Elektrochemische Wasserspaltung

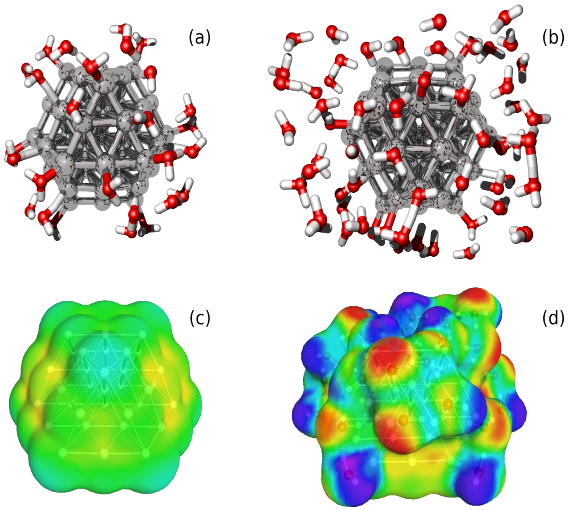
Forschung im Rahmen der
Max Planck MAXNET Energy Initiative

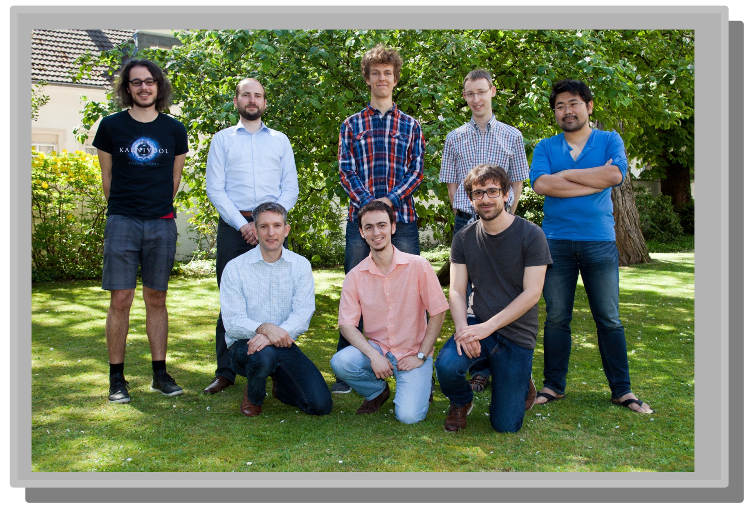
Prof. Dr. Alexander A. Auer, Dr. Ioannis Spanos

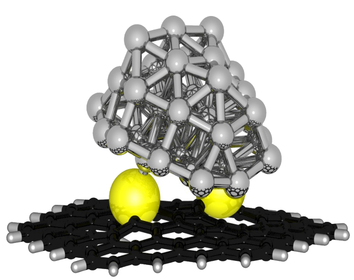
Herbstsitzung Arbeitskreis Energie der DPG, 19. Oktober 2017, Bad Honnef

Theoretical Methods and Heterogeneous Catalysis

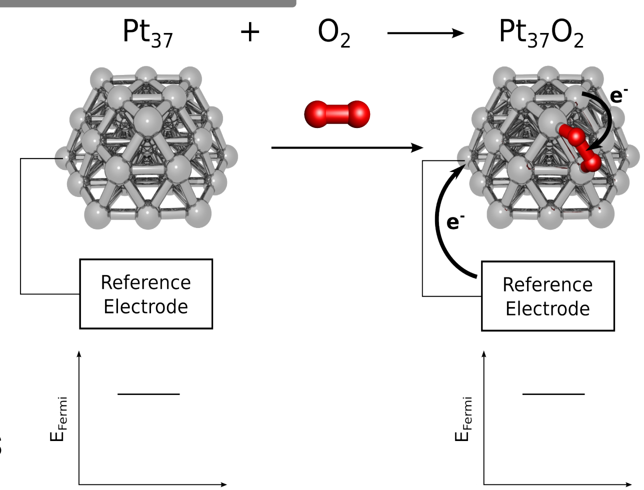
Electrocatalysis:
ORR on Pt nanoparticles,
nanoparticle catalyst systems







Method development
– constant chemical potential DFT approaches



The MPI for Chemical Energy Conversion

1958 Gründung der Selbständigen Abteilung für Strahlenchemie des MPI für Kohlenforschung.

1981 Gründung des **MPI für Strahlenchemie**

2003 Aus dem MPI für Strahlenchemie wird **das MPI für Bioanorganische Chemie**

2011 Frank Neese wird als Direktor berufen

2011 Robert Schlögl wird Leiter des MPI für bioanorganische Chemie

2012 Neugründung des **Instituts Max-Planck-Institut für chemische Energiekonversion** mit Robert Schlögl als geschäftsführender Direktor

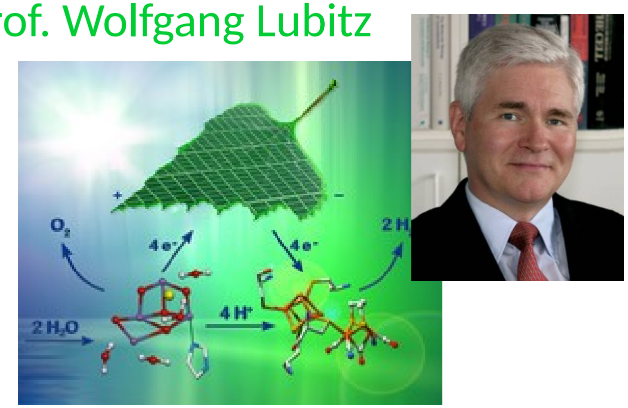
2013 Erteilung des Zuschlags für die bauliche **Erweiterung des Instituts**

2017 **Serena DeBeer** und **Walter Leitner** werden neue Direktoren am MPI CEC

Spatenstich für die Erweiterung des Instituts

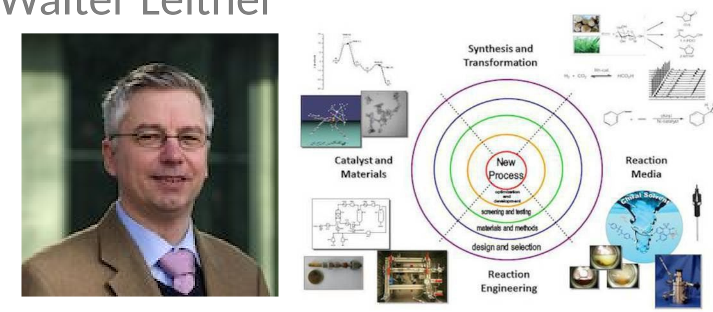
The MPI for Chemical Energy Conversion

Prof. Wolfgang Lubitz



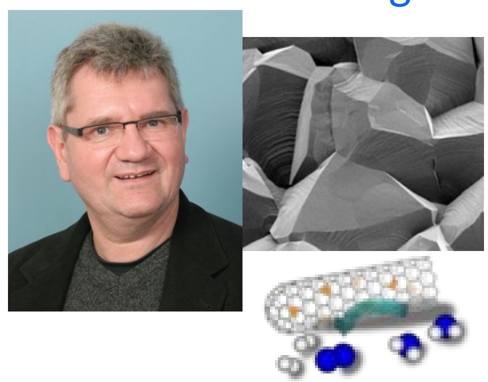
Biocatalysis,
Bioinorganic Chemistry

Prof. Walter Leitner



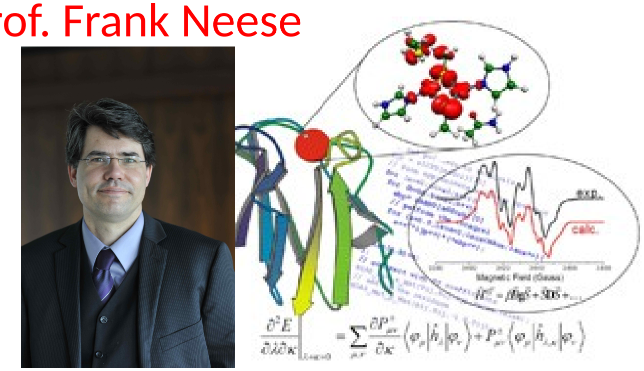
Heterogeneous Catalysis,
Green Chemistry

Prof. Robert Schlögl



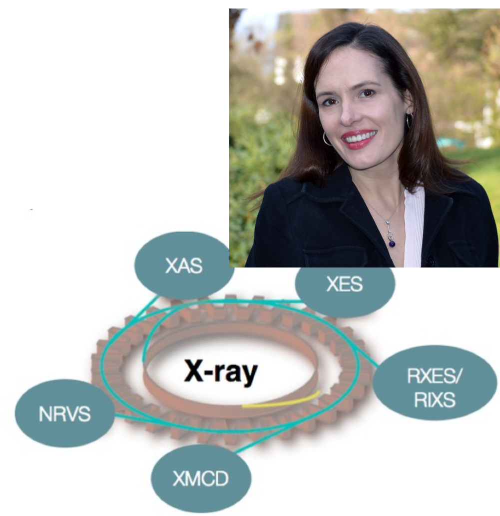
Heterogeneous Catalysis,
Materials Science

Prof. Frank Neese



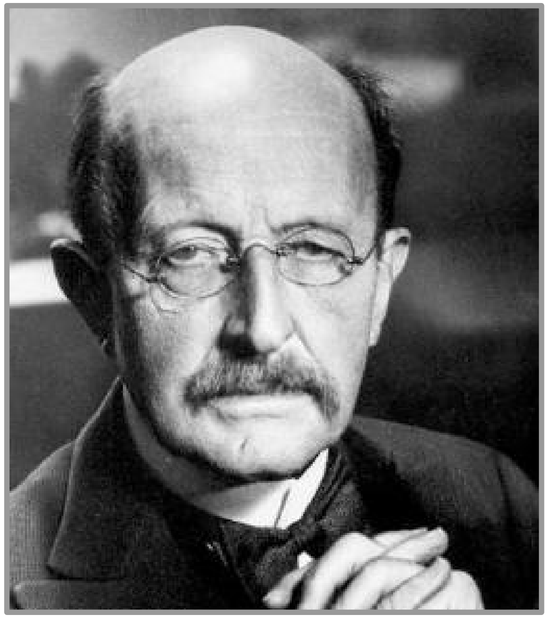
Theoretical Chemistry, Spectroscopy

Prof. Serena DeBeer



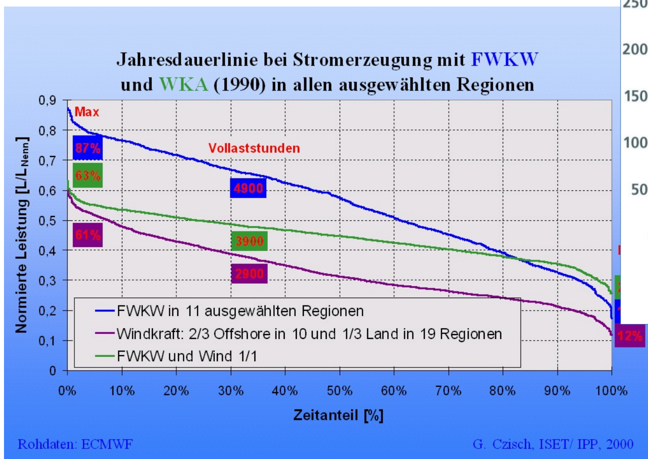
X-Ray Spectroscopy, Catalysis

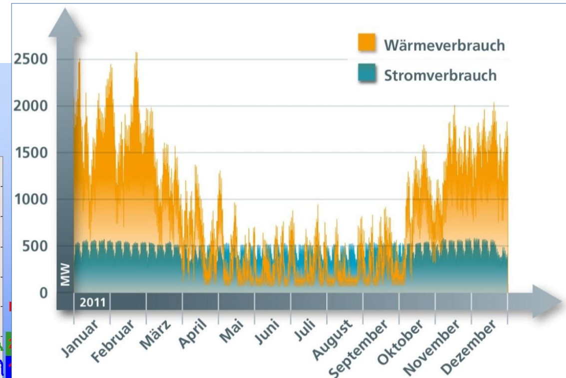
Spirit of the Max Planck Society

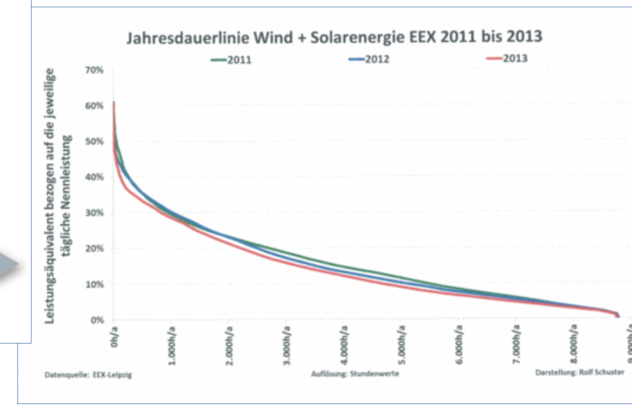


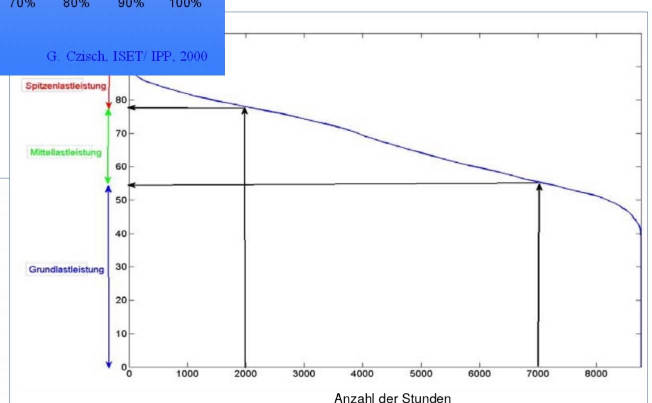
„Dem Anwenden
muss das Erkennen vorausgehen."

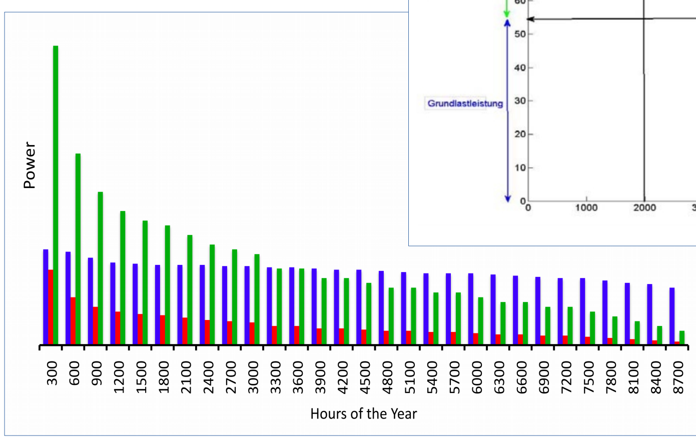
Energy problem – or storage problem ?











Sonntag, 17. August 2014 – Erneuerbare Energien decken ***75%*** des deutschen Strombedarfs

Sonntag, 8. Mai 2016 – Erneuerbare Energien decken ***87%*** des deutschen Strombedarfs

Mittwoch, 22. Februar 2017 – Einspeiserektord Windkraft, 817 Gwh

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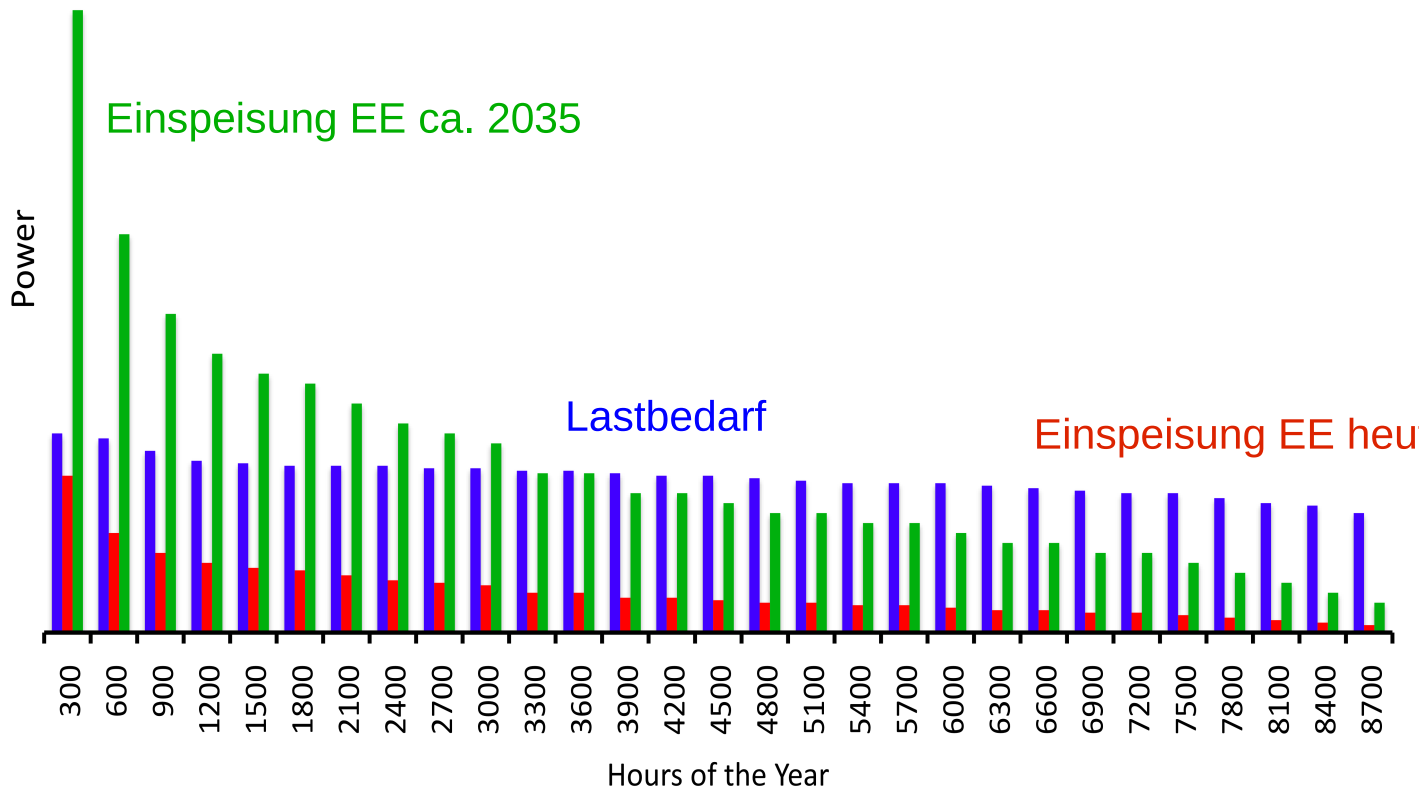
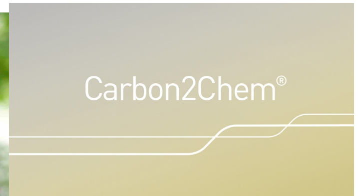
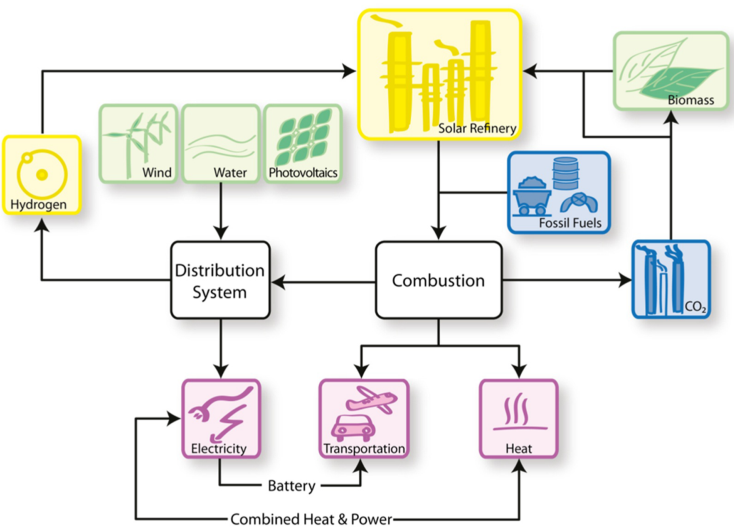
Energy problem – or storage problem ?

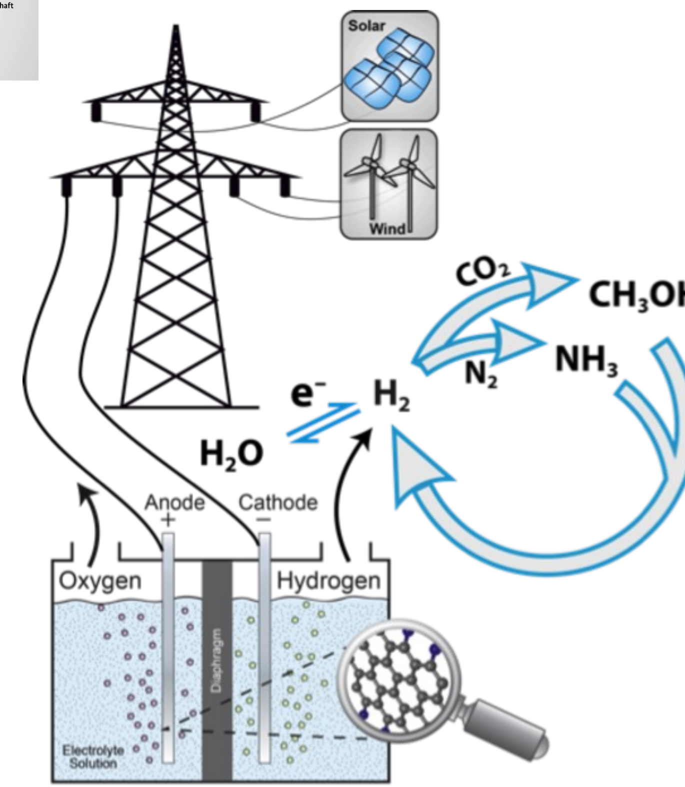


Scientific focus: Water splitting

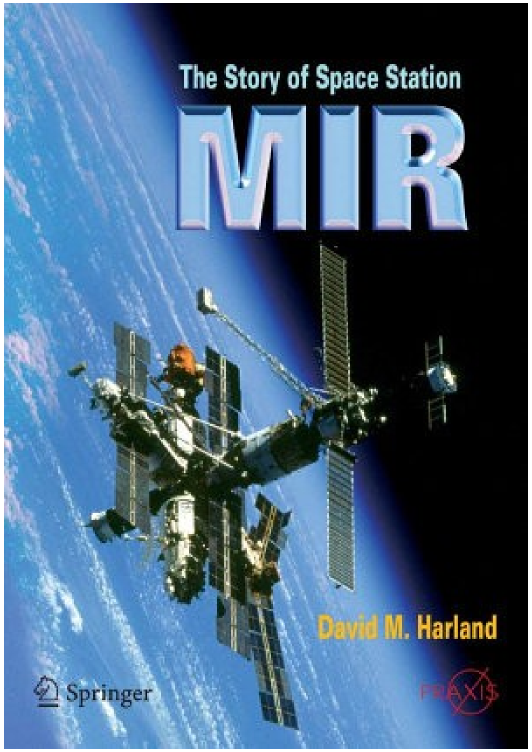


25 Mn MANGAN





Scientific focus: Water splitting



and longer exposure periods (in some cases, 40 hours).

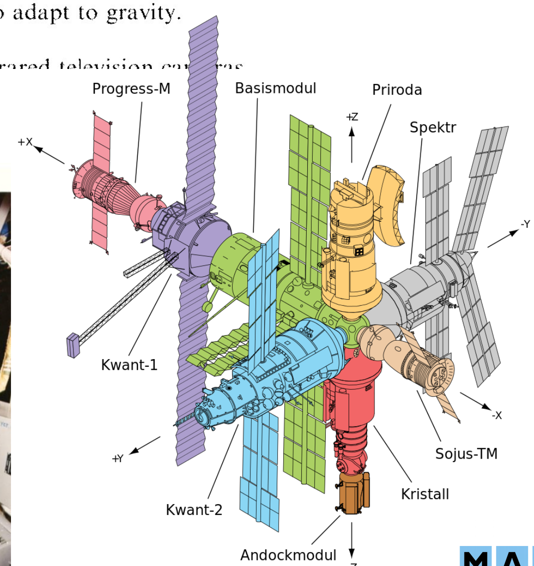
Electrotopograph-7K
An apparatus on Mir used to measure surface distortions of advanced plastics and high-temperature superconductors exposed to space in the scientific airlock for various times.

Elektron
This produced oxygen by electrolysing a 30 per cent potassium hydroxide (KOH) solution, to maintain the required composition of the gaseous environment within the Mir complex without requiring so much liquefied air to be delivered by Progress ferries. It was connected by flexible tubes which were to be distributed throughout the complex. There were twelve electrolysis cells in the unit, which were cooled by the base block's primary coolant loop. It consumed about 4 kilogram of water per day; whenever possible water recycled from urine was employed. The hydrogen released was vented.

Eleutheroccus
A drug taken over a prolonged period (a daily dose of 4 ml) towards the end of a long spaceflight to act as a tonic, to stimulate the body to work harder, and thereby increase long-term stamina to help cosmonauts prepare to adapt to gravity.

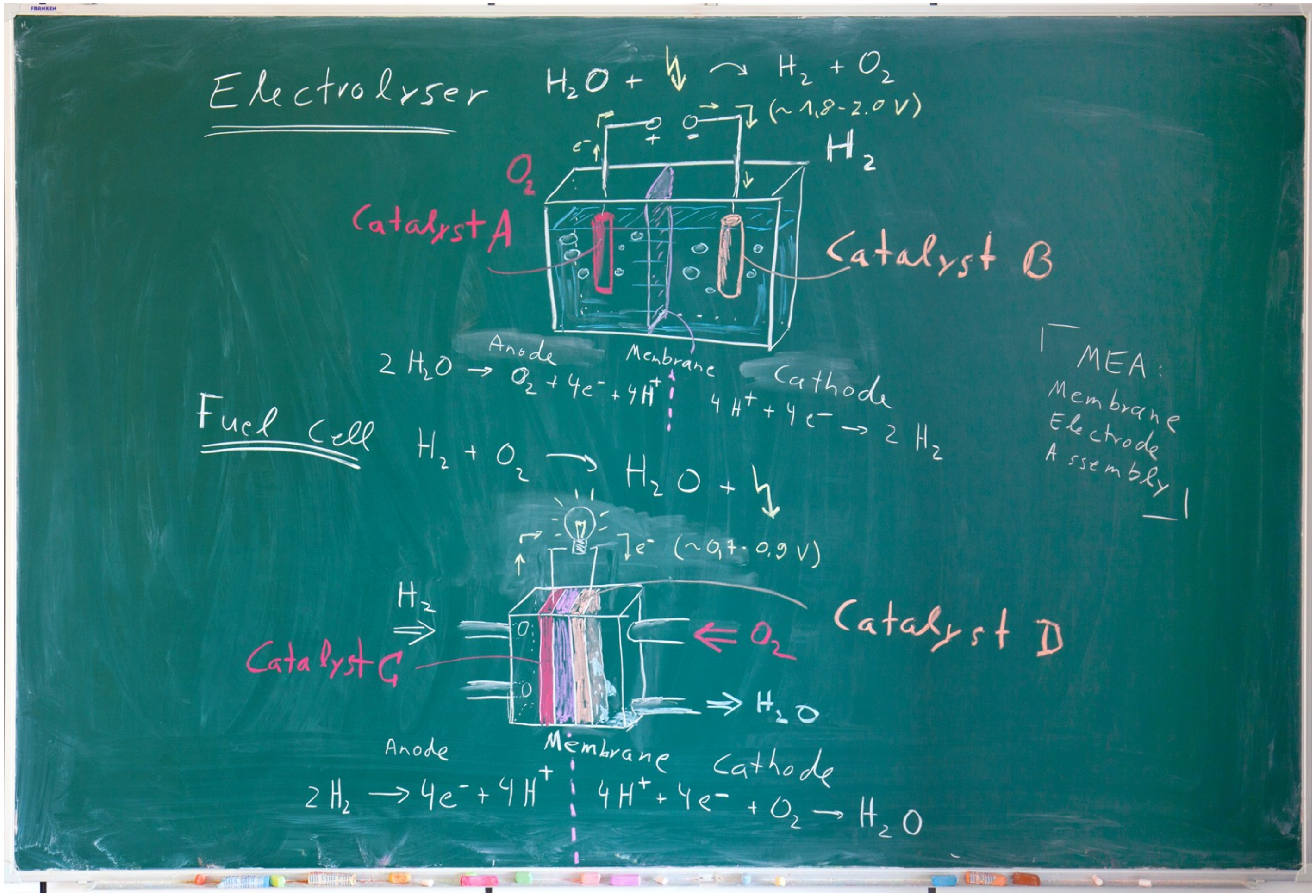
ELITE
A European Space Agency experiment that used four infrared television cameras

First prototype electrolysis unit, aboard Mir-Kvant, 1987

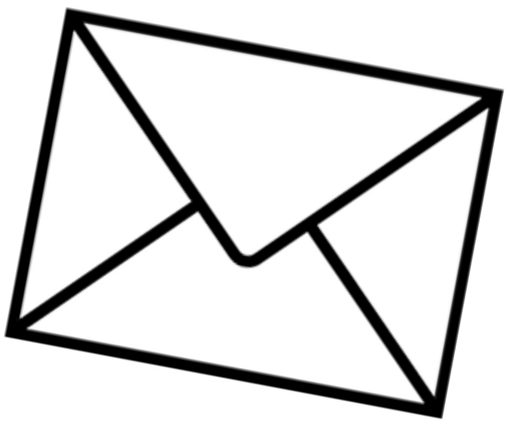


MIR space station, 1986-2001

Scientific focus: Water splitting



Scientific focus: Water splitting



Storing 10% of germany's renewables (60 TWh for 2015) would require electrolysis of roughly 1-2 mio t of H_2O. Today in germany, every year more than 5 mio t of Cl_2 are produced ...

Termodynamics of hydrogen / oxygen to water system:
Calorimetry yields $H_2 + ½ O_2 \rightarrow H_2O$
Reaction enthalpy 571,6 kJ/mol,
Maximum potential possible: 1,23 V (4 e^-)

Fuel cell: typical cell voltages 0.5 – 1.0 V
Electrolysers : typical cell voltages 2.0-2.5 V

- ohmic losses
- membrane ion conductivity
- diffusion limitation (flow field)
- material degradation
- side reactions
- catalyst performace

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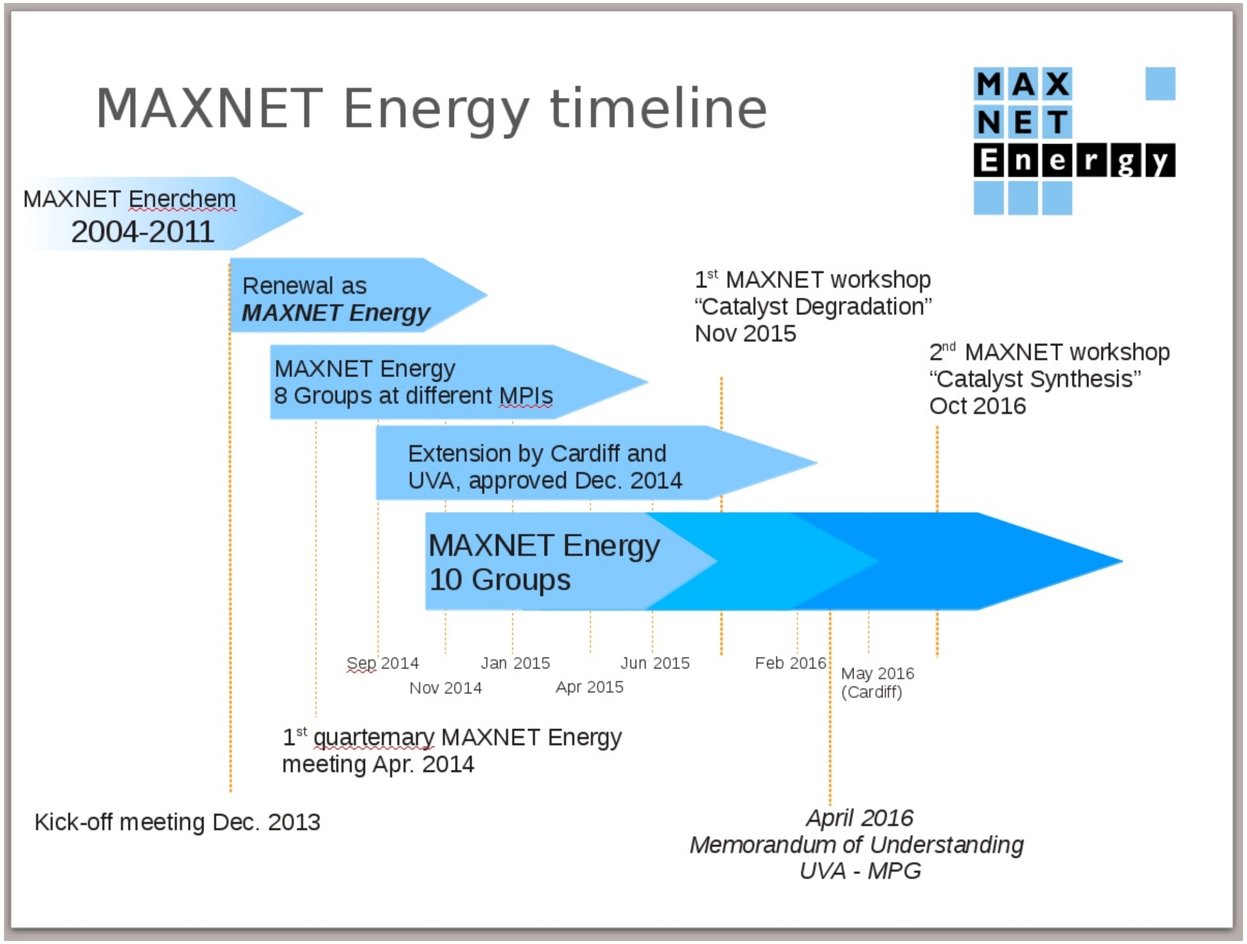
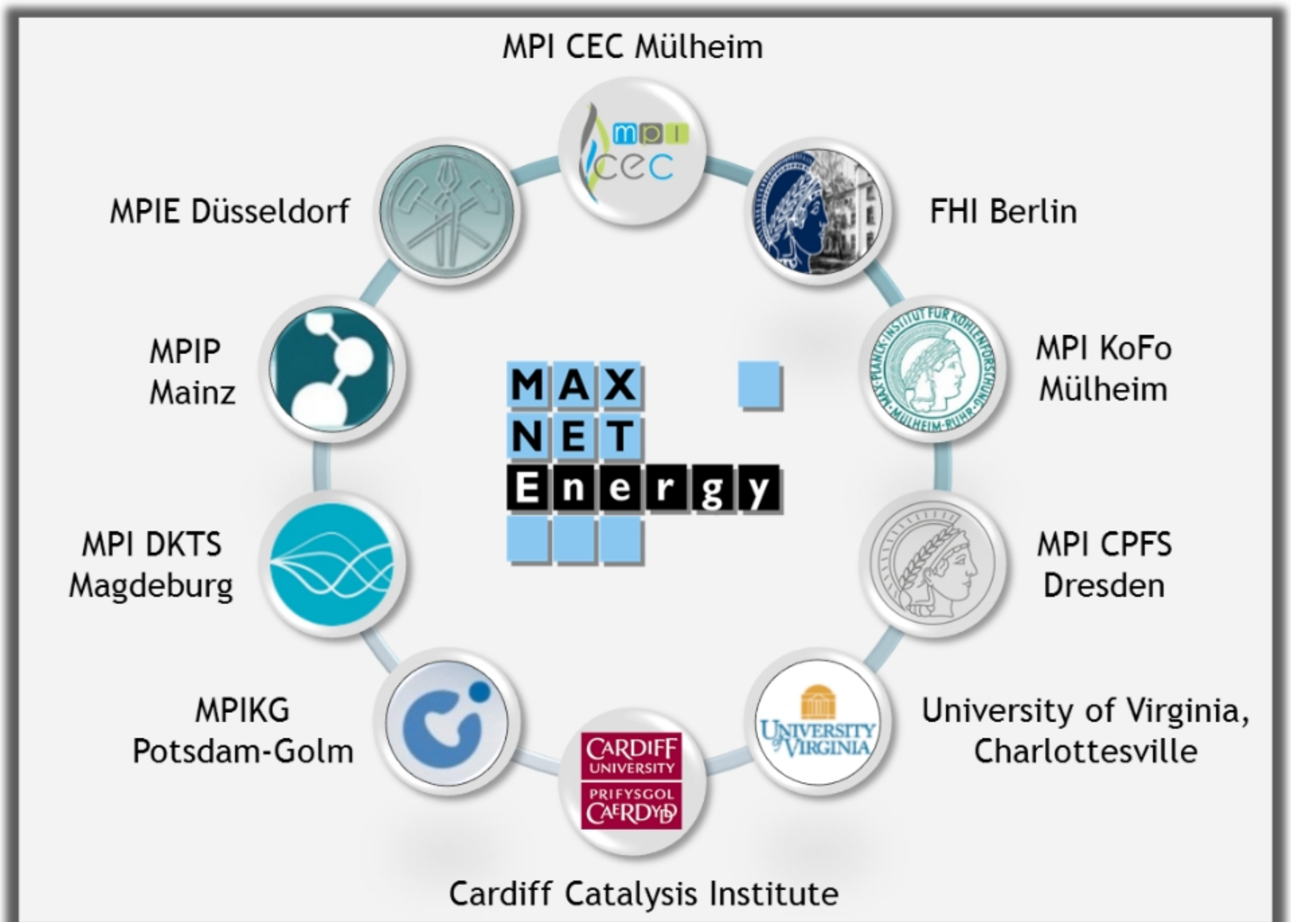
"Membrane electrolysis - History, current status and perspective", M. Paidara , V. Fateevb, K. Bouzeka, *Electrochimica Acta* **209**, 737 (**2016**)

The MPG MAXNET Energy Reserach Initiative

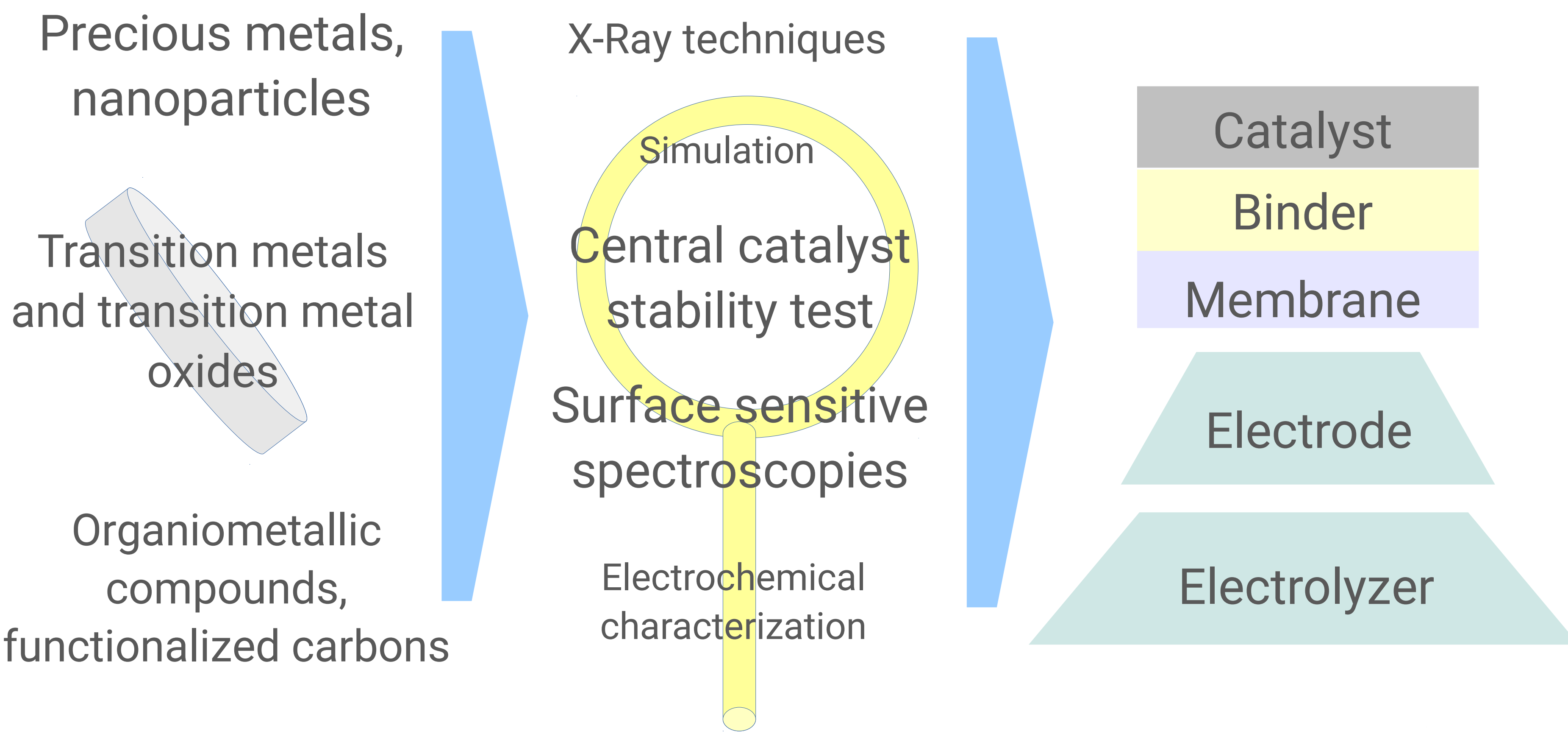
The MPG MAXNET Energy Reserach Initiative



The MPG MAXNET Energy Reserach Initiative

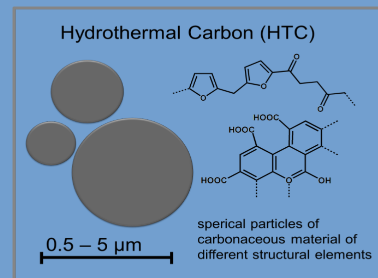


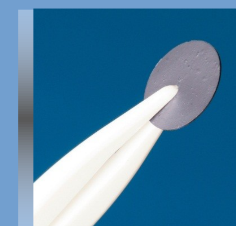
The MPG MAXNET Energy Reserach Initiative



The MPG MAXNET Energy Reserach Initiative

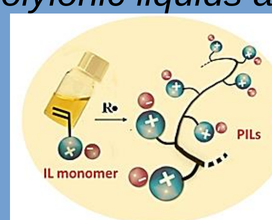
Hydrothermal carbon as binder free functionalized support

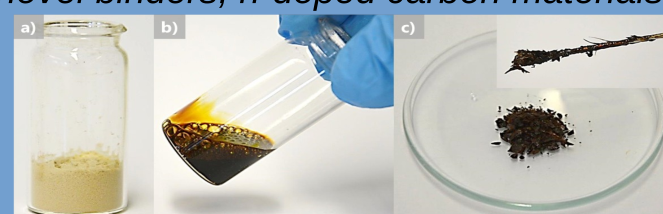




Dept. Schlögl, S. Reiche, S. Buller, MPI CEC Mülheim

Polyionic liquids as novel binders, n-doped carbon materials





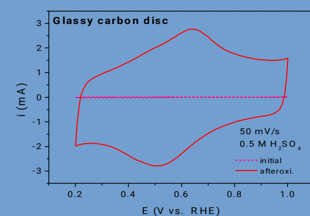
Dept. Antonietti, N. Fechler, R. Guterman MPIKG Golm

The MPG MAXNET Energy Reserach Initiative

Carbon corrosion at OER conditions

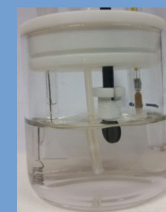
Dept. Schlögl,
Youngmi Yi,
MPI CEC Mülheim

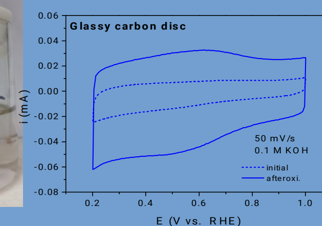
Acid



118.5 → 118.5 mg

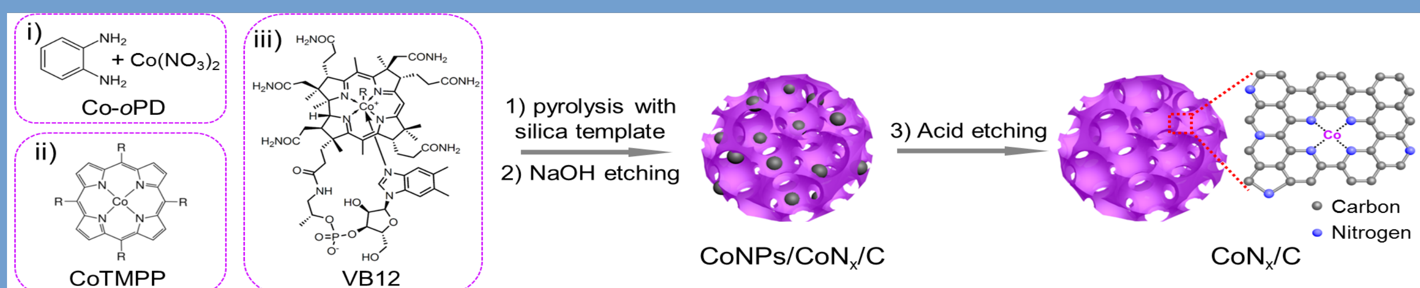
Alkaline





116.3 → 115.86 mg

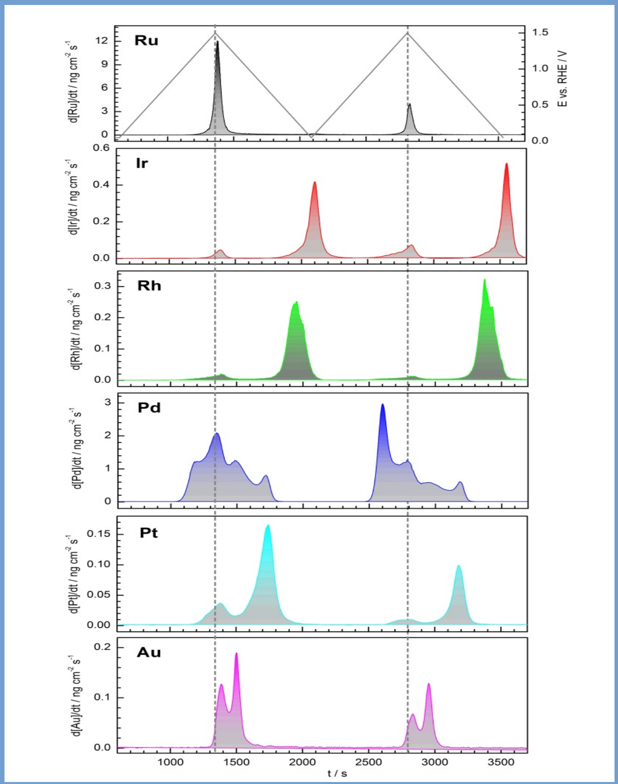
Carbon-based electrocatalysts with molecular active sites



Dept. Müllen, S. Brüller, H. Liang, MPIP Mainz

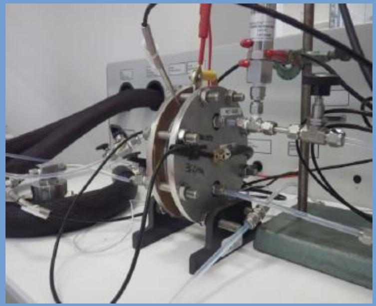
The MPG MAXNET Energy Reserach Initiative

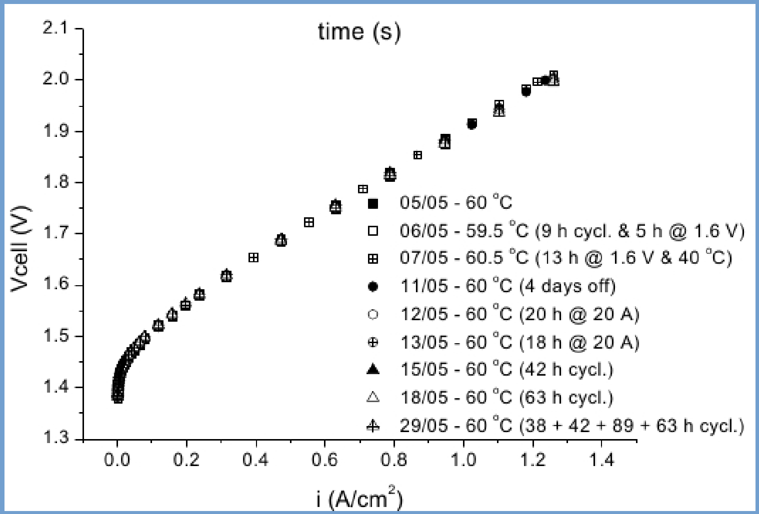
Noble metal corrosion SFC/ICP-MS



Dept. Stratmann, K. Mayrhofer,
MPIE Düsseldorf

OER electrolyzer test cell

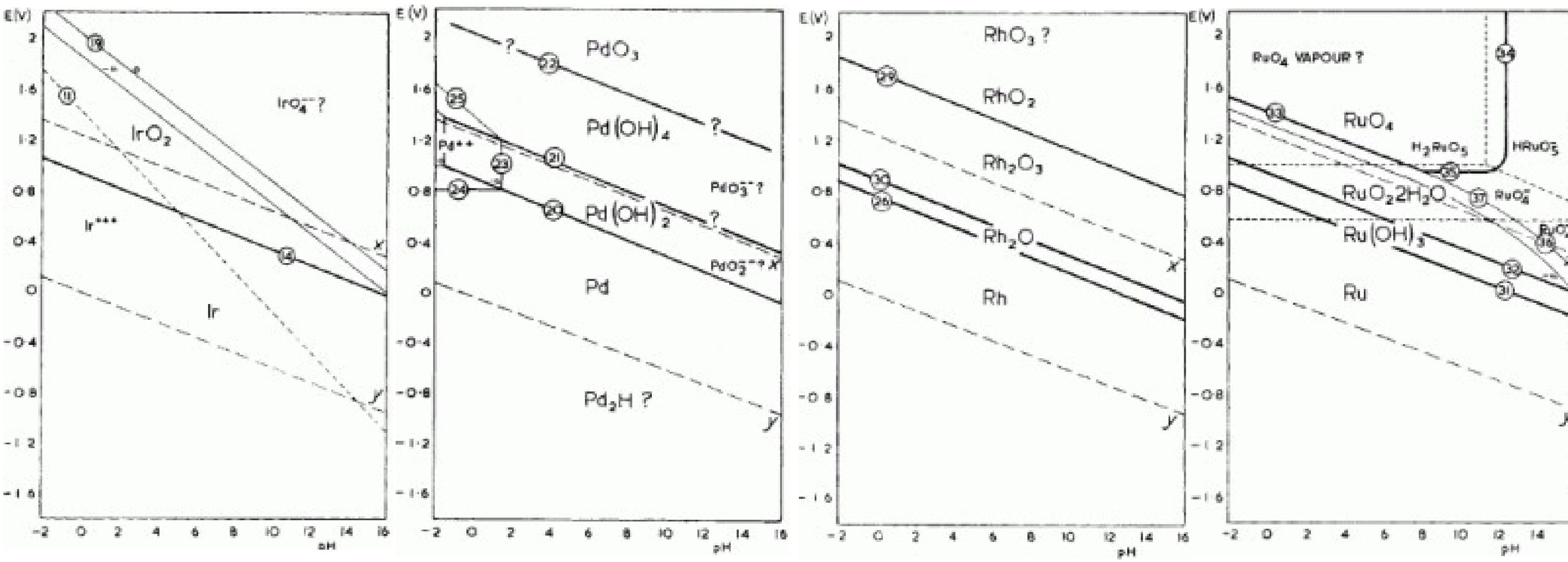




Dept. Sundmacher, T. Vidakovic-Koch,
G. Papakonstantinou, MPI DKTS Magdeburg

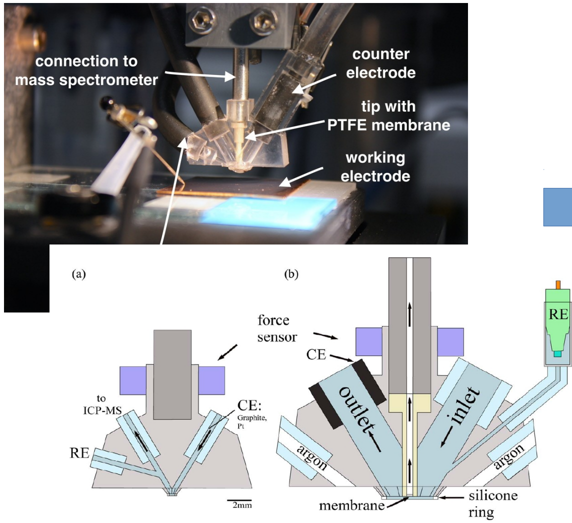
“MAXNET Energy – Focusing Research in Chemical Energy Conversion on the Electrocatalytic Oxygen Evolution”, *Green* **5** (1-6), 7–21, (**2016**)

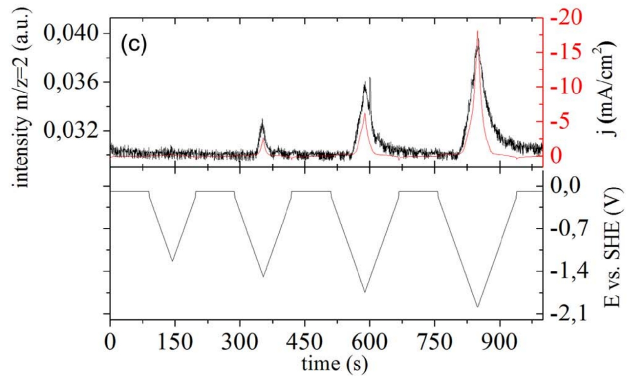
Precious metal corrosion

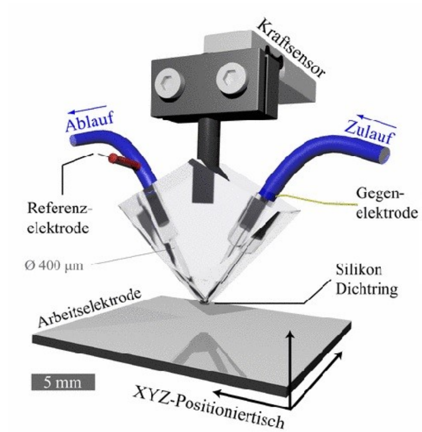


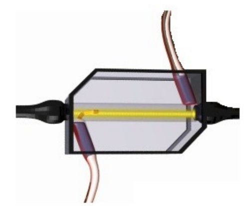
N. de Zoubov J. Van Muylde, M. J. N. Pourbaix, *Platinum Metals Rev.* **3**, (3), 100 (**1959**)

Precious metal corrosion







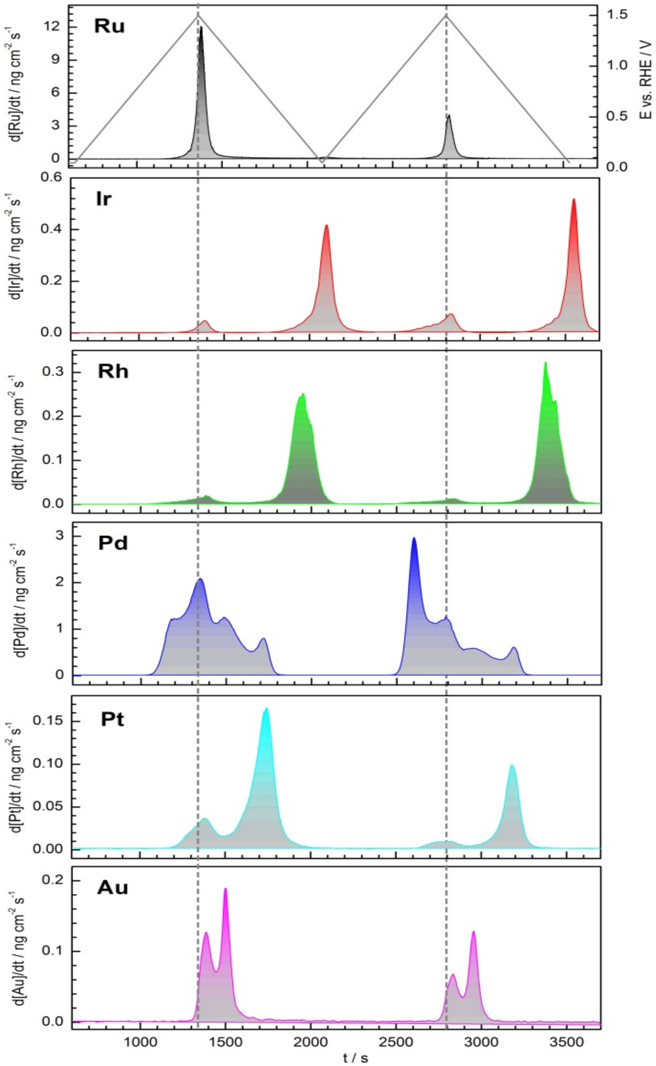


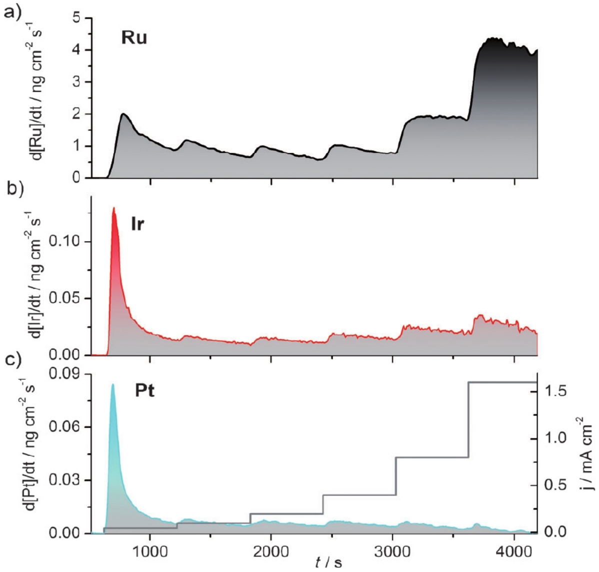
Scanning flow cell (SFC) coupled to an inductively coupled plasma mass spectrometer (ICP-MS)

Karl. Mayrhofer - MPIE Düsseldorf, HI Erlangen-Nürnberg

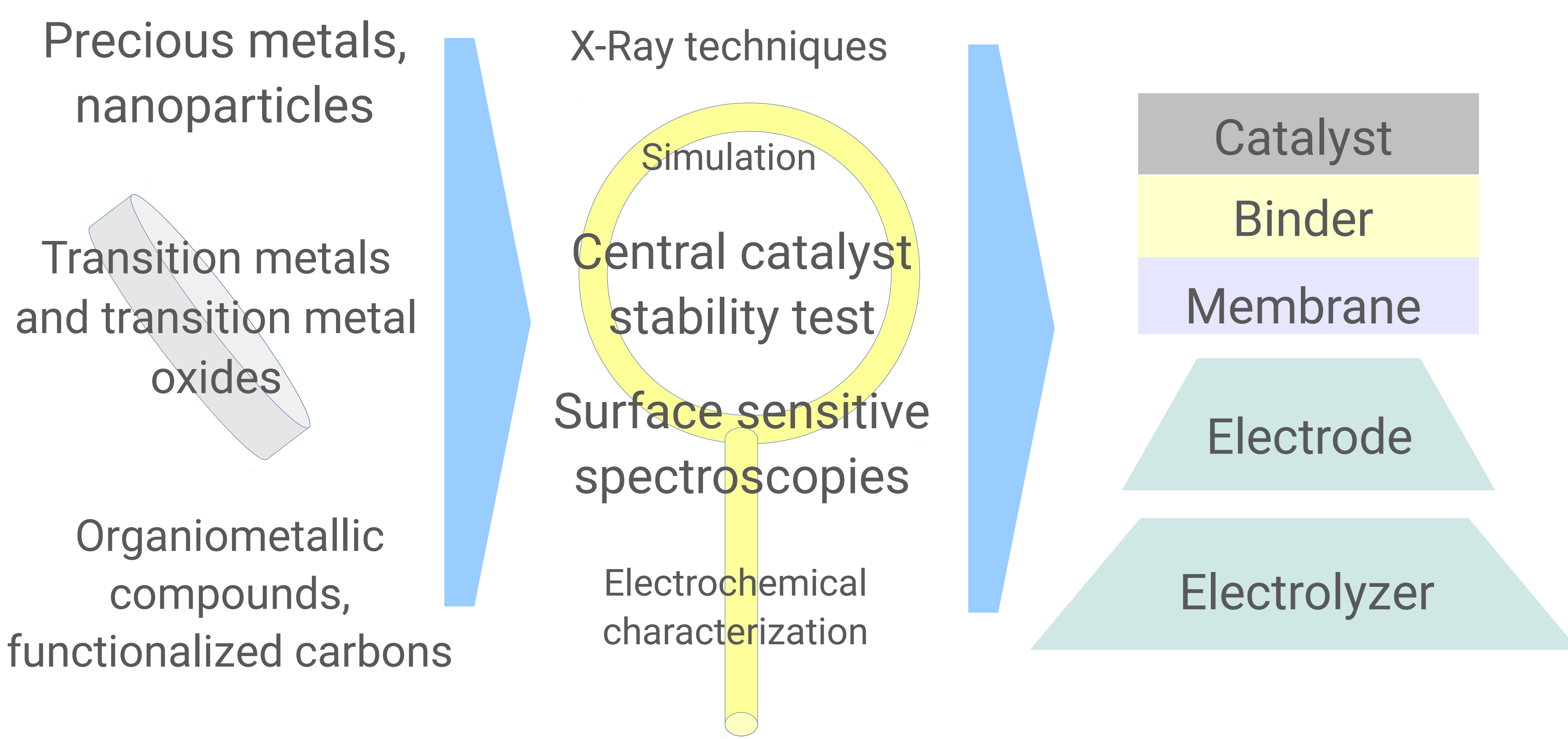
J.-P. Grote, A. R. Zeradjanin, S. Cherevko, and K. J. J. Mayrhofer, *Review of Scientific Instruments* **85**, 104101 (**2014**)

Precious metal corrosion





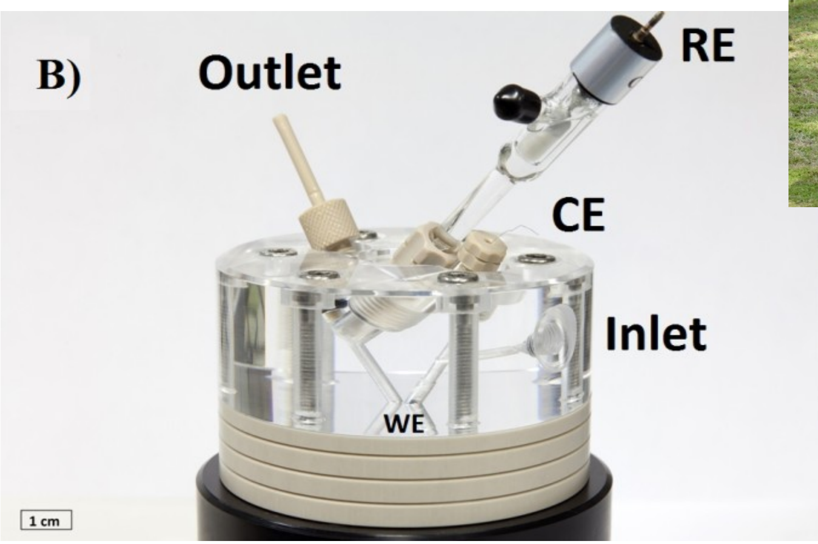
The MPG MAXNET Energy Reserach Initiative



Evaluating OER catalysts

Central test setup

- scalable: larger sample size
- on-line analysis: oxygen and catalyst traces
- versatile: alkaline and acidic
- simple: easy to reproduce
- service: marker analysis for all samples



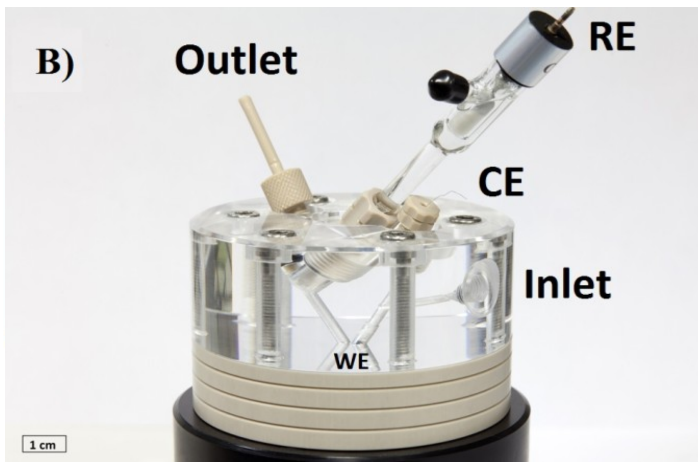
Anna Mechler – Electrocatalysis Group
Dept. Schlögl, MPI CEC

Ioannis Spanos – design and operation of the central test facility

Evaluating OER catalysts

Static and dynamic OER evaluation

Corrosion evaluation



Flow Cell

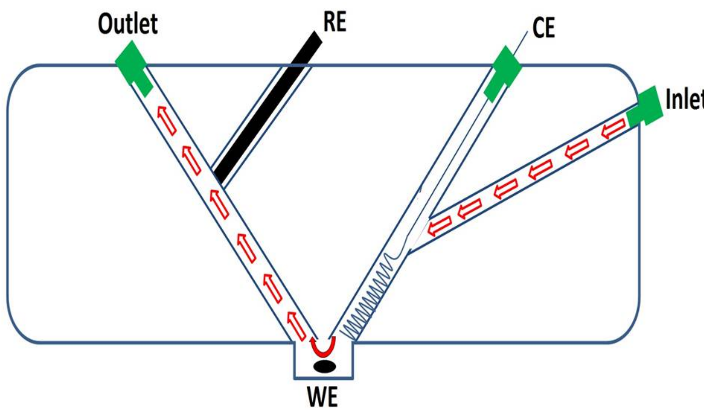
Faradaic efficiency

Spanos, I.; Auer, A. A.; Neugebauer, S.; Deng, X.; Tüysüz, H.; Schlögl, R. *ACS Catal.* **2017**, *7* (6), 3768−3778.

Evaluating OER catalysts

Static and dynamic OER evaluation

Corrosion evaluation



Flow Cell

Faradaic efficiency

Spanos, I.; Auer, A. A.; Neugebauer, S.; Deng, X.; Tüysüz, H.; Schlögl, R. *ACS Catal.* **2017**, *7* (6), 3768−3778.

Evaluating OER catalysts

Pre-analysis

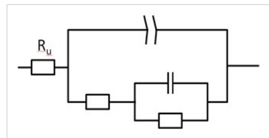
- **OCP**
- LSV from OCP to start potential, 5mV/s
- **Conditioning**

Acidic or alkaline conditions, room temperature, various catalyst loadings

MANGAN (25 Mn)

Catalyst evaluation

- **OCP, Impedance** — **iR-drop**



- LSV from OCP to 1.2 V_{RHE}, 5 mV/s
- **LSV: 1.2-1.7V_{RHE}** — **1.2 – 1.7 V_{RHE}, iR-corrected, 5 mV/s**
- **Faradaic Efficiency: Chronoamperometry (CA) or Chronopotentiometry (CP)** — **O_2 evolution at 1 Coulomb of charge**
- Galvanodynamic from 0 mA to 10 mA/cm²
- LSV from OCP to 1.7V_{RHE}, 5mV/s
- **Stabilty: - CA or CP**
  - Potential steps — **2 h at 10 mA/cm² or 2h at 1.7V_{RHE}**; **OCP to 1.7V**
- **ICP-OES analysis**
  Activity/stability markers — **$E_{J=10mAcm^2}$, ΔJ_{LSV}%, $n_{Faradaic}$, $E_{OER,\ onset}$, $n_{CP,2h}$%, $\Delta cor_{CP,\ 2h}$**

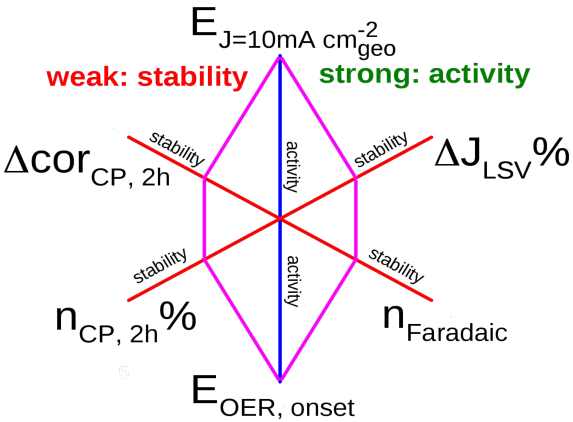
Post-analysis

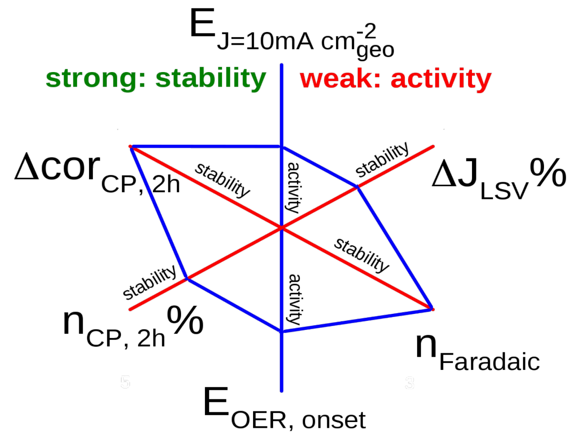
- **OCP, Impedance** — **iR-drop**
- LSV from OCP to 1.2 V_{RHE}, 5 mV/s
- **LSV: 1.2-1.7V_{RHE}** — **1.2 – 1.7 V_{RHE}, iR-corrected, 5 mV/s**
- **Faradaic Efficiency: Chronoamperometry (CP) or Chronopotentiometry (CA)** — **O_2 evolution at 1 Coulomb of charge**

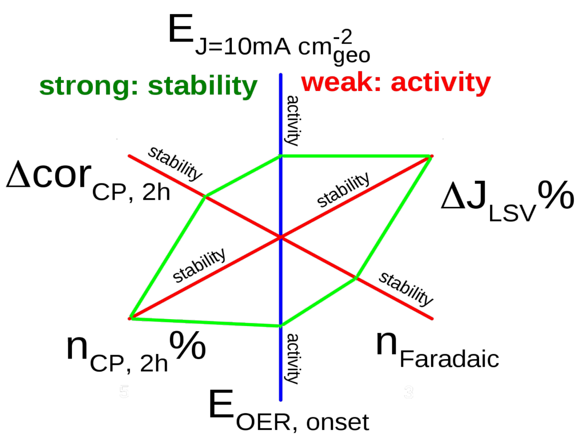
Evaluating OER catalysts

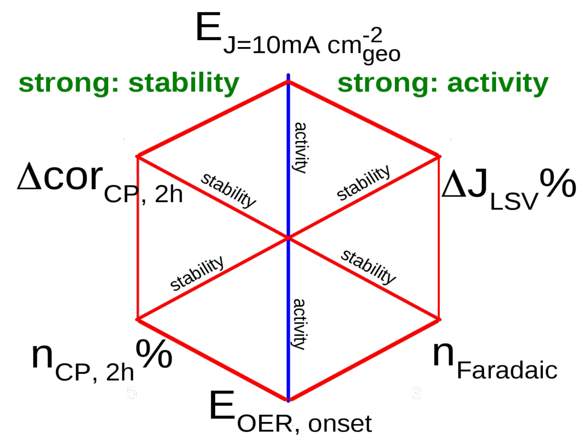
Activity markers	
$E_{J=10mA/cm^2}$	The potential at a current density value of 10mA/cm^2, taken from the LSV.
$E_{OER,\ onset}$	OER onset potential, taken from the LSV.
Stability markers	
$\Delta J_{LSV}\%$:	The relative difference of the maximum current density during an LSV before and after the stress test.
$n_{CP,2h}\%$:	The relative difference of the oxygen evolution overpotential at 0h and 2h of the CP stress test at 10mA/cm^2.
$n_{Faradaic}$	Faradaic efficiency before the stress test.
$\Delta cor_{CP,2h}$	Total metal corrosion, calculated by integrating the area under the corrosion peaks taken by ICP-OES analysis during the stress test between the 300th and 1200th sec.

Evaluating OER catalysts

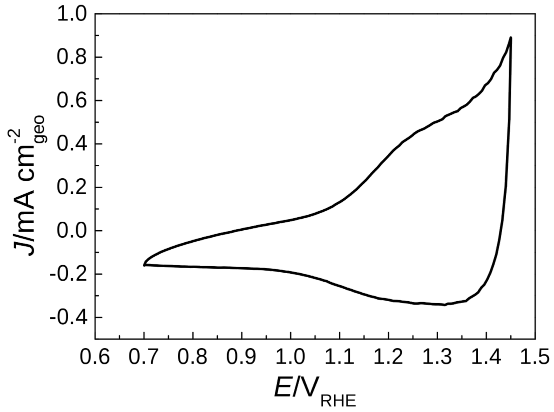




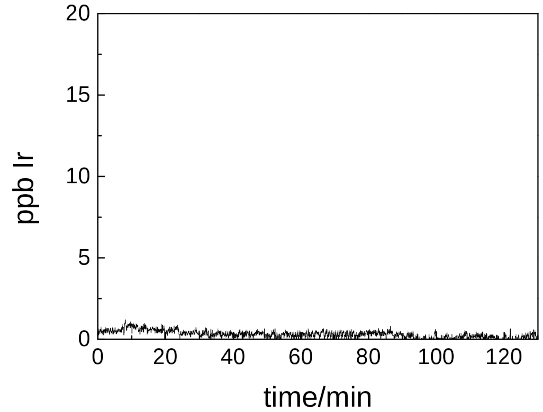


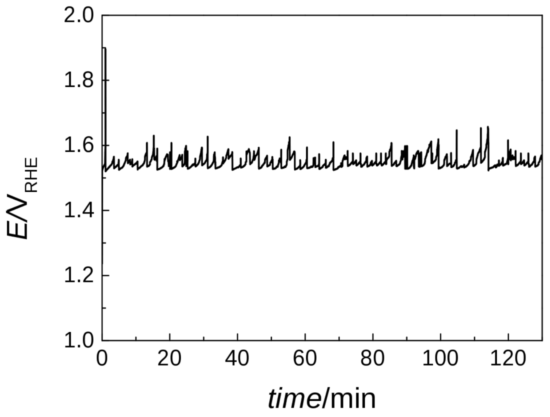


IrO_2 - 0.1M $HClO_4$ 100µg/cm²

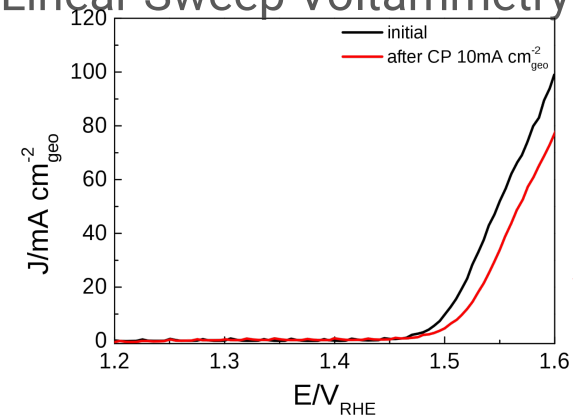


ICP-OES profiles during CP 10mA/cm²





Linear Sweep Voltammetry

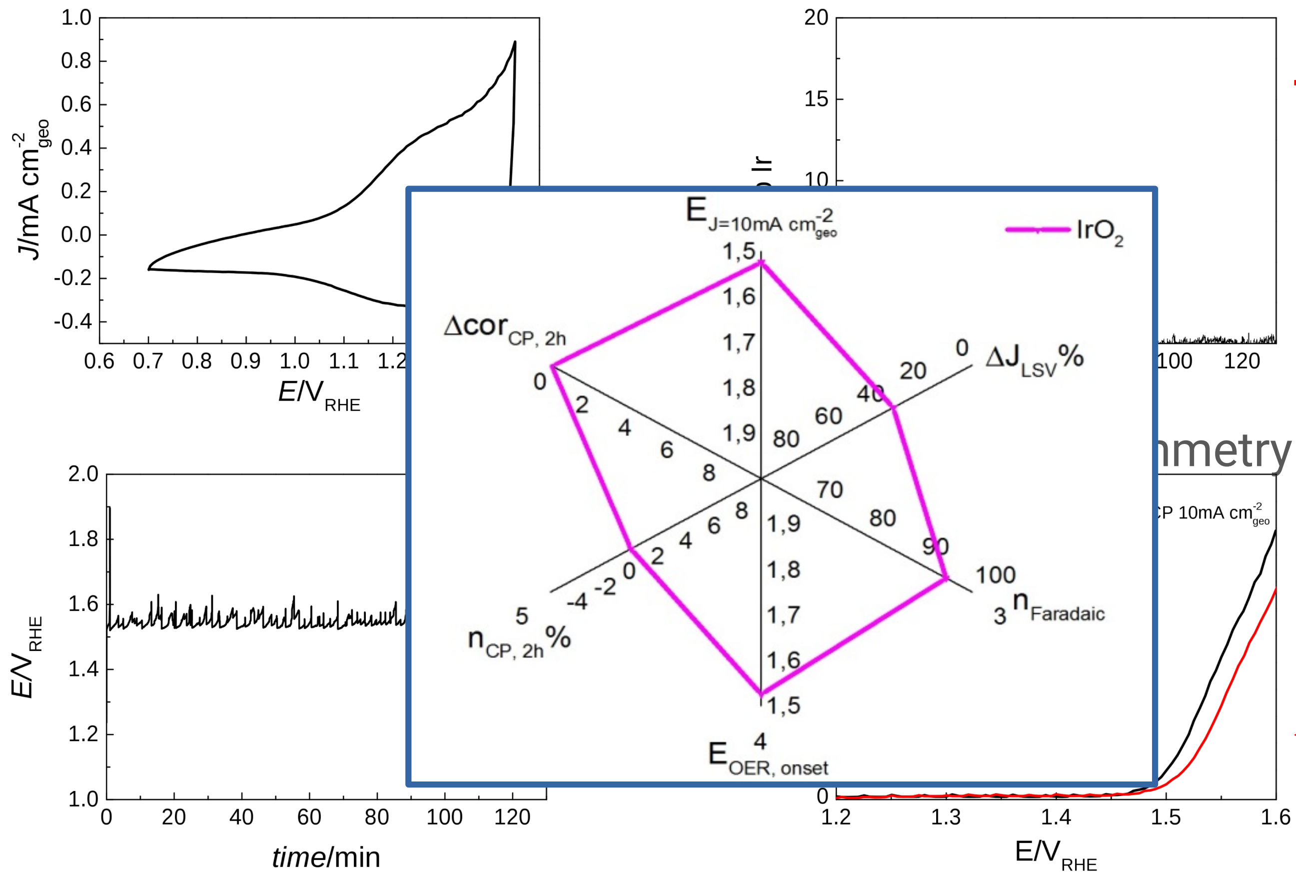


Minimal catalyst corrosion

LSV – High stability

IrO_2 - 0.1M $HClO_4$ 100µg/cm²

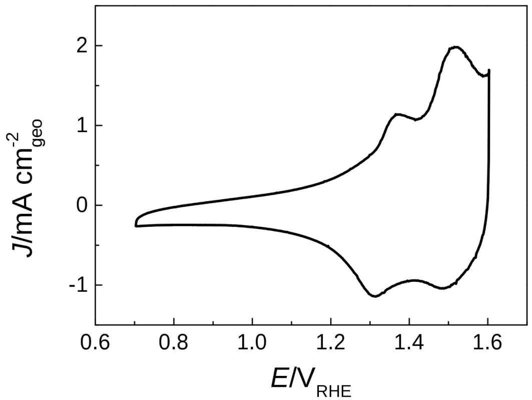
ICP-OES profiles during CP 10mA/cm²



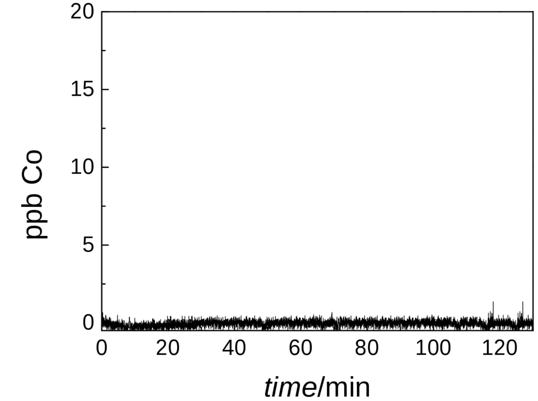
LSV – High stability

Minimal catalyst corrosion

Co_3O_4 - 1M KOH 100µg/cm²

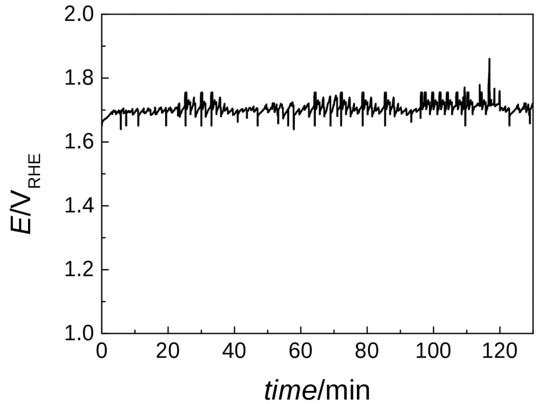


ICP-OES profiles during CP 10mA/cm²

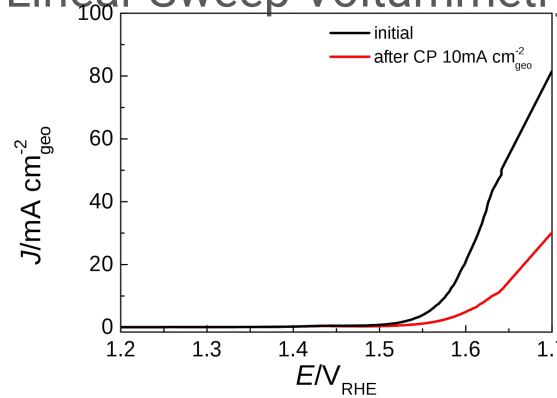


Minimal catalyst corrosion

LSV – Low stability



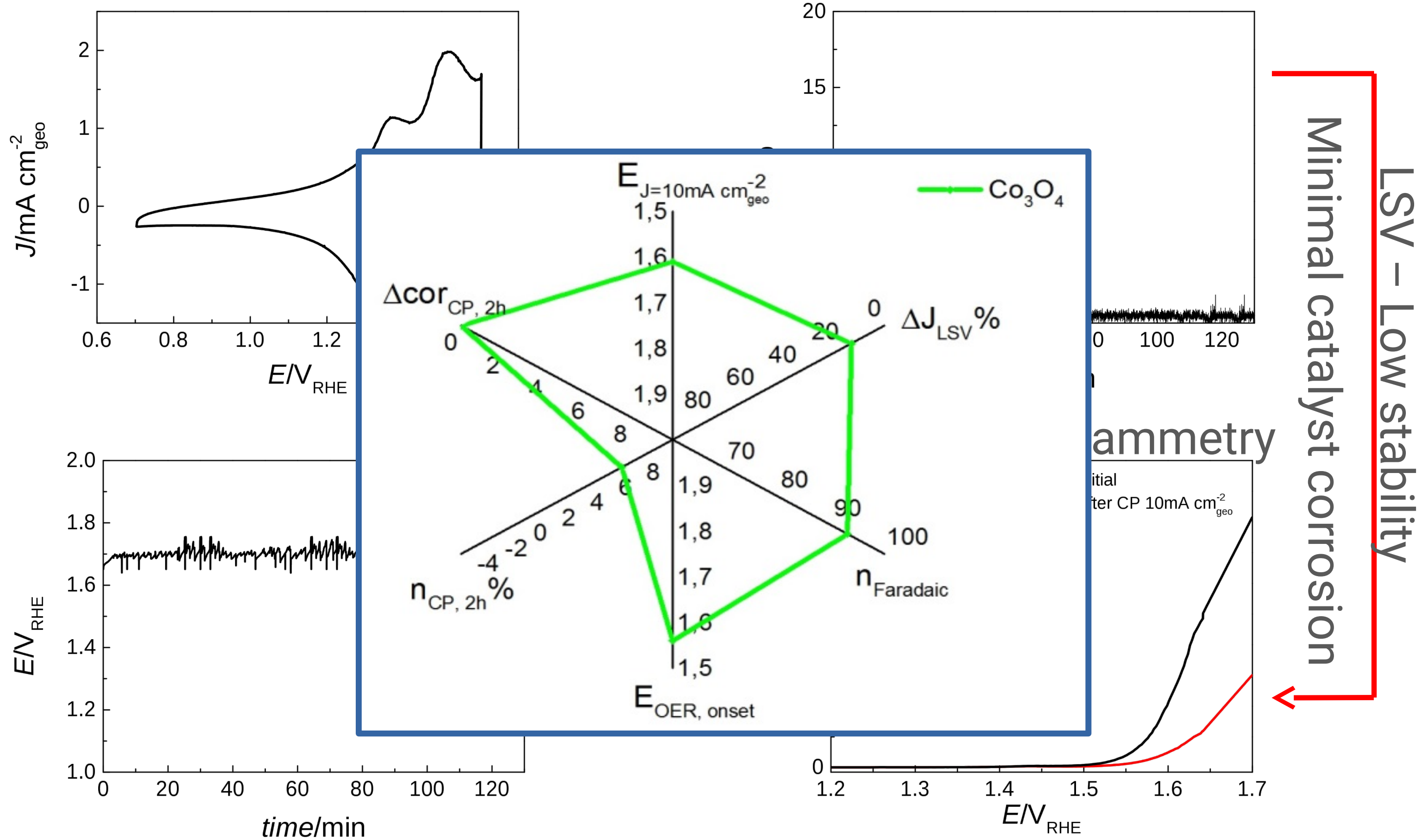
Linear Sweep Voltammetry



Different deactivation mechanism

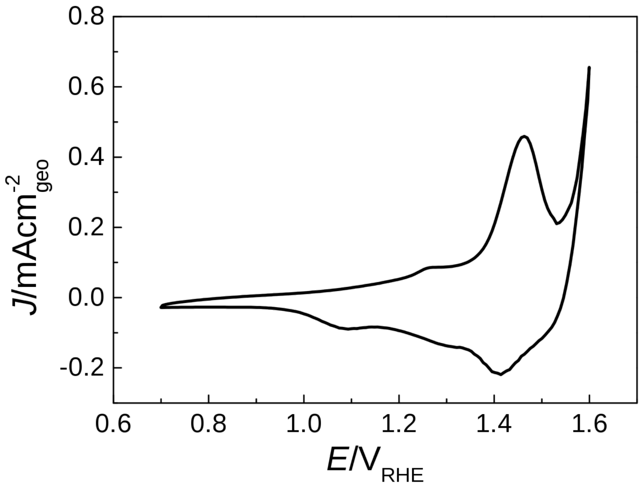
Co_3O_4 - 1M KOH 100µg/cm²

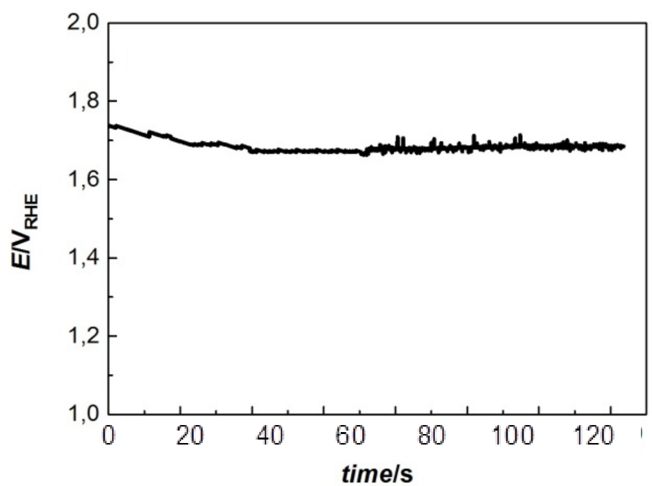
ICP-OES profiles during CP 10mA/cm²



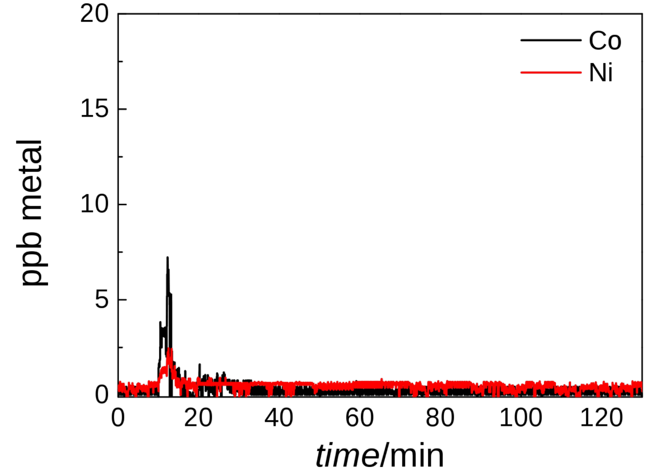
Different deactivation mechanism

$NiCo_2O$ - 1M KOH 100µg/cm²

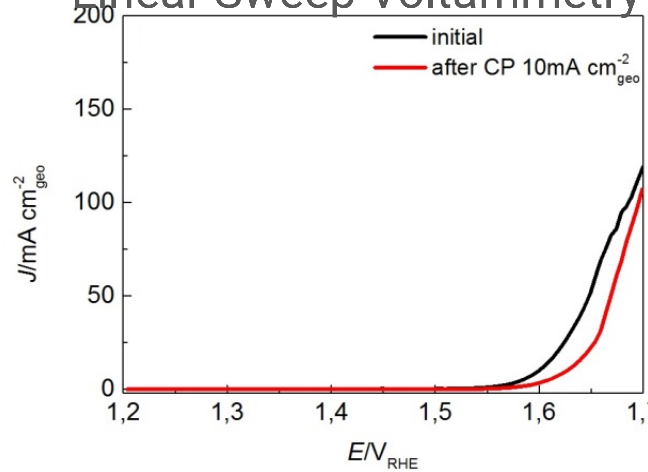




ICP-OES profiles during CP 10mA/cm²



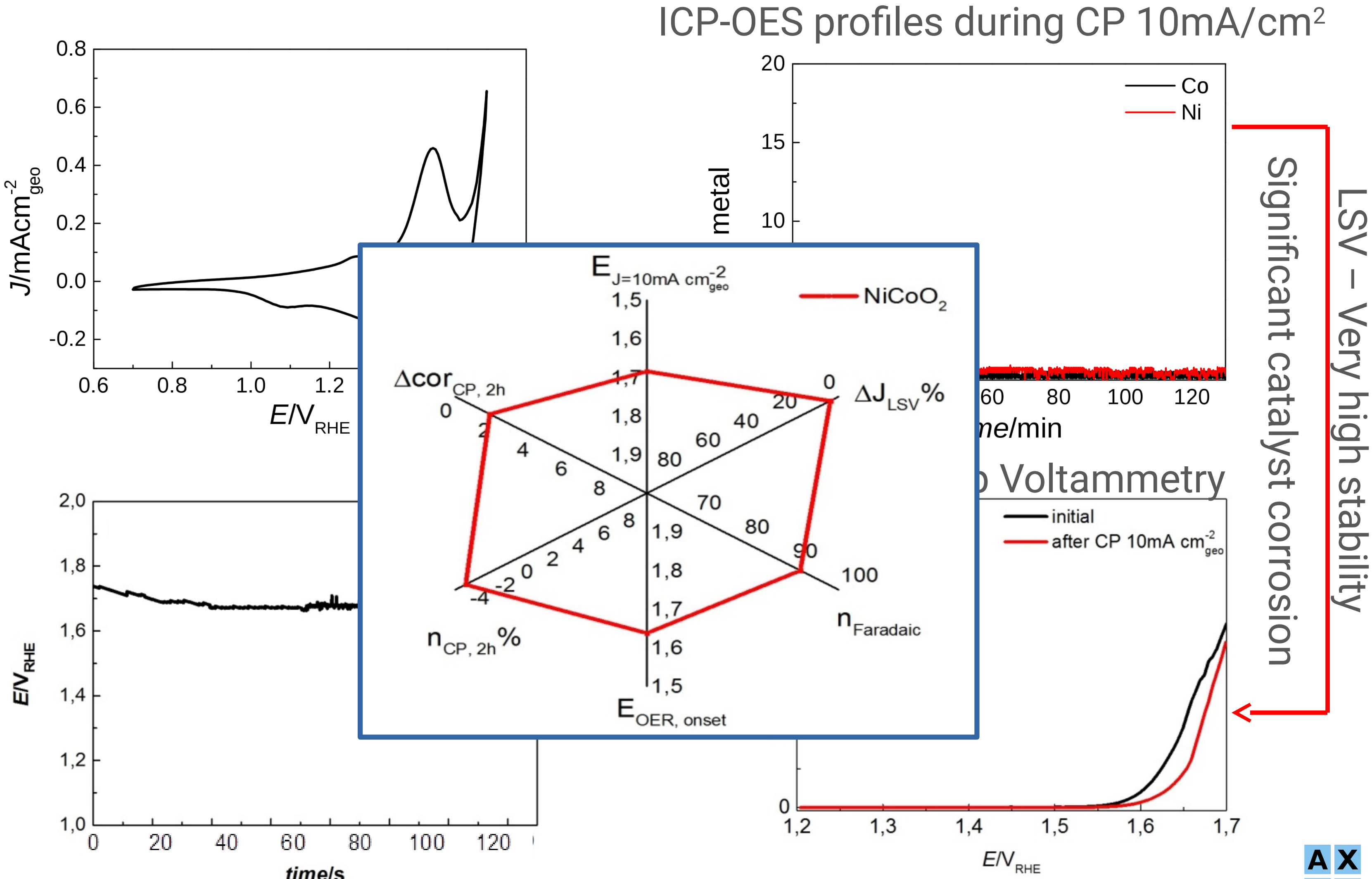
Linear Sweep Voltammetry



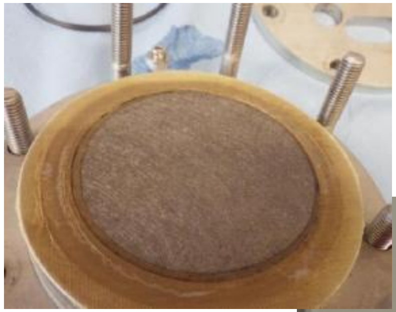
Significant catalyst corrosion

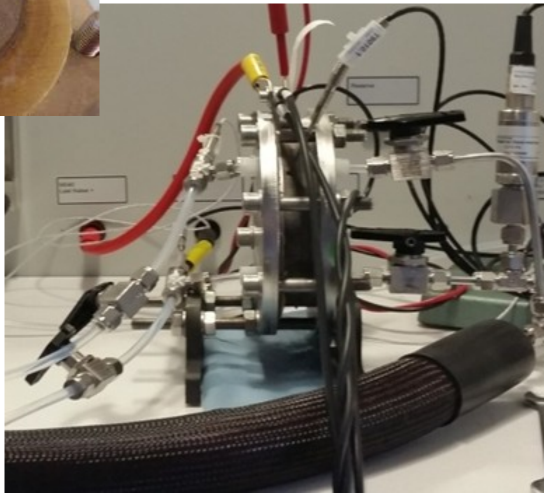
LSV – Very high stability

$NiCo_2O$ - 1M KOH 100µg/cm²



Reserach on different lengthscales





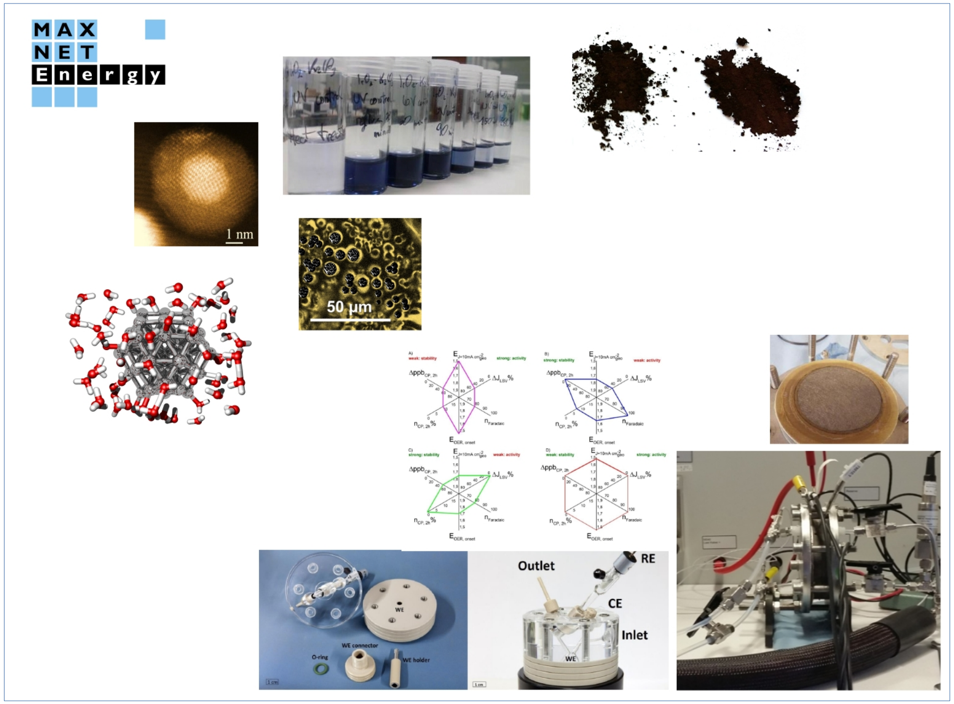
<u>MAXNET Energy Electrolysis Cell</u>

- MPI-DKTS / Dept. Sundmacher
- full electrolysis cell, 10 cm^2
- two setups: acidic and new alkaline
- scale up platform
- pre- and post-analysis
- common ground for material scientists, electrochemists, analytical chemistry and chemical engineers

<u>Presentation in November 2017 – "scientific" alkaline electrolysis cell:</u>

- Cell design and operation MPI DKTS
- Hydrogen evolution catalyst Pt@C from MPI CEC
- Oxygen evolution catalyst Fe/Co/Ni catalysts from CEC, FHI, MPI KoFo
- Binder and membranes: MPI KG Golm

Vielen Dank für Ihre Aufmerksamkeit



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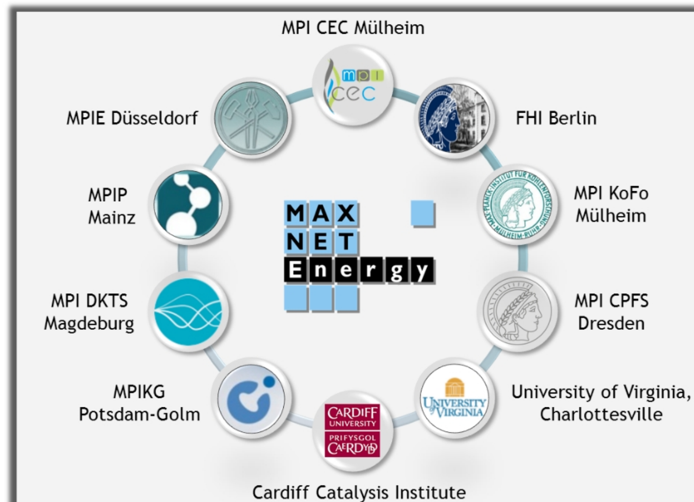

http://maxnetenergy.cec.mpg.de