Development of Highly Efficient Raney Nickel Electrodes for Alkaline Water Electrolysis

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Outline

- Introduction
- Electrode development by applying plasma spray technology
- Electrochemical results
- Cost reduction by applying atmospheric plasma spraying (APS)
- Electrode fabrication for power-to-gas plant in Wyhlen, Germany
- Summary

HYSOLAR – Hydrogen from Solar Energy (1986-1995)

German - Saudi-Arabian project for solar hydrogen production

Erection of research and demonstration plants:

- Hydrogen production (350 kW in Riad, 10 kW in Stuttgart)
- Hydrogen usage (Hydrogen combustion engines, AFC, PAFC, catalytic burner)
- Total efficiency: 5,2 %,
  Efficiency PV panel: 8,1 %,
  Efficiency electrolyzer: 80,0 %

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Electrolyzers of HYSOLAR Project: Experimental/Test systems
P = 2 – 350/500kW, p = 1 -10bar$_{abs}$, T = 40 – 95°C

HT

HT/DLR

HT/

DLR

Supplier:

HYDROTECHNIK

3 / 2 kW

HS

HS/DLR

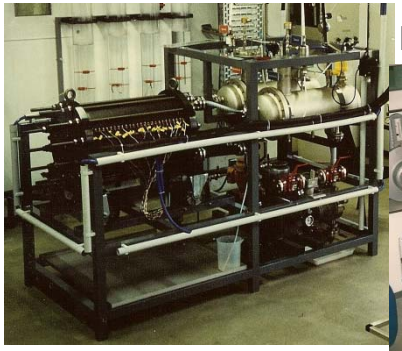
Supplier:

HYDROGEN SYSTEMS /

METKON ALYZER 10kW

MA

MA/DLR



FZJ

FZJ/DLR

Supplier:

FZ JÜLICH

10 kW

FZJ/DLR

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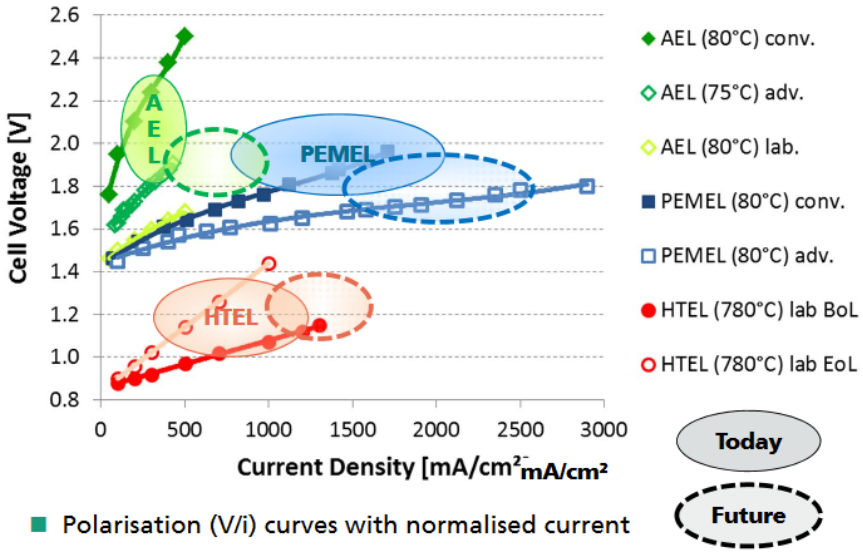
Targets of DLR Electrode Development

(1) Performance and Efficiency of Water Electrolysis
Comparison of different EL technologies at stack level.



Source: http://www.fch.europa.eu/sites/default/files/2%20Water%20Electrolysis%20Status%20and%20Potential%20for%20Development.pdf

Performance: Operation at >0.6 A cm^{-2} with a cell voltage of 1.8 V

Durability: 10 000 hours with 2 000 on-off cycles with less than 10% degradation

Cost: Reduction by 30% at stack level

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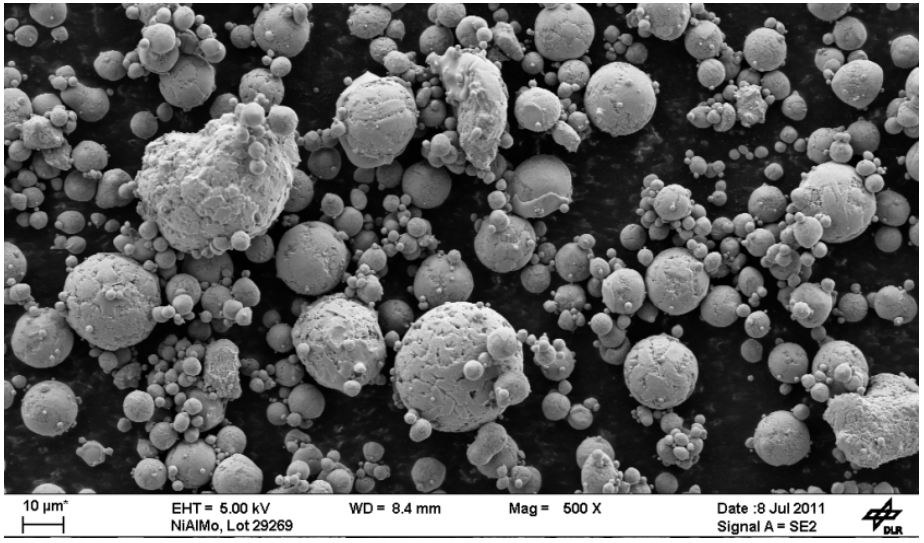
Benchmarked Catalyst for Alkaline Water Electrolysis

Raney Ni — 100 mV overpotential at 500 mA cm^{-2} — 28 wt% KOH, 80°C

HER	OER
NiAl (54:46 wt%) alloy NiAlMo (39:44:17 wt%) alloy	NiAl (54:46 wt%) alloy NiAl + Co_3O_4



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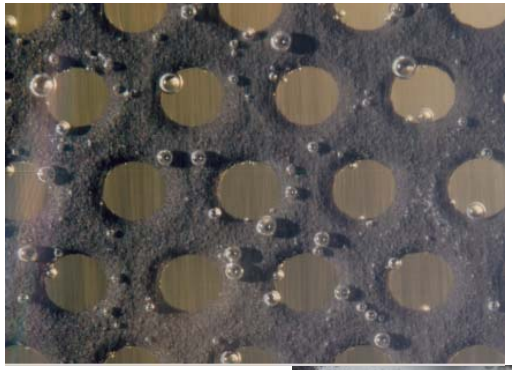
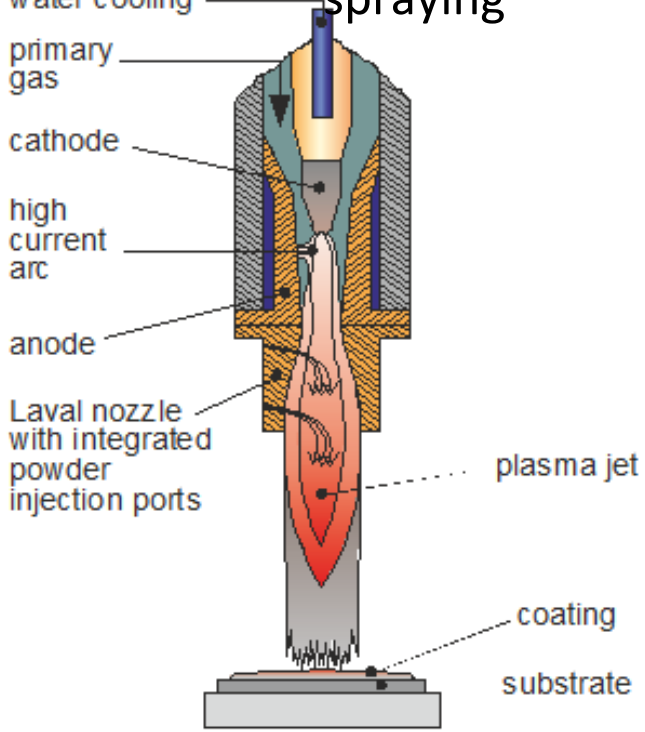
VPS Raney Ni Coating

Electrode development for low overpotential, long lifetime and low costs

Using VPS coating technology electrodes were developed with low-cost materials that have a high efficiency/low overpotential and little degradation in intermittent operation

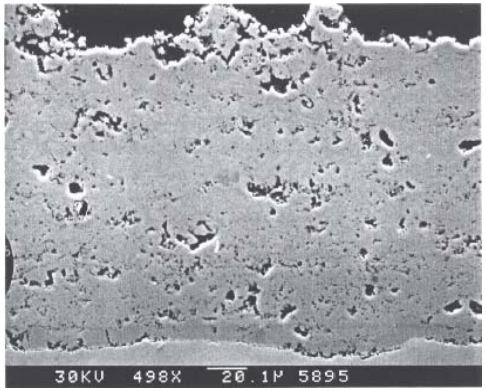


Vacuum plasma spraying

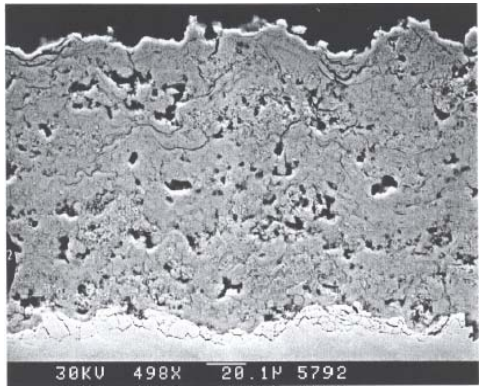


VPS Raney Ni Coating

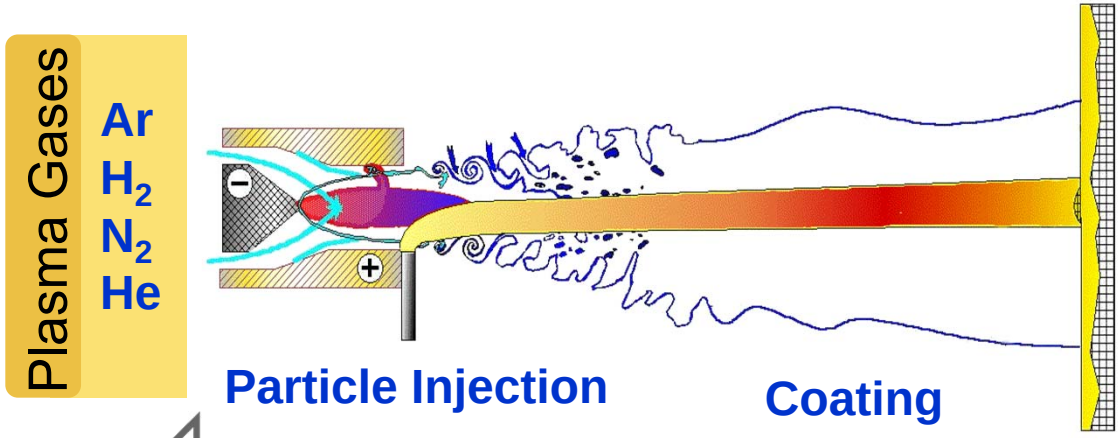
Plasma-sprayed Raney Nickel cathode before activation

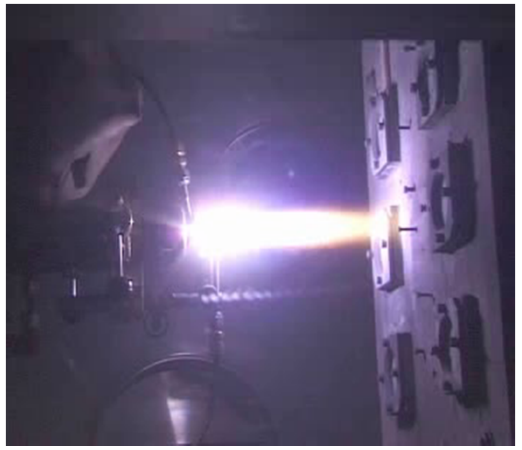


Plasma-sprayed Raney Nickel cathode after activation



Principle of Vacuum Plasma Spraying





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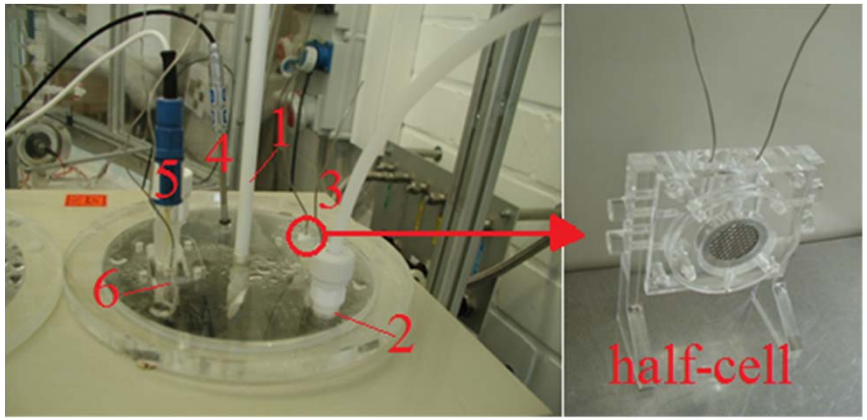
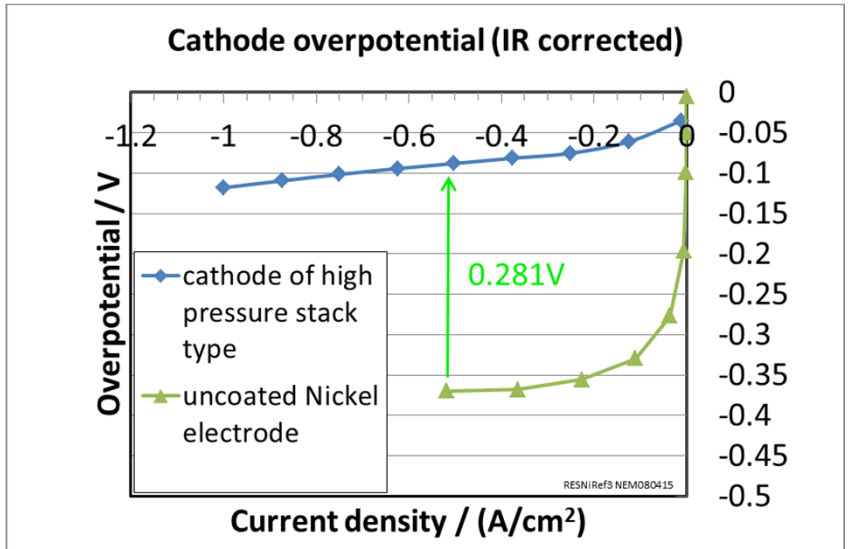
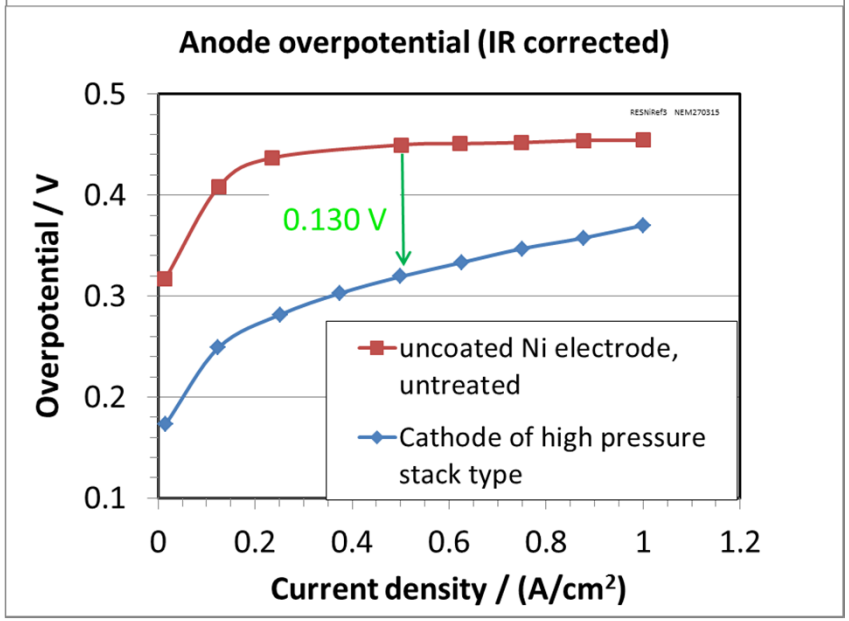
Electrode Performance – Half Cell Test Configuration

Half cell measurement
Electrode area: 4 cm^2 ; Cathode: NiAlMo
Anode: NiAl; Conditions: 70 °C, 30 wt.% KOH



1. Stirror fixer
2. Gas collector
3. Working electrode
4. Count-electrode
5. Reference electrode (Hg/HgO)
6. Thermocouple





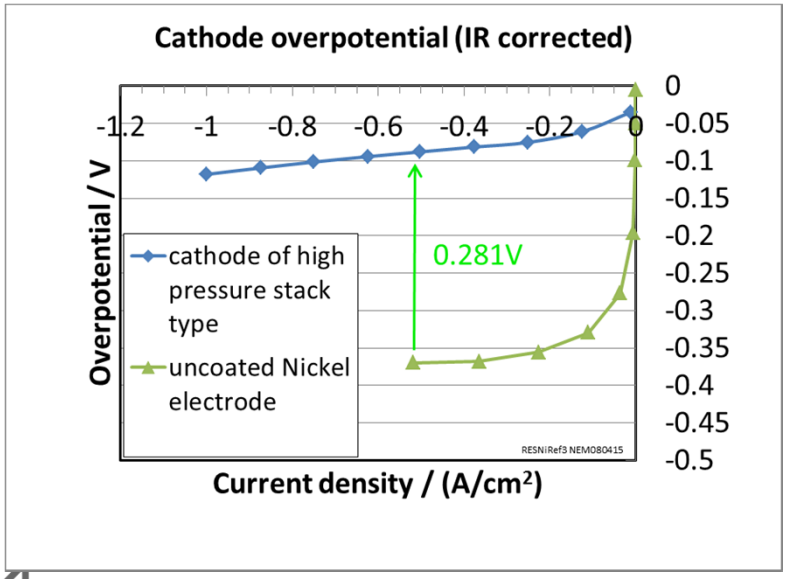
Electrode Development for Low Overpotential, Long Lifetime and Low Costs

Progress achieved:

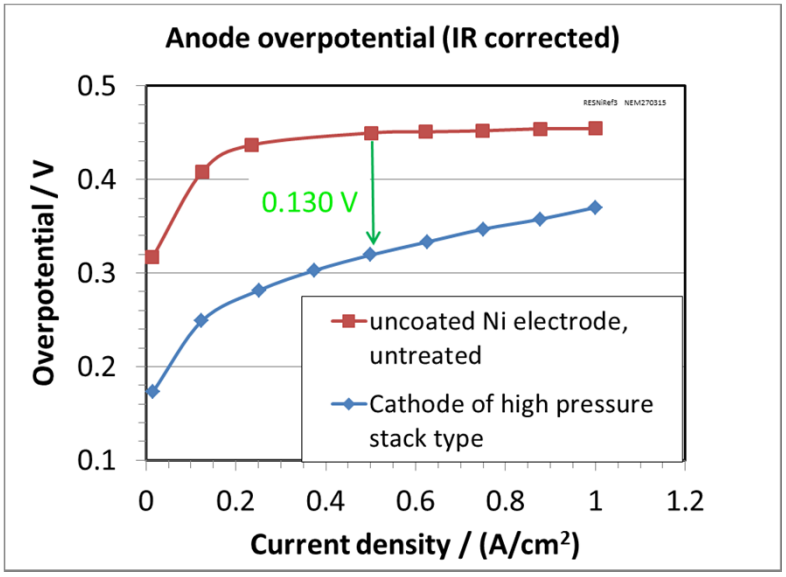
Long term test in intermittent operation, 0.5 A/cm², 70°C:

- After 1100 on-off cycles

cathode -10 mV



anode + 23 mV,



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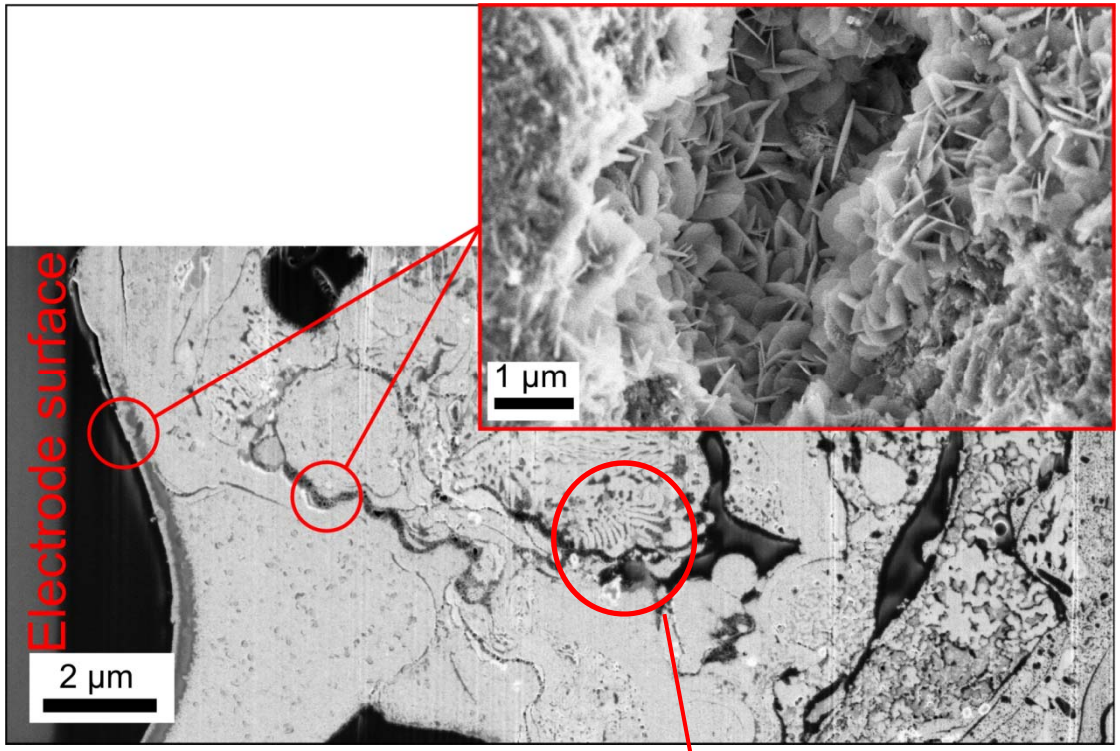
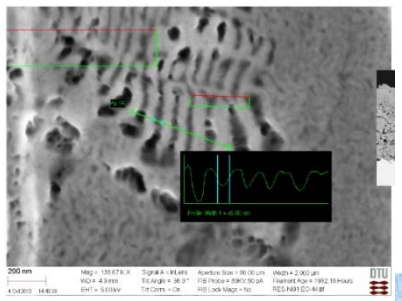
Investigation of Electrode Microstructure





Technical University of Denmark

- Highly heterogeneous microstructure with many subdomains.
- Dendritic structures stemming from the dissolution of Al from the Raney type NiAl alloy particles.
- Desert rose like nano flake structures ($Ni(OH)_2$) observed in the pores especially after long term operation

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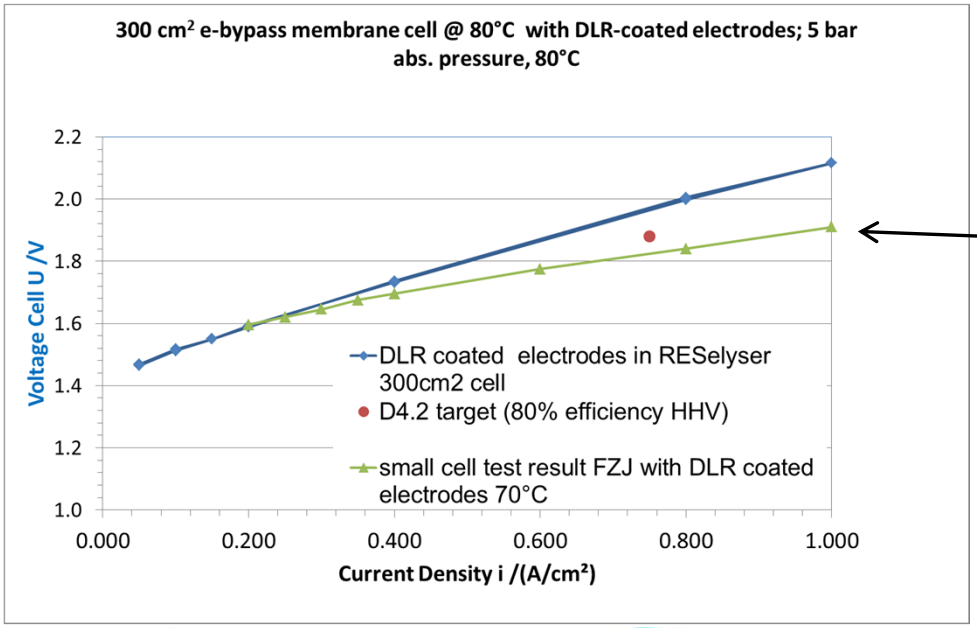
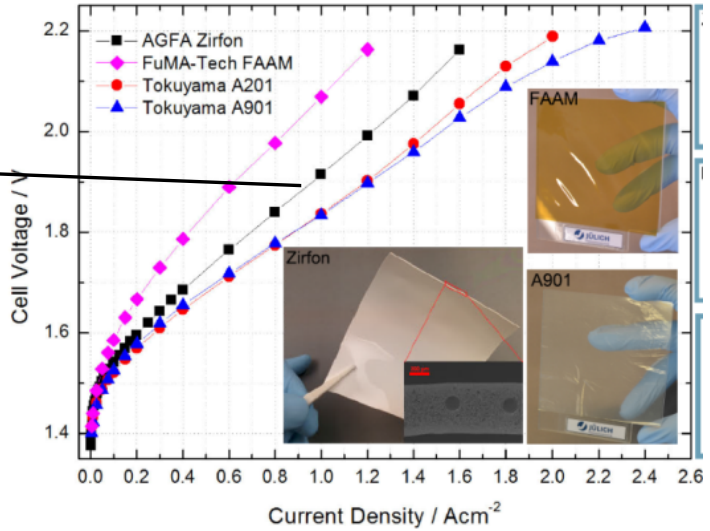
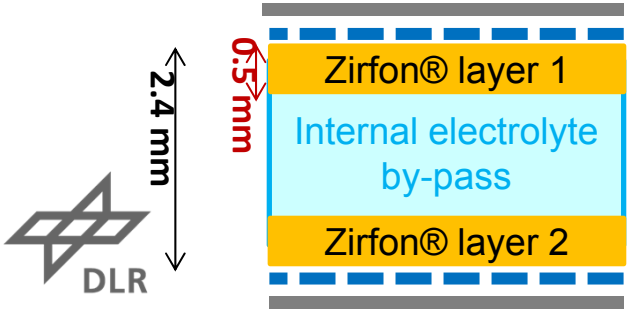
Electrode Performance – Full Cell Test







- Double side coated PPS spacer-fabric, Zirfon® (ZrO_2/polymer composite) dual layer
- Variation of permeability of Zirfon layers: from 120 l/(h m² bar) to 900 l/(h m² bar)
- Separators of 300 cm² delivered for cell and stack integration
- Technical scale (2500 cm²) producibility demonstrated

FCH FUEL CELLS AND HYDROGEN JOINT UNDERTAKING

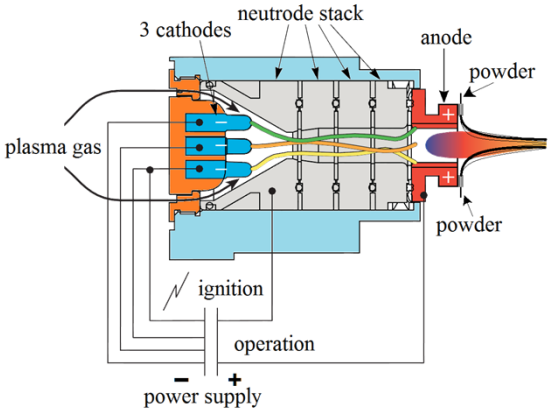
Electrode Fabrication by Air Plasma Spraying

- Variation of coating parameters by using an industrial-type APS torch (Triplex)

  -> significant cost reduction compared to VPS

- Impact on coating porosity by varying gas flow rates and hence particle velocities

Standard APS Torch



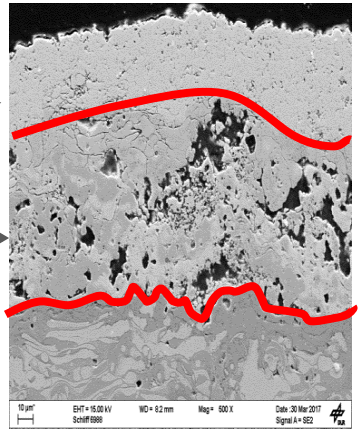
APS Triplex Torch

Flame: 30 mm - 100 mm
T: 2000 °C; v: < 300 m/s

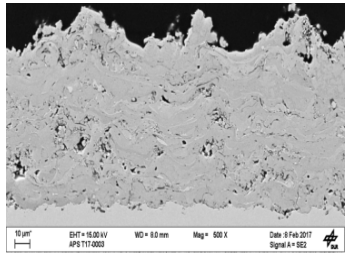
Flame: 50 mm – 200 mm
T: 3000°C; v: < 700 m/s

VPS →

APS → (standard)

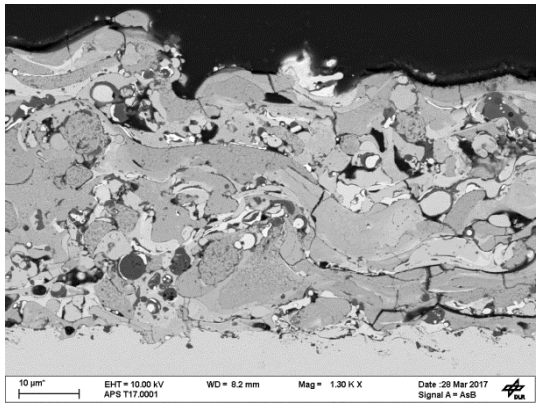


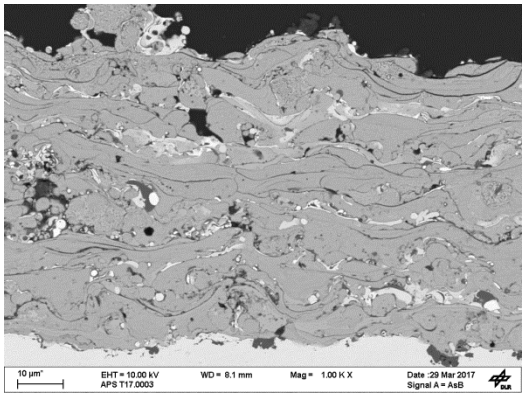
APS → (Triplex)

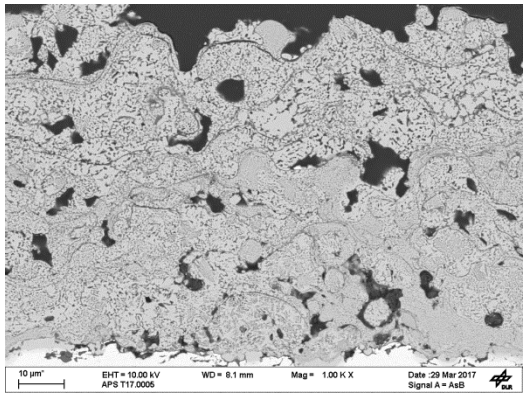


APS Electrodes Performance – Half Cell Configuration

NiAlMo coating cross section after spraying with APS Triplex with different particle velocity and activation







Plasma in-flight particle velocity

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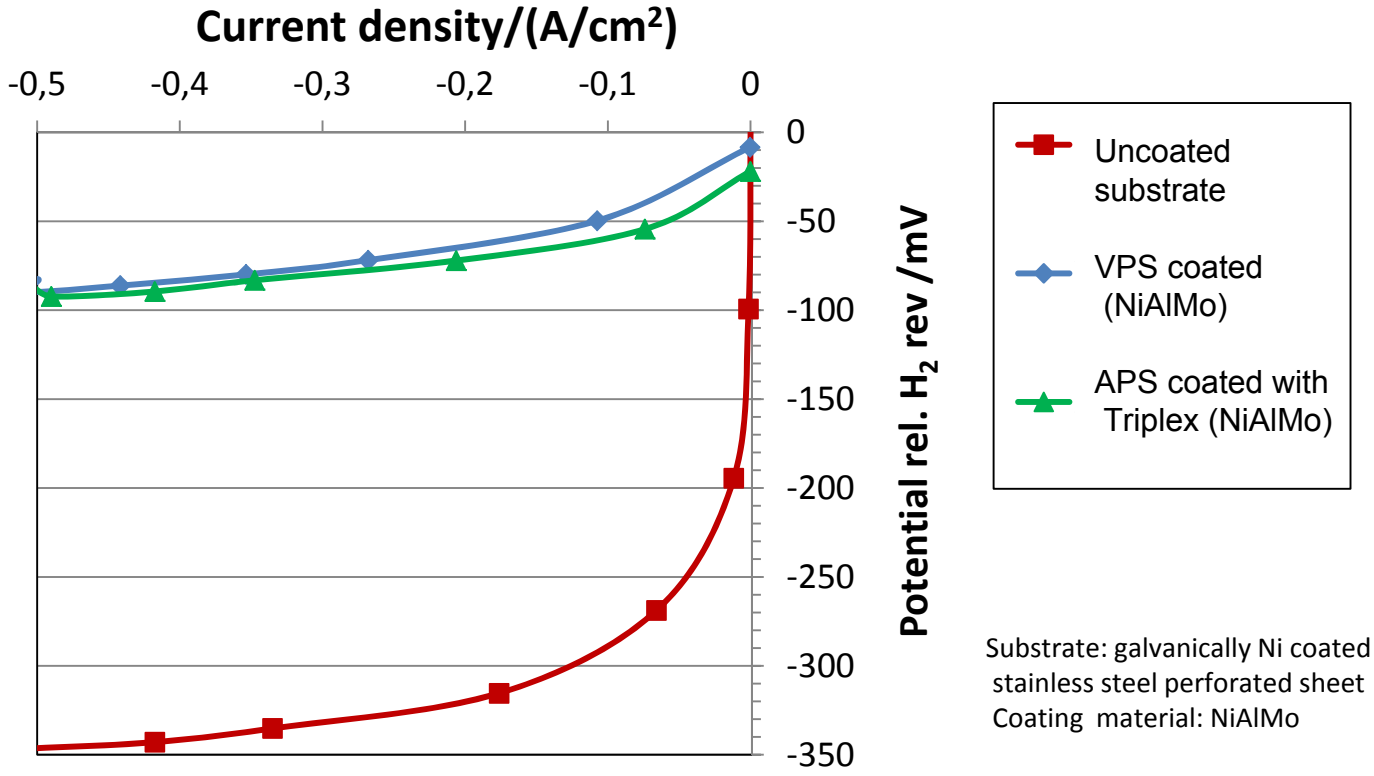
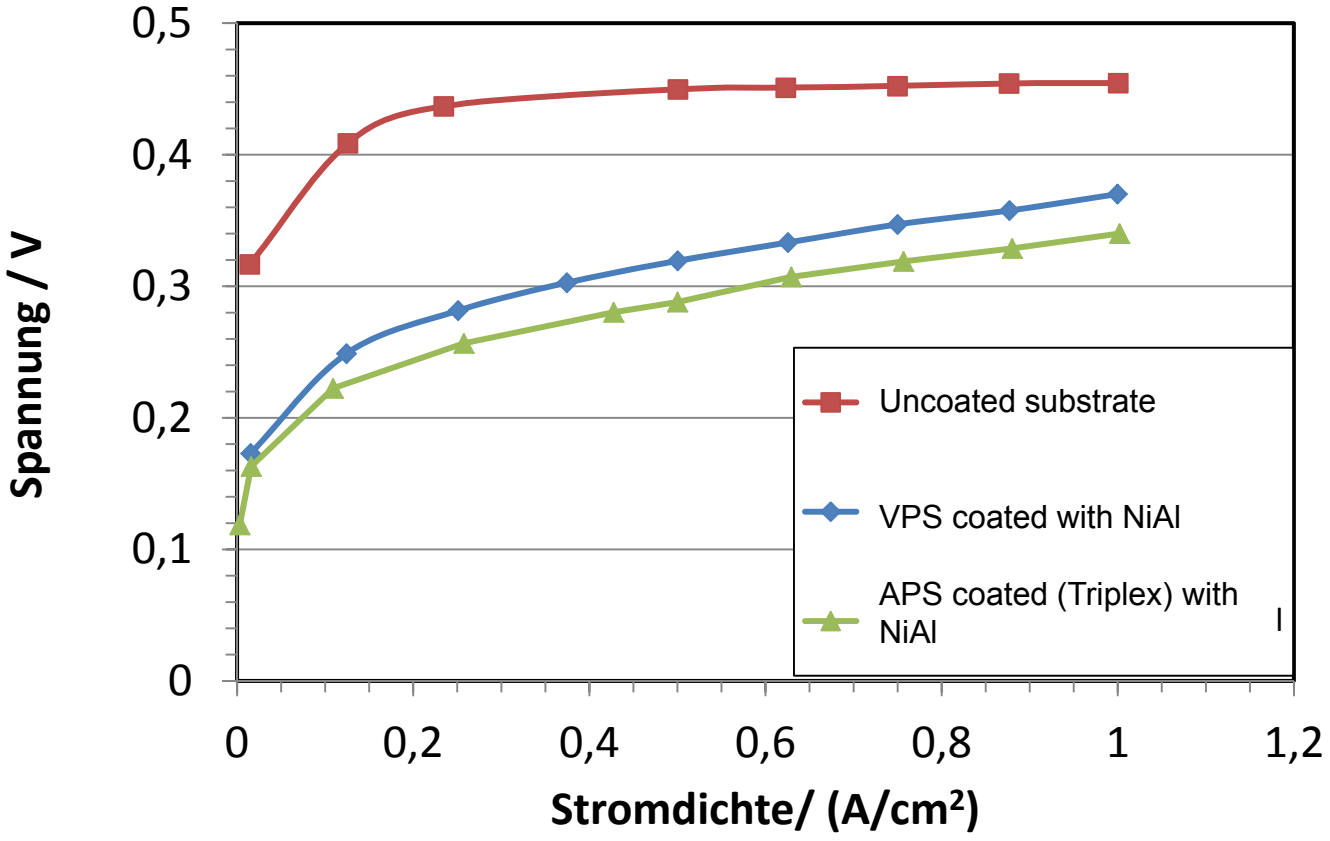
Recent Electrochemical Results of Coated Cathodes



Substrate: galvanically Ni coated stainless steel perforated sheet
Coating material: NiAlMo

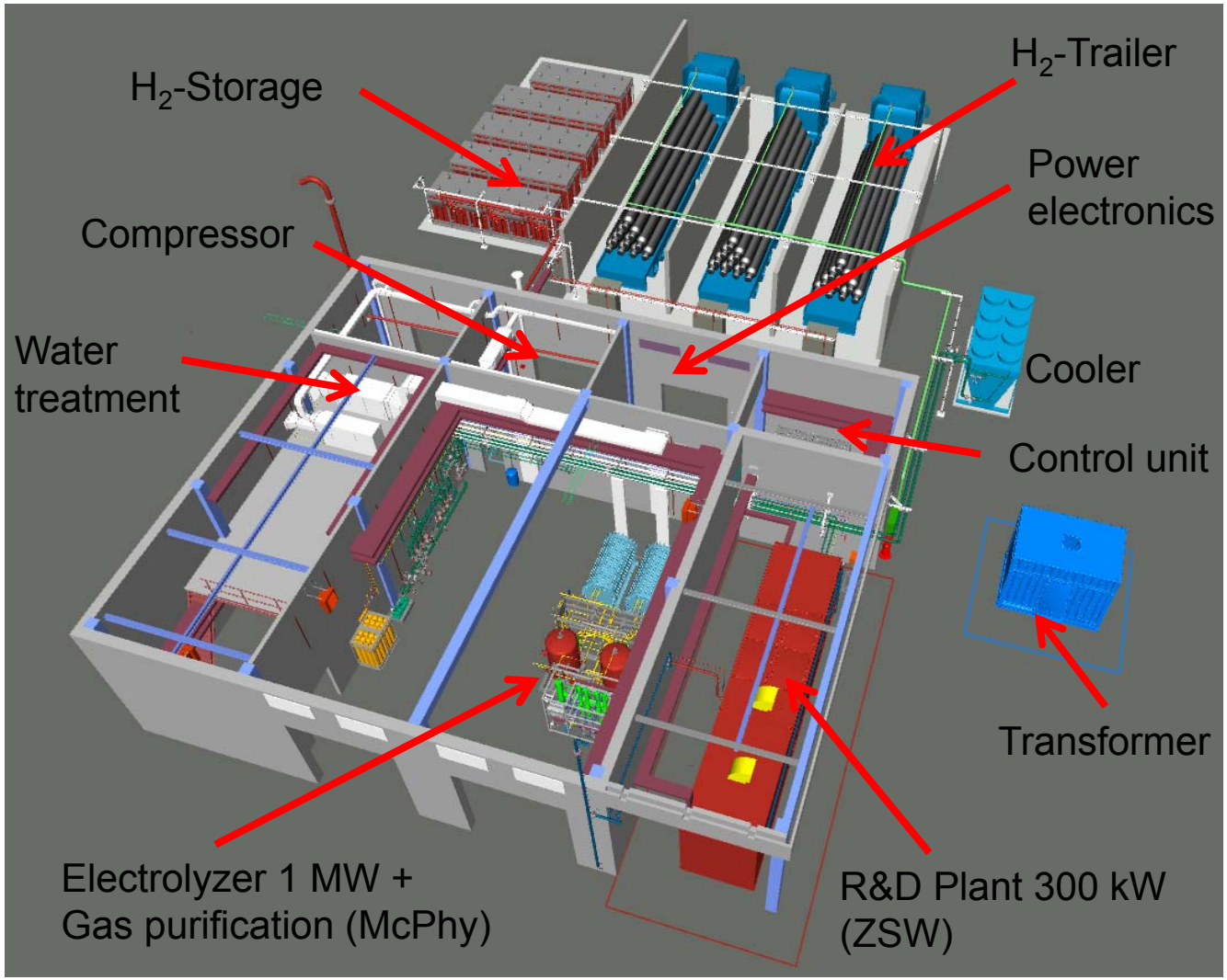
Recent Electrochemical Results of Coated Anodes



Power-to-Gas Plant in Wyhlen, Germany
Planning of Site

Source: Energiedienst

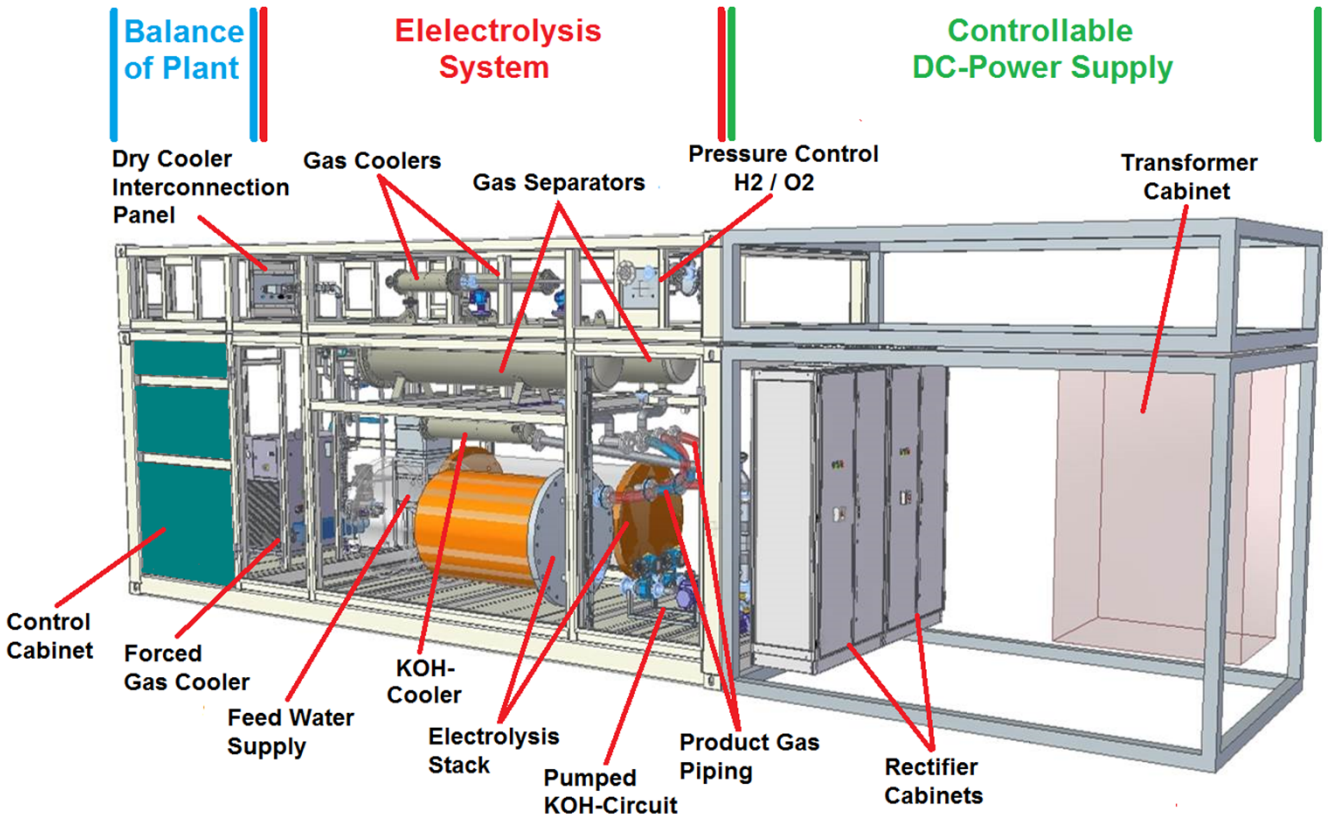
Power-to-Gas Plant in Wyhlen, Germany
Planning of Site



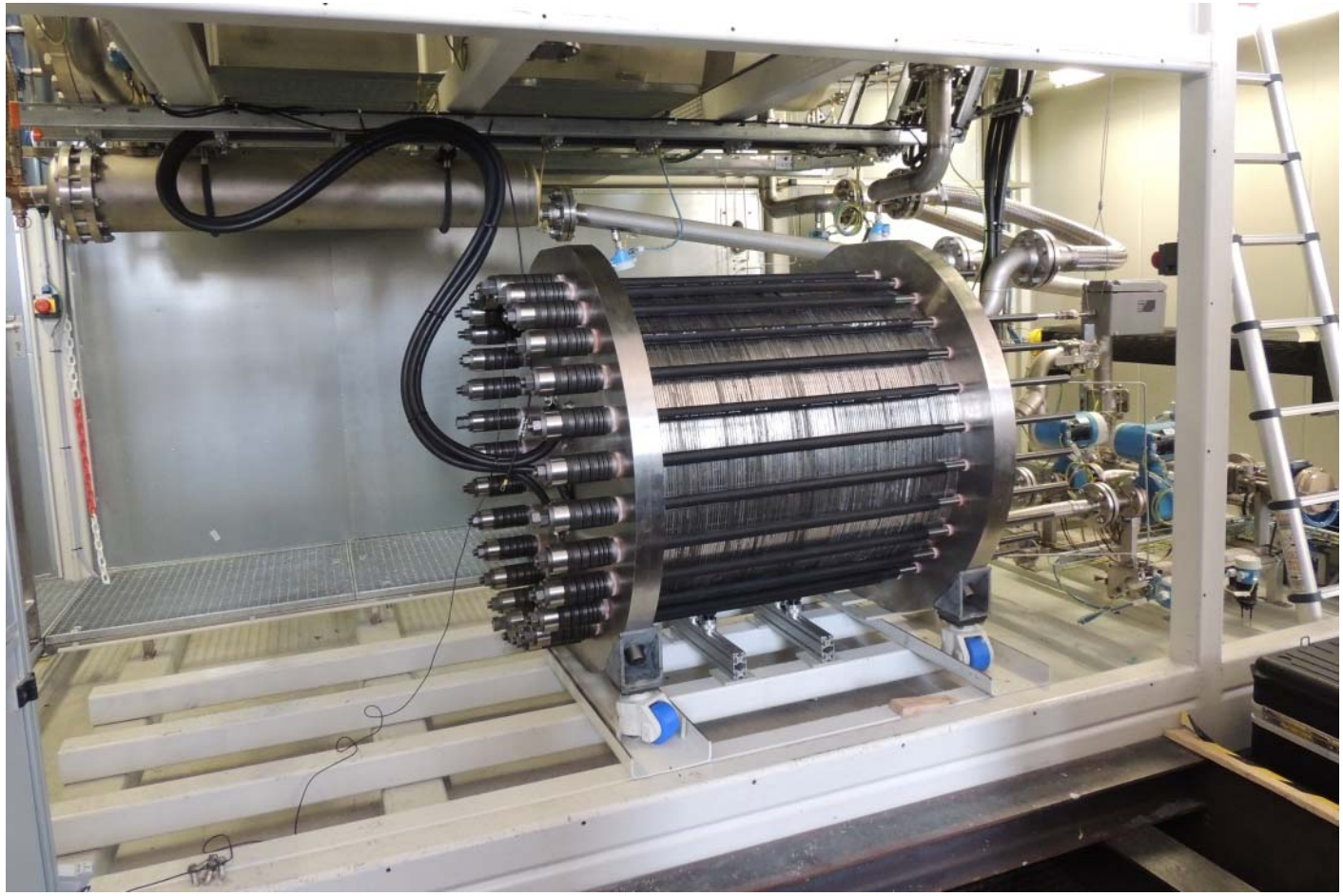
Source: Energiedienst / Haas Engineering

Fraunhofer ISE DVGW DLR ZSW

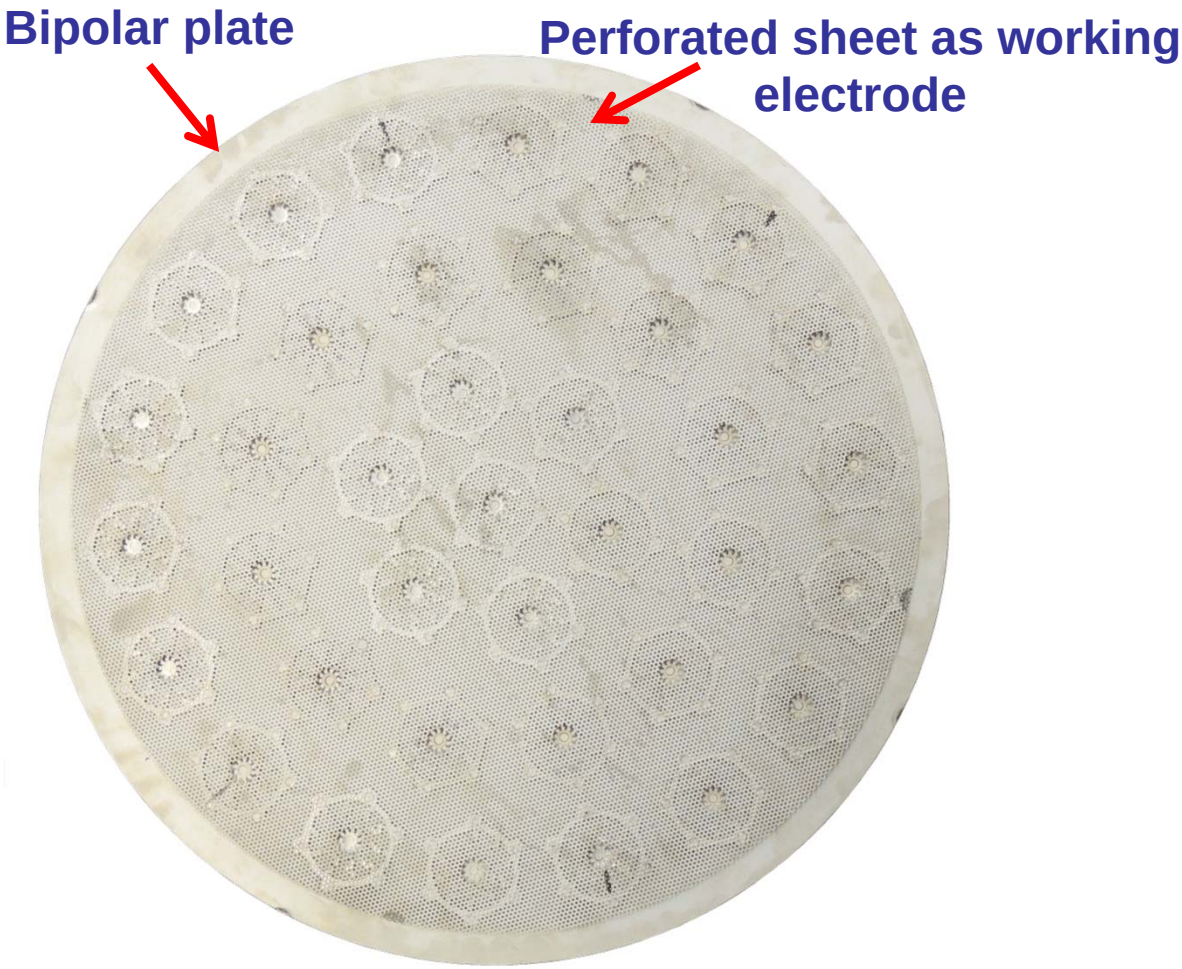
Light House Project „Power to Gas“
Pressurized Alkaline Electrolyzer of ZSW



Advanced Alkaline Electrolysis Stack of ZSW (300 kW Stack for Pressurized Operation)



3000 cm^2 Electrode Packages (Effective area 2750 cm^2) for Pressurized Alkaline Electrolyzers



Summary

- Based on former experience DLR continues with the development of efficient and cost-effective electrodes for alkaline water electrolysis.
- Hydrogen and oxygen evolution electrodes using Raney alloy materials are developed by applying plasma spray technology and are electrochemically characterized.
- Low cell voltage around 1.8 V at a current density of 0.6 A/cm^2 was achieved.
- The change from vacuum plasma spraying to atmospheric plasma spraying results in a significant cost reduction for electrode fabrication.
- Electrodes with a size of 3.000 cm^2 will be manufactured in the coming months to equip a 300 kW electrolyzer for a power-to-gas R&D plant in the frame of the lighthouse project „P2G-BW“

Acknowledgment

Financial support through the Ministry of Economics of the State of Baden-Württemberg (Lighthouse Project „Power-to-Gas-BW“) and the FCH-JU Project „RESelyzer“ (Contract N° 278732) is gratefully acknowledged.

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Jake Bowen

Marcelo Carmo

Thank you

Dr. Günter Schiller

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APS vs VPS Electrodes Cost

	VPS	APS
Yield per day	3 m²	3 m²
CAPEX	2,8 million €	0,480 million €
Depreciation time	10 years	10 years
Machine cost per day	1272 €	218 €
Other operating costs per day	212 €	196 €
Machine + other operating cost per m²	494 €	138 €
Staff cost per day	528 €	528 €
Coating cost per m²	**670 €**	**314 €**

Cost reduction from VPS to APS can be above 50% and as much as 72%

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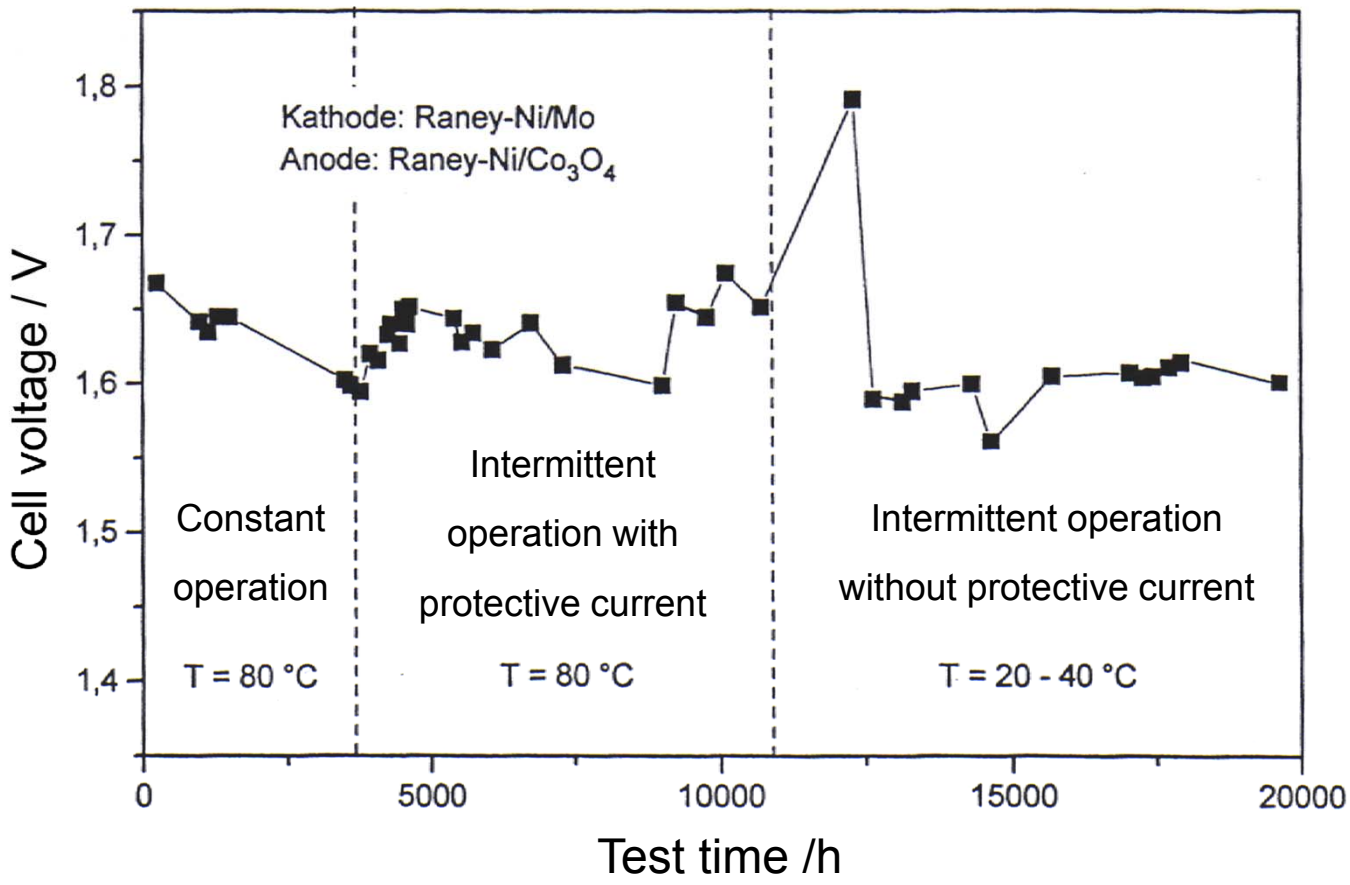
Long-Term Tests of Single Cell VPS Coated Electrodes at DLR



250 cm^2,
Cell voltage
at 0.3 A/cm^2
at 80°C

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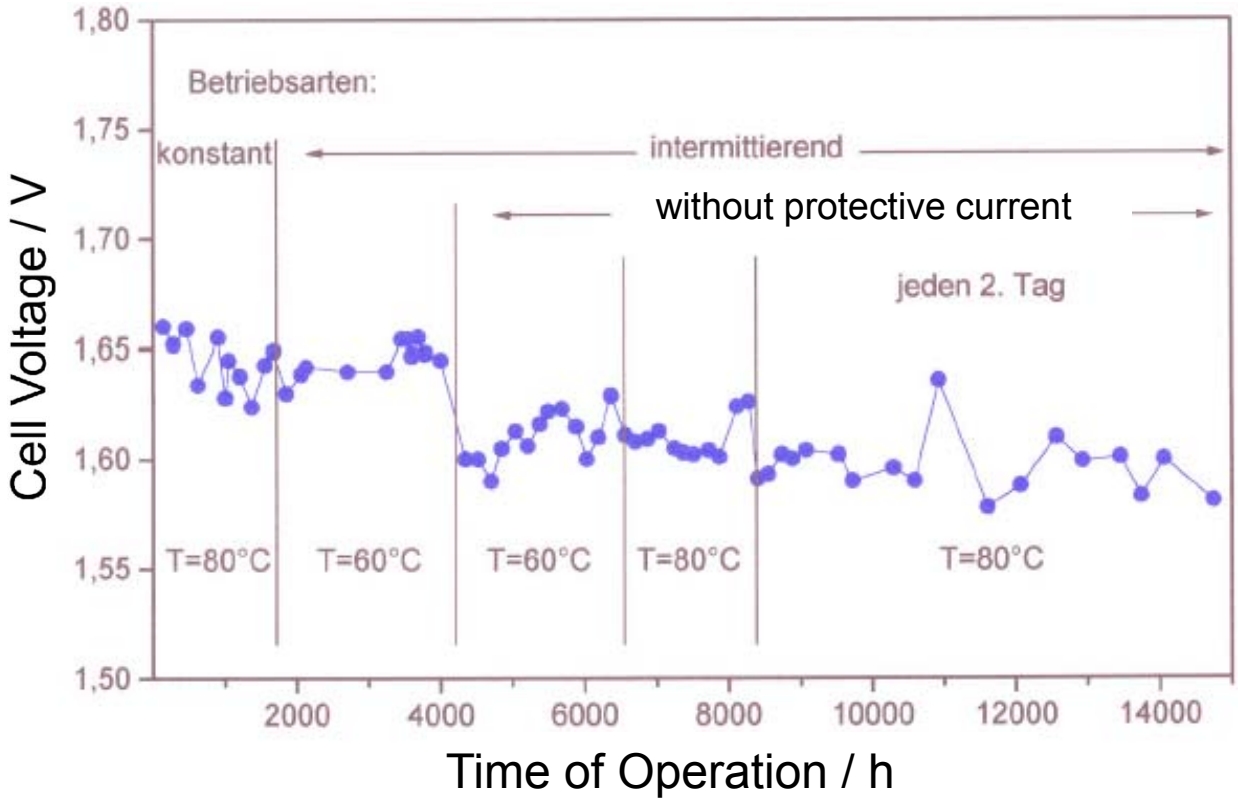
Long-Term Measurement with Plasma Sprayed Electrodes

Time evolution of cell voltage with plasma-spayed electrodes (600 cm^2) at reference conditions (300 mA/cm^2, 80° C)



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