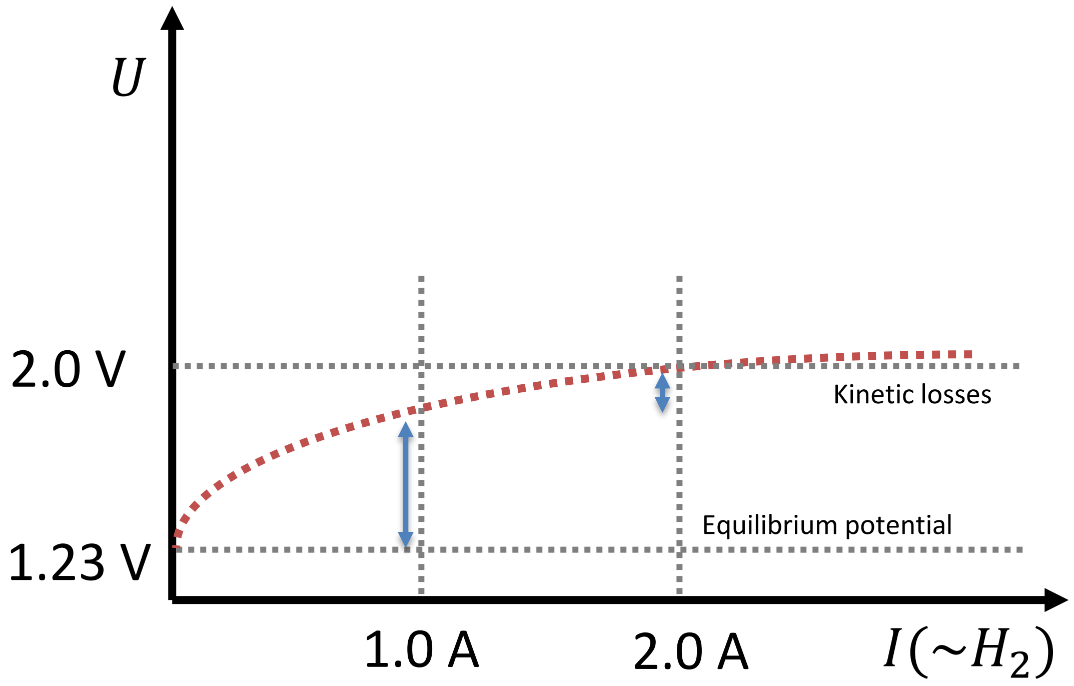


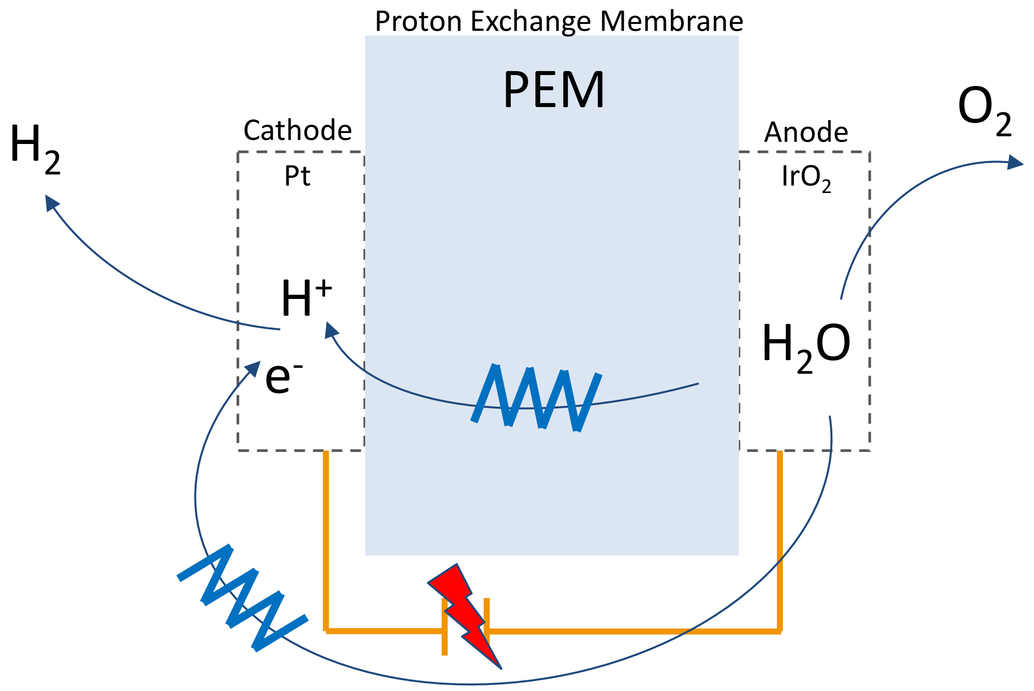
Implications of Reaction Kinetics on Polarization Curve

- **Low overpotentials and slow reaction kinetics lead to logarithmic losses in the Polarization curve**

Can you think of other losses?



Losses in Electrolyis



$$4H^+ + 4e^- \rightarrow 2H_2$$

$$2H_2O \rightarrow O_2 + 4H^+ + 4e^-$$

$$2H_2O \rightarrow O_2 + 2H_2$$

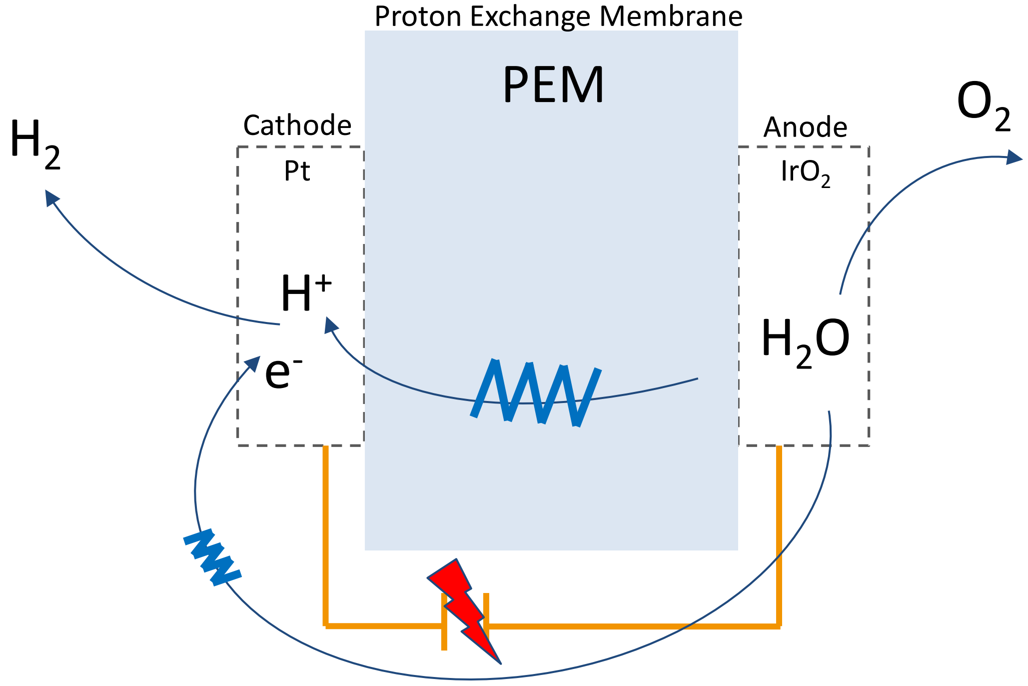
Ohmic Losses in Electrolyis

- **Protons and electrons are subjected to Ohmic losses**

$$R_{\Omega,eff} = R_{\Omega,+} + R_{\Omega,-}$$

$$R_{\Omega,+} \gg R_{\Omega,-}$$

$$\mathbf{4H^+ + 4e^- \rightarrow 2H_2}$$

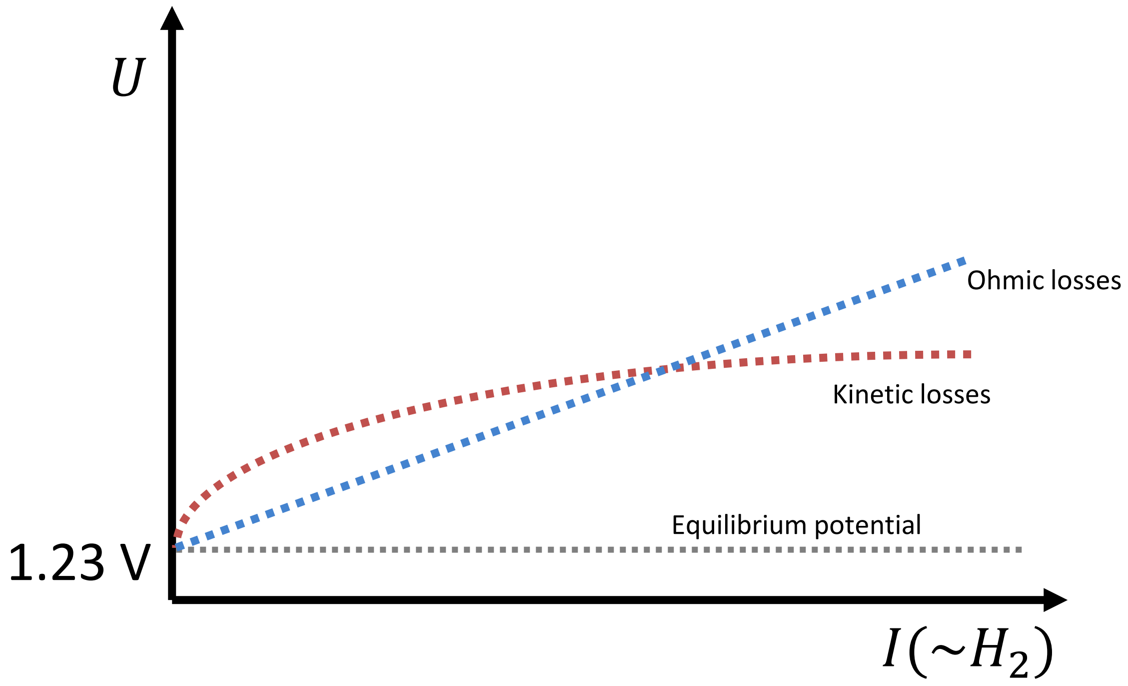


$$\mathbf{2H_2O \rightarrow O_2 + 4H^+ + 4e^-}$$

$$\mathbf{2H_2O \rightarrow O_2 + 2H_2}$$

Implications of Ohmic losses on Polarization Curve

- Ohmic resistances lead to linear losses in the Polarization curve



The Typical Electrolyzer Polarization Curve

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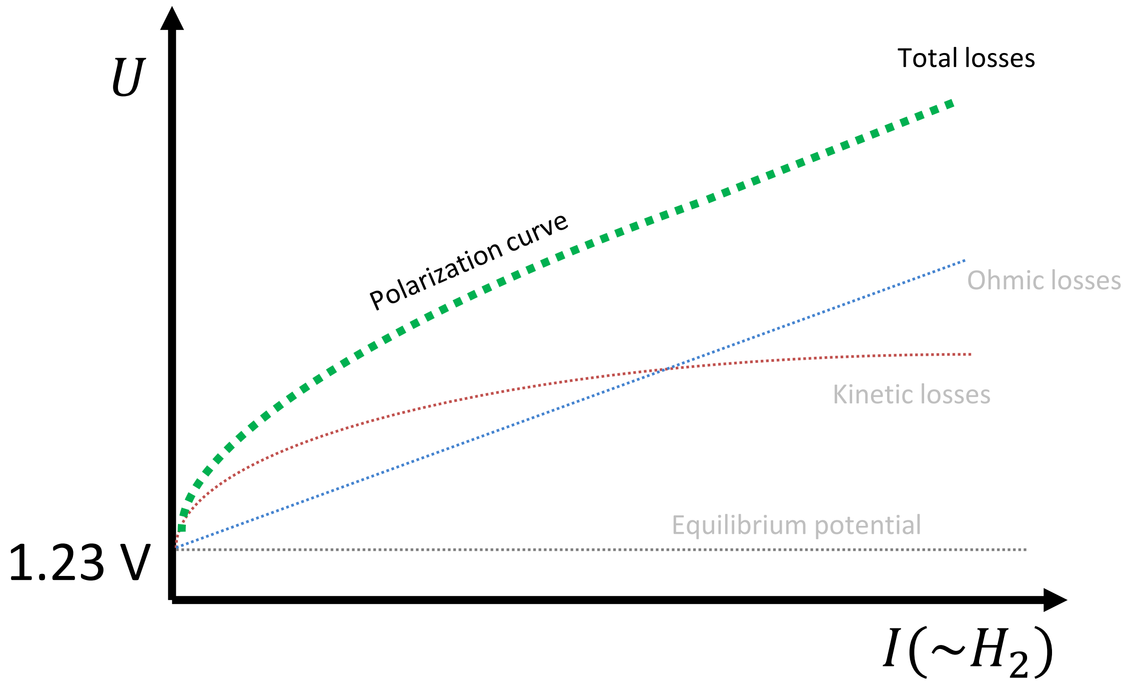
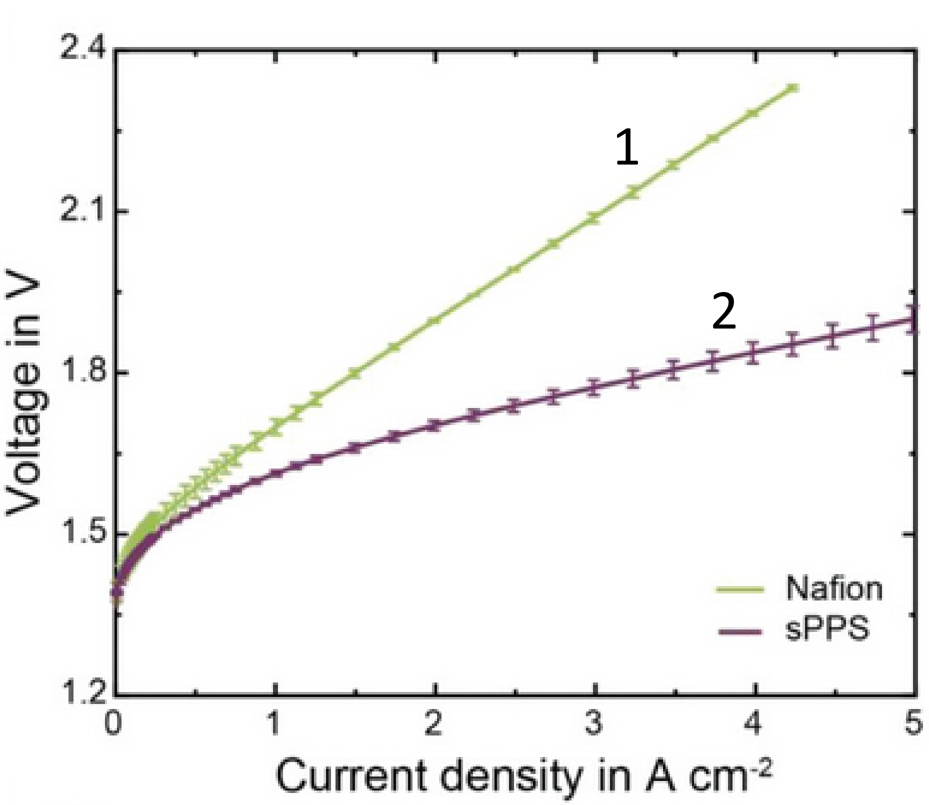
- The sum of all losses leads to a characteristic polarization curve (aka „U-I-Kennlinie“)
- Low current densities:
  Dominated by kinetic losses
- High current densities:
  Dominated by Ohmic losses



Quiz: Example from Reality



Klose, Carolin, et al. "All-hydrocarbon MEA for PEM water electrolysis combining low hydrogen crossover and high efficiency." *Advanced Energy Materials* 10.14 (**2020**): 1903995.

- **Which electrolyzer works more efficient?**
- **Which loss mechanism has been improved?**

In Reality

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- **Lab Scale**
  - For research purposes

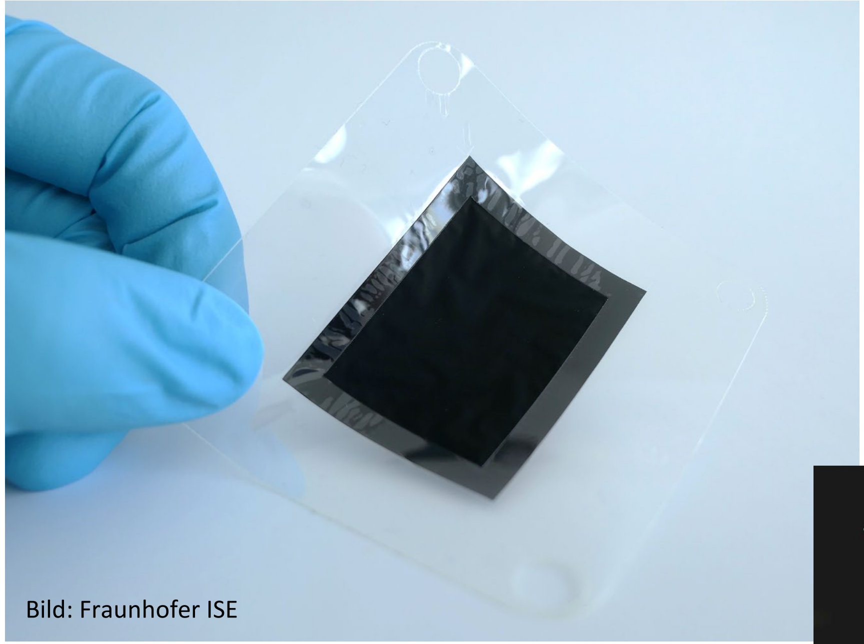
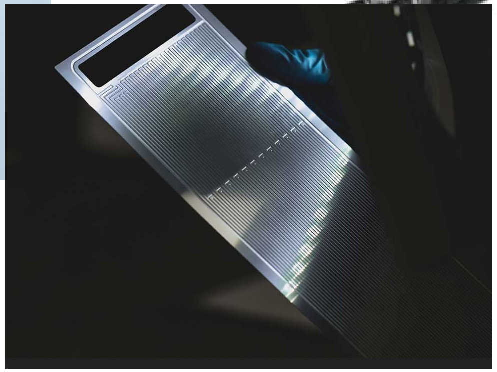
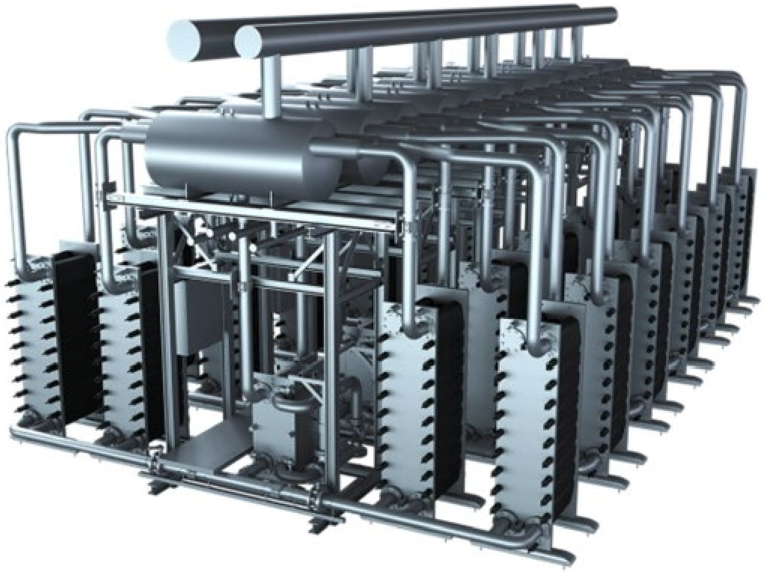


Bild: Fraunhofer ISE

- **Industry Scale**
  - For making Hydrogen





Bilder: Siemens „Sylizer 300“

Remember SMR

- High TRL technology
- Capacity of up to 18 tons H_2/h

What‘s possible with state of the art Electrolysis?

Interesting Questions for Engineers…

- What‘s the Hydrogen production throughput in state-of-the-art electrolyzers?
- How much electrical energy do I need to invest for hydrogen production?
- What‘s the efficiency of an electrolyzer?
- How does this change with temperature and pressure?

Do it yourself ☺

