JÜLICH FORSCHUNGSZENTRUM
1. Workshop der SVI-Topics 2 & 4
Potenziale neuer Hoch- und Niedertemperaturmaterialien
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Aula im Technologiezentrum Jülich

Materials for low-cost components of proton exchange membrane water electrolyzers

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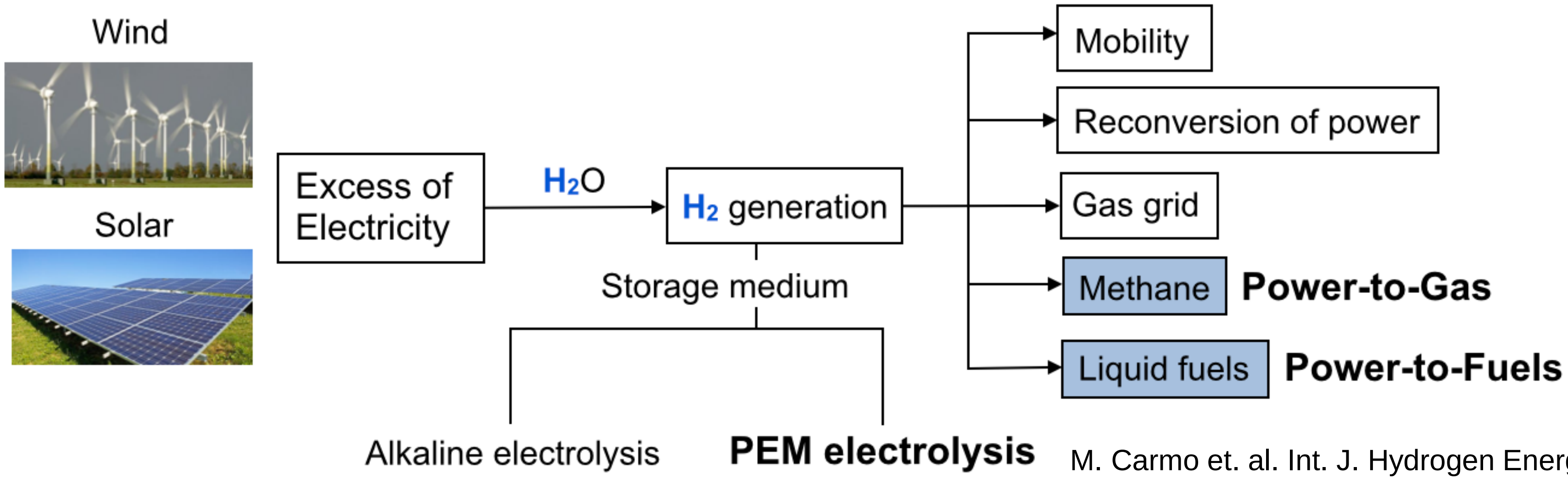
Outline

- H_2 as an energy vector, PEM electrolyzer component cost breakdown
- Oxygen evolution reaction (OER) catalysts
- Coatings for stainless steel bipolar plates (BPP)
- Coatings for gas difussion layers (GDL) / current collectors (CC)
- Summary

Hydrogen as energy vector



M. Carmo et. al. Int. J. Hydrogen Energy **2013**, *38*, 4901–4934.

Total energy waste from renewables in Germany has increased from **555 GWh** in 2013 to **1581 GWh** in 2014

Yearly Monitoring Report 2015, German Grid Agency, German Energy Supply

Advantages

- Low footprint by compact design
- Scalability by modular construction
- Overload capability (> 6 A/cm^2)
- Rapid response (dynamic operation)

Drawback

- Expensive components

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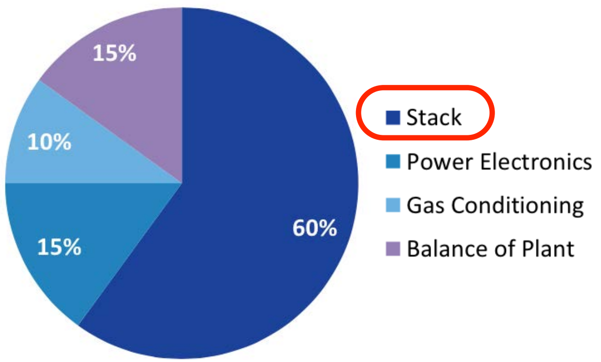
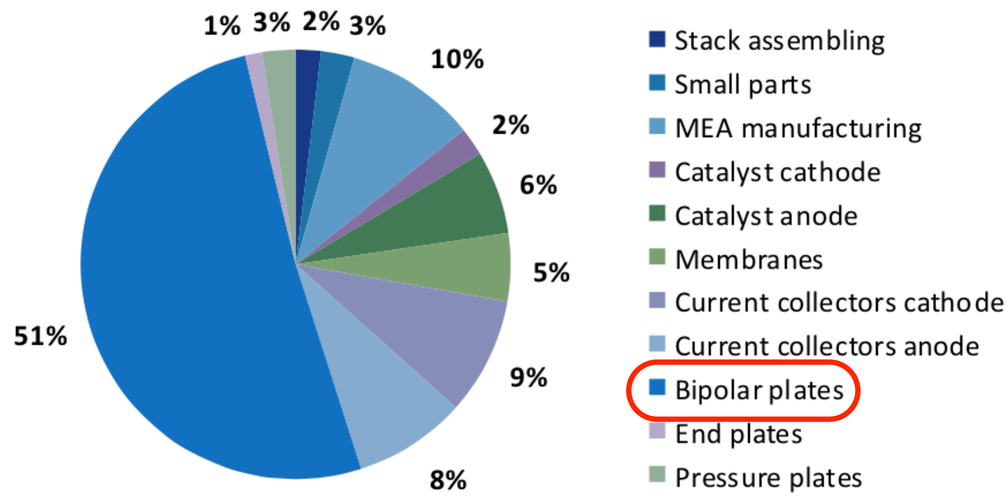
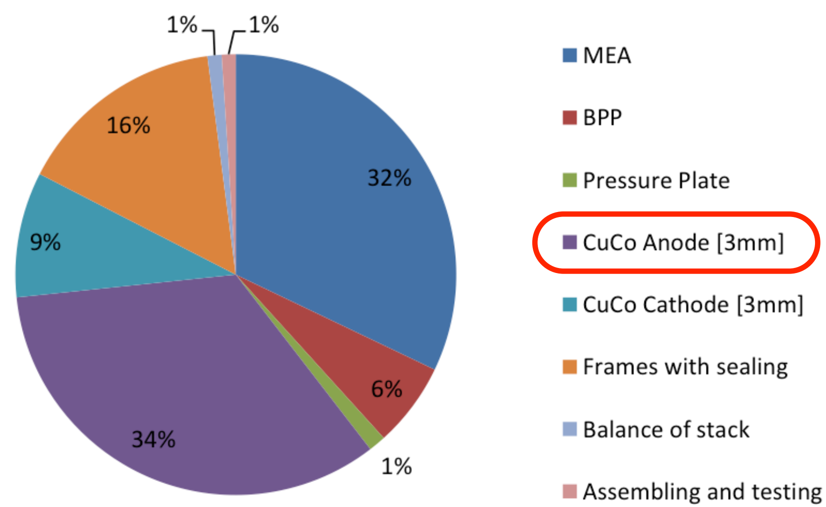
Cost breakdown of PEM electrolyzer system and stack



[a]Study on development of water electrolysis in the EU. Final Report. E4tech Fuel Cells and Hydrogen Joint Undertaking; 2014





- Stack comprises 60 % of the total cost of the PEM Electrolyzer system[a]
- Bipolar plates are the most expensive component (51%) of the stack[a].
- Currently the cost of the PMG catalyst (Ir and Pt) comprise only 8%
- Bipolar plates without flow field (6%). Anode current collectors (34%)[b]

[b]K. A. Friedrich, Studie über die Planung einer Demonstrationsanlage zur Wasserstoff - Kraftstoffgewinnung durch Elektrolyse mit Zwischenspeicherung in Salzkavernen, 2015.

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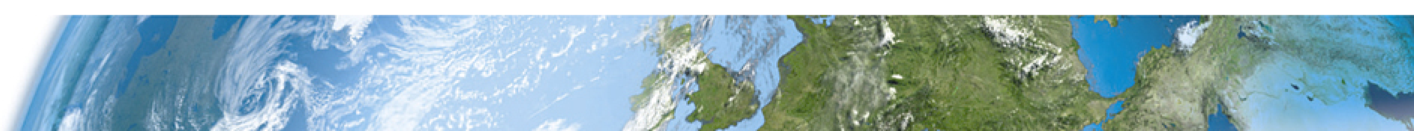
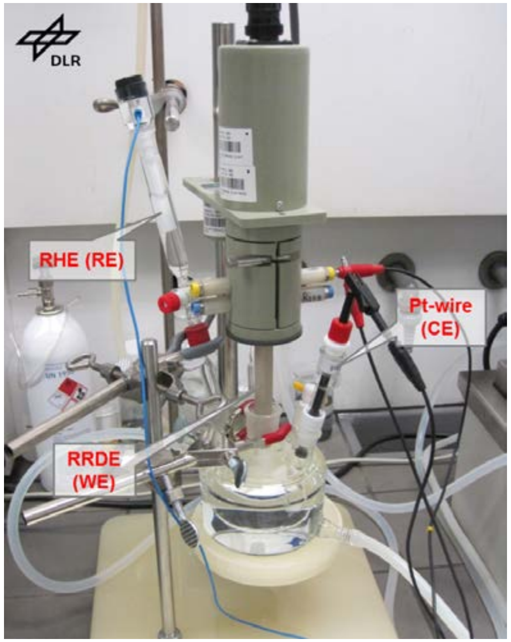


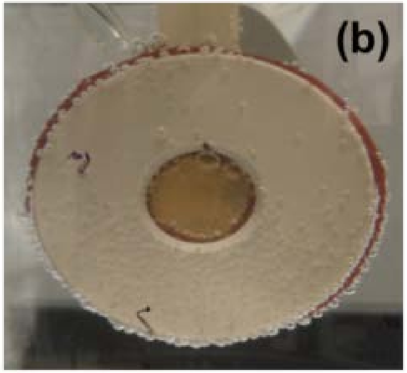
Evaluation of catalysts and coatings

HYDROGENICS
Advanced Hydrogen Solutions

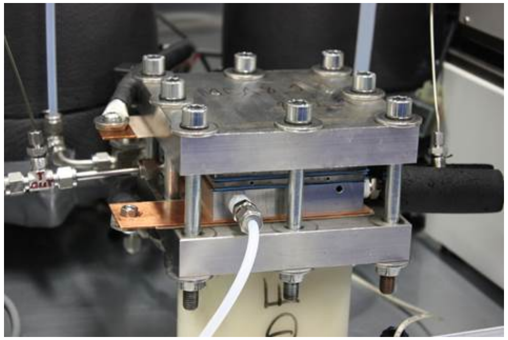
Rotating ring disc electrode (RRDE)



Sample holder for corrosion measurements (1 cm^2 exposed area)



4 Cell - 25 cm^2 - stack



6 Cell - 120 cm^2 – stack (E92 model)

0.75 - 2.5 Nm^3 H_2 h^{-1} “Hylyzer” PEM electrolyzer unit, 8 bar

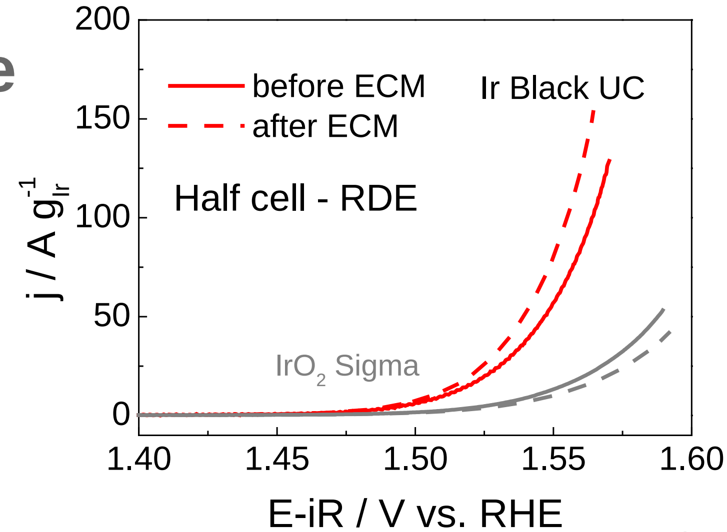
Oxygen evolution reaction catalysts

Benchmark PEM electrolyzer anode

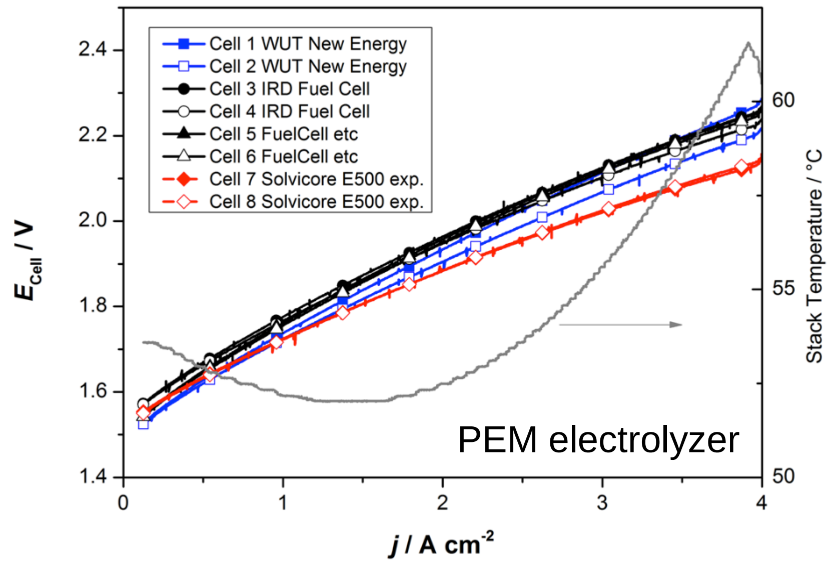
- Half cell measurements: OER activity of Ir-black (Umicore) is 3x higher than thermally treated IrO_2 (at 1.48V, 25 °C)
- MEAs with IrO_2 (thermally treated) show lower performance compared to those with Ir-black
- Half cell and single cell measurements correlates well with the PEM electrolyzer results
- Ir-black can be considered as benchmark anode in PEM electrolyzers

Company	Anode (mg cm^{-2})	Membrane	Cathode (mg cm^{-2})
Wuhan WUT	2	N115	0.8
IRD	2.3	N115	0.5
FuelCellsEtc	3	N115	3
E500 (Ir-black)	1	N115	0.9

*ECM: Electrochemical measurements



a)



Electrochim. Acta, **2016**, 210, 502–511

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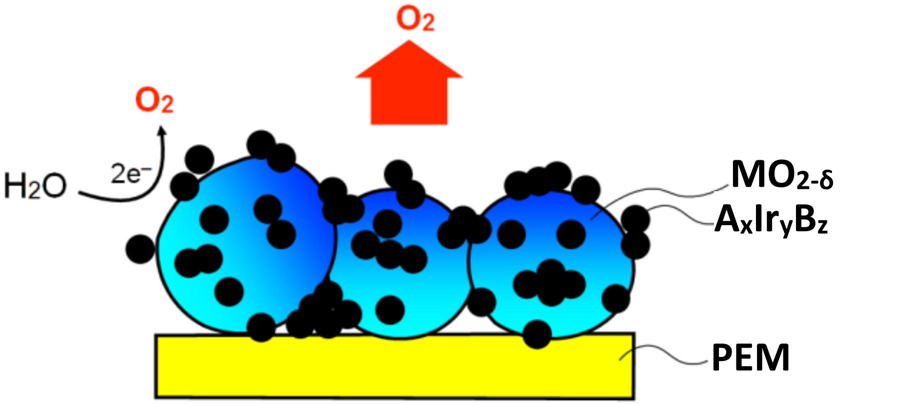
Designing a cost effective, active and durable electro-catalyst for OER

Challenge: Develop a catalyst than can be mass-produced at a reduced cost

- **Ir** as active and stable metal center for OER
- Enhancement of activity of Ir by adding **A**. Reduction of Ir content
- Enhancement of durability of Ir by adding **B** (PMG metal) / HOR (less H_2 crossover)
- Increase of ESA by using an electro-ceramic support $MO_{2-\delta}$. Cost reduction

Target material: $\mathbf{A_xIr_yB_z/MO_{2-\delta}}$



Examples:

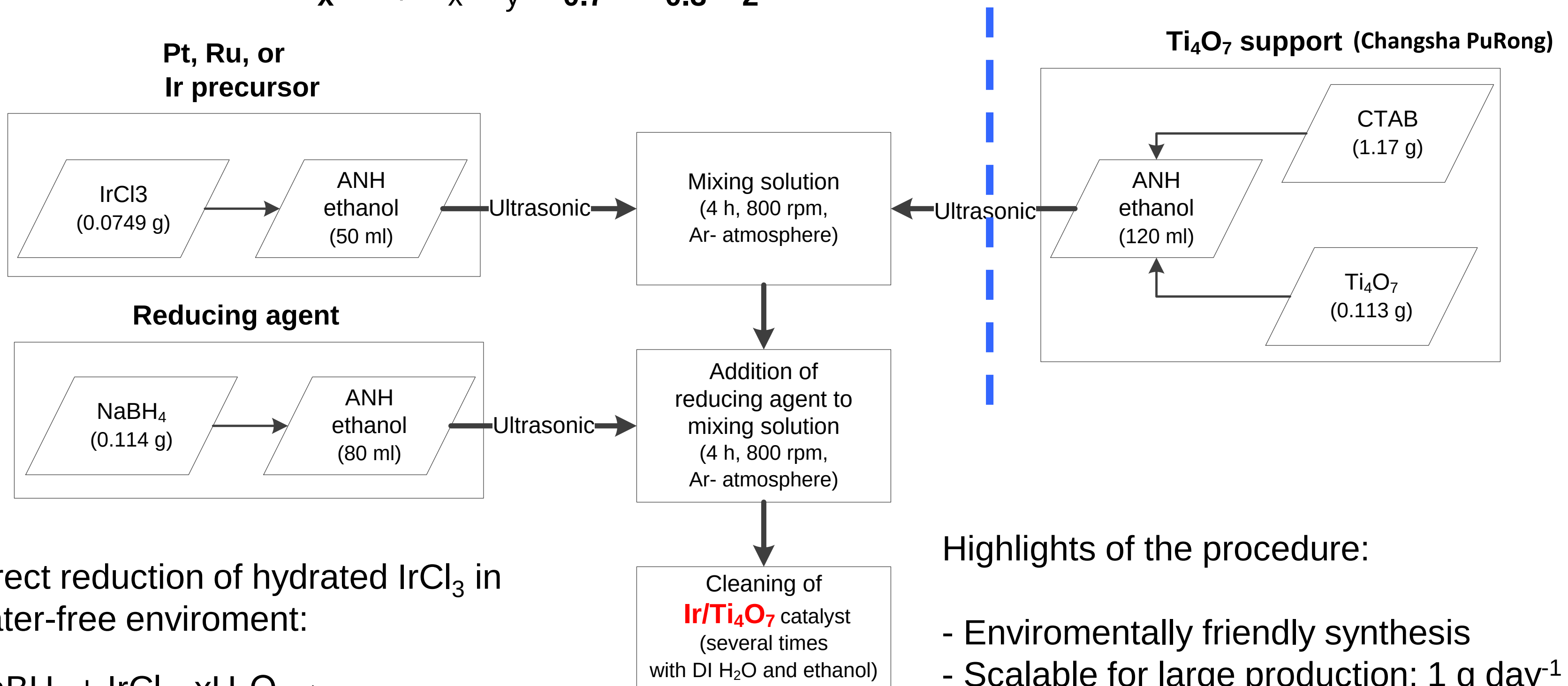
A = Ru, Ir-Ru has a higher electro-catalytic activity than Ir[1,2,3]
B = Pt, Ir-Pt is more stable than Ir at high potentials[3]/HOR (less H_2 crossover)
$\mathbf{MO_{2-\delta}}$ = Ti_4O_7 Corrosion resistant support at high potentials, conductive, commercially available in large quantities

[1,2,3]E. Mayousse et al. Int. J. Hydrogen Energy **2011**, *36*, 10474; L. E. Owe et al. Electrochim. Acta **2012**, *70*, 158–164; S. Siracusano et al. Appl. Catal. B Environ. **2015**, 164, 488–495.
[4]K.M. Papazisi et al. Int. J. Hydrogen Energy 37 (2012) 16642

Synthesis of OER catalysts

IrO_x-Ir[a], Ir_xPt_y **$Ir_{0.7}Ru_{0.3}O_2$**[b]

Pt/TiO_2, **Ir/Ti_4O_7**[c]



Direct reduction of hydrated $IrCl_3$ in water-free enviroment:

$NaBH_4 + IrCl_3 \cdot xH_2O \rightarrow$
$Ir^0 + H_3BO_3 + NaCl + HCl + yIrCl_3 + H_2$

Highlights of the procedure:

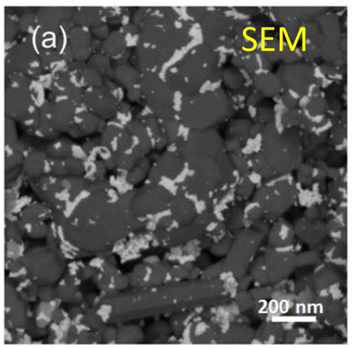
- Enviromentally friendly synthesis
- Scalable for large production: 1 g day^{-1}
- Estimated cost < 100 € g^{-1}

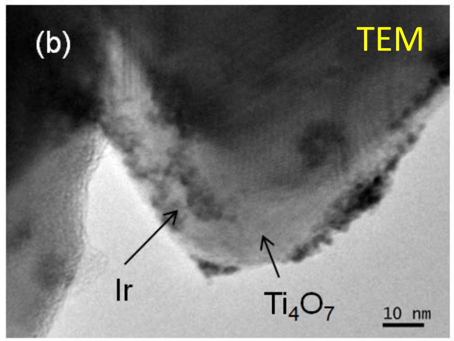
[a]Angew. Chemie **2016**, *128*, 752–756.
[b]J. Phys. Chem. Lett. **2016**, *7*, 3240–3245.
[c]Phys. Chem. Chem. Phys. **2016**, *18*, 4487–4495.

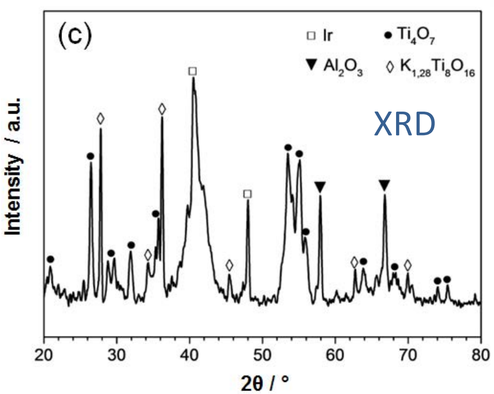
Patent DE 102015101249 A1

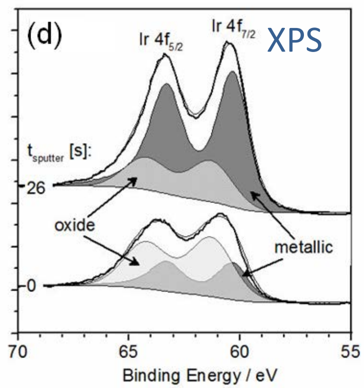
Higly active and cost effective OER electrocatalysts

- High surface area ($m^2\ g^{-1}$): IrO_x-Ir: 60, Ir-black: 8.04, and Ir/Ti_4O_7: 38.03
- Similar crystal and surface properties of IrO_x-Ir and Ir-black

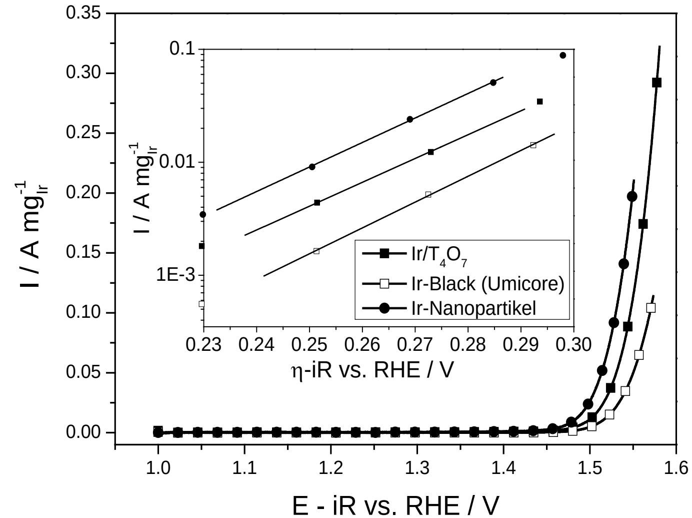








Half cell - RDE



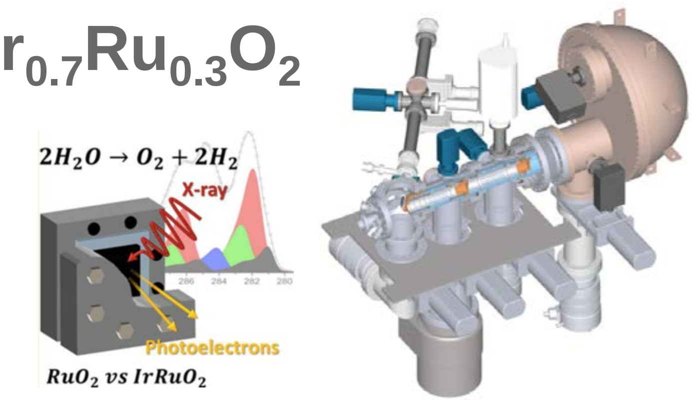
Catalyst	Activity (A/g_{Ir})[a]	Company
Ir-Black	1.6	Umicore
IrO_x-Ir	9	DLR
30 wt% Ir/Ti_4O_7	4.2	DLR

[a]@ 0.25 V Overpotential, T=25°C

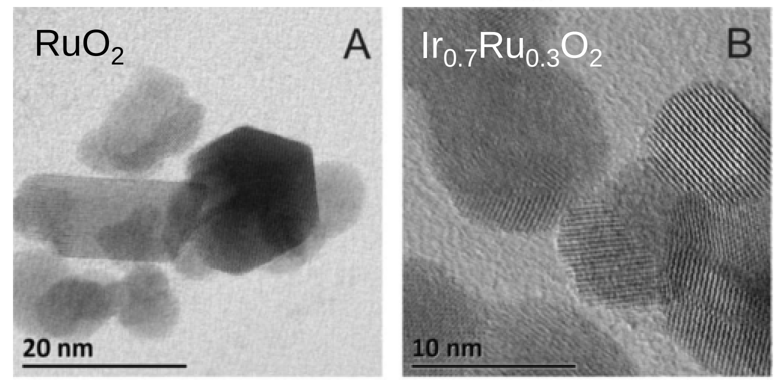
Angew. Chemie, **2016**, *128*, 752–756
Phys. Chem. Chem. Phys., **2016**, *18*, 4487–4495

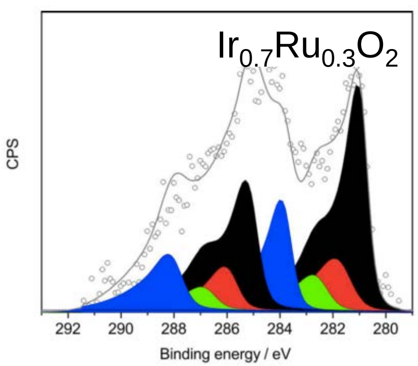
NAP-XPS set-up at BESSY II

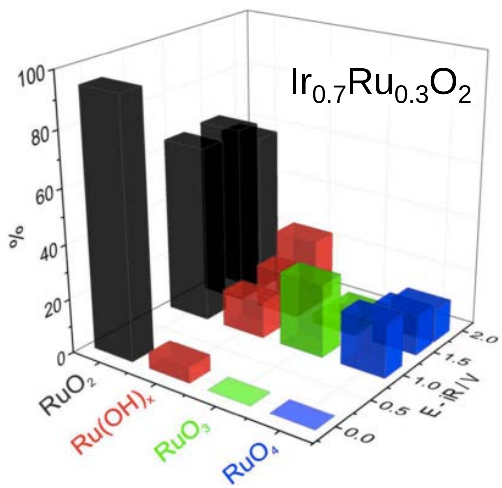
Stabilization mechanism of Ru in $Ir_{0.7}Ru_{0.3}O_2$

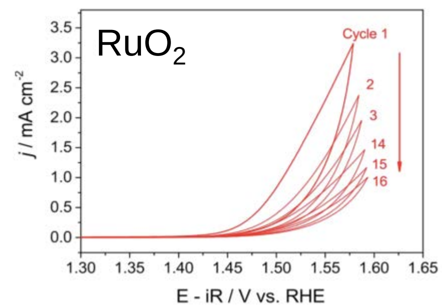


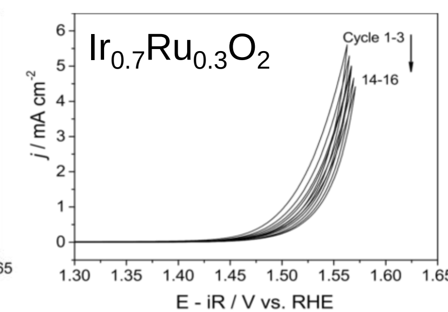
- Near ambient pressure X-ray photoelectron spectroscopy (NAP-XPS) is appliedfor in situ monitoring of the surface state of MEA swith RuO_2 and bimetallic $Ir_{0.7}Ru_{0.3}O_2$ anodes during water splitting
- Ir protects Ru from the formation of an unstable hydrous Ru(IV) oxide
- Water splitting occurs through a surface Ru(VIII) intermediate











J. Phys. Chem. Lett., **2016**, *7*, 3240–3245

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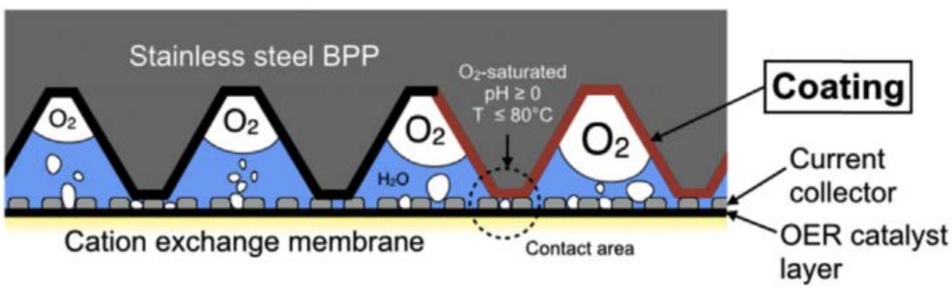
UNIVERSITÉ DE STRASBOURG

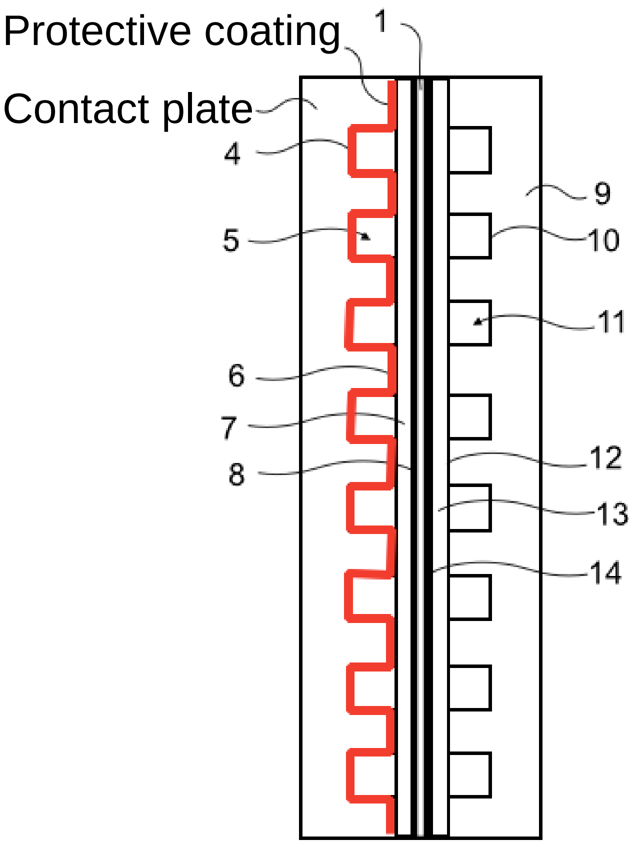
Coatings for stainless steel bipolar plates

Requirements of the protective coating

1. **Resistant to corrosion**
2. **Low electrical resistivity / High electrical conductivity**
3. Strong adherence to the substrate
4. Low cost material, facile and scalable deposition technique
5. Withstand mechanical loads during operation
6. Minimal differences in the coefficient of thermal expansion
7. Resistant to H_2 embrittlement (cathode side)



J. Power Sources, **2016**, *307*, 815–825



No limitations in weight and thickness!

Strategy for coating stainless steel

Coatings for PEM fuel cells:

Standard approach:

Coating 1 **Coating 2**

Corrosion resistant and conductive coating on stainless steel

Coatings for PEM electrolyzers:

Our approach:

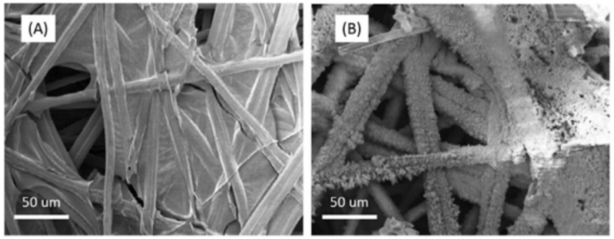
Coating 1: Titanium coating by vacuum plasma spraying (VPS)

Coating 2: Surface modification of the Ti coating by electrodeposition or PVD magnetron sputtering

The released Fe^{2+} poison the CCM of the electrolyzer

S. Sun et al., J. Power Sources 267 (2014) 515.

Fresh GDL Fresh GDL



J. Mo, et al., Int. J. Hydrogen Energy **2015**, *40*, 5.

Cost reduction?

PEMFC: PVD coatings alone meet the DOE requirements.

PEM electrolyzers: current Ti bipolar plates have to be coated to reduce passivation.

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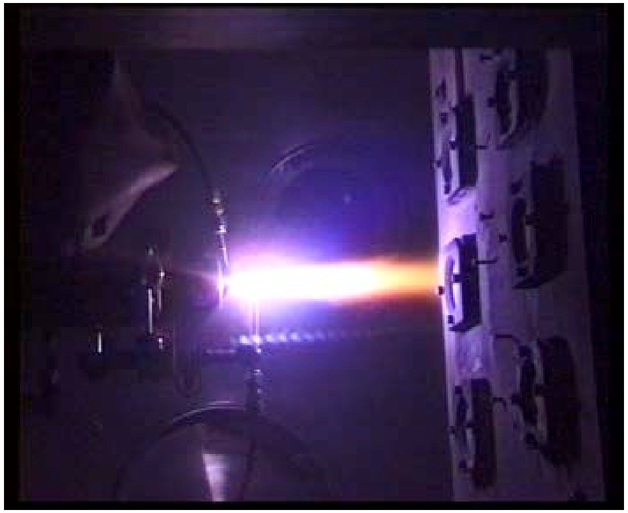
Vaccum plasma spraying (VPS) coatings

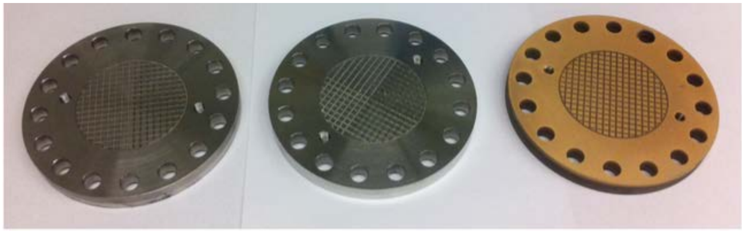
DLR coatings for:

- SOFC components
- Catalysts for alkaline electrolysis
- Thermal barriers
- BPP of PEM electrolyzers

Vacuum chamber

Plasma torch



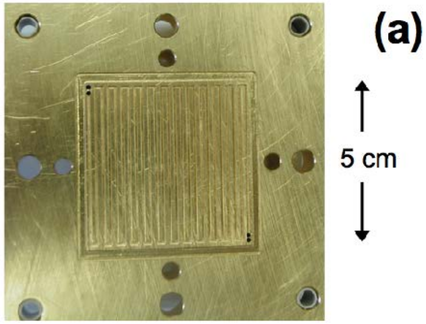


Ti ss Au/Ti/ss

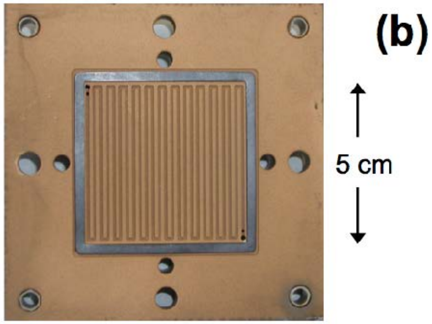
ECS Trans., **2014**, *64*, 1039–1048.
ECS Trans., **2015**, *69*, 223–239.

*Electrodeposition

Au*-coating



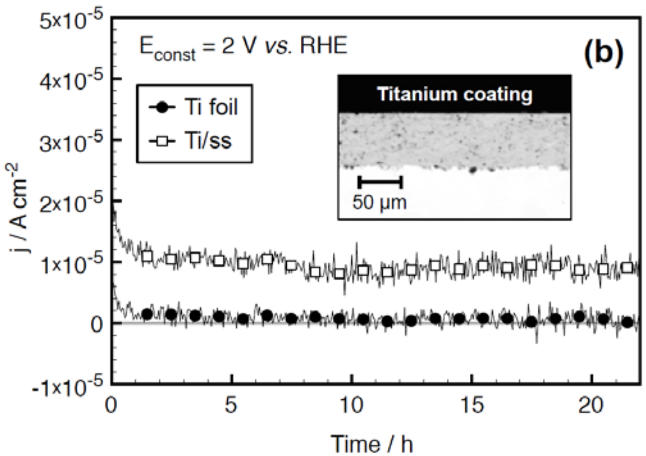
Au*/Ti-coating

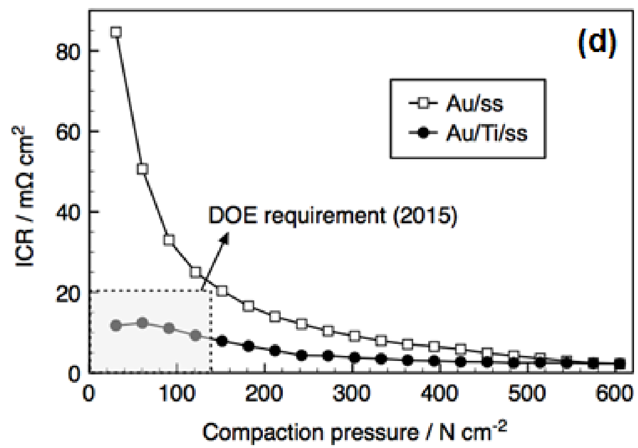


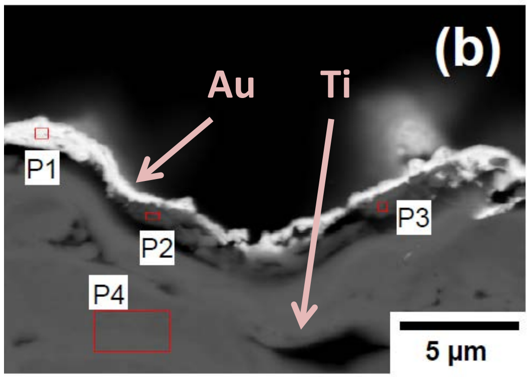
Thermally sprayed Ti coatings modified with Au and Pt

O_2-saturated 0.5 M H_2SO_4, 80 °C

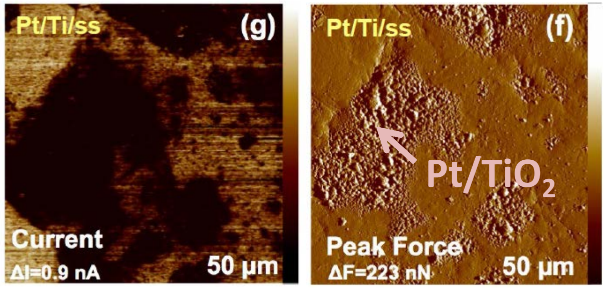
ECS Trans., **2015**, *69*, 223–239.







AFM after corrosion test



J. Power Sources, **2016**, *307*, 815–825

Patent WO 2015000925 A1

- Dense Ti coatings on stainless steel were developed by vaccum plasma spraying (VPS)
- The Ti coatings fully protect the stainless steel substrate against corrosion in simulated enviroment of the PEM electrolyzer anode. $[Fe^{2+}] = 0$ at the end of the test
- Modifications with Pt and Au reduce significantly the interfacial contact resistance (ICR)

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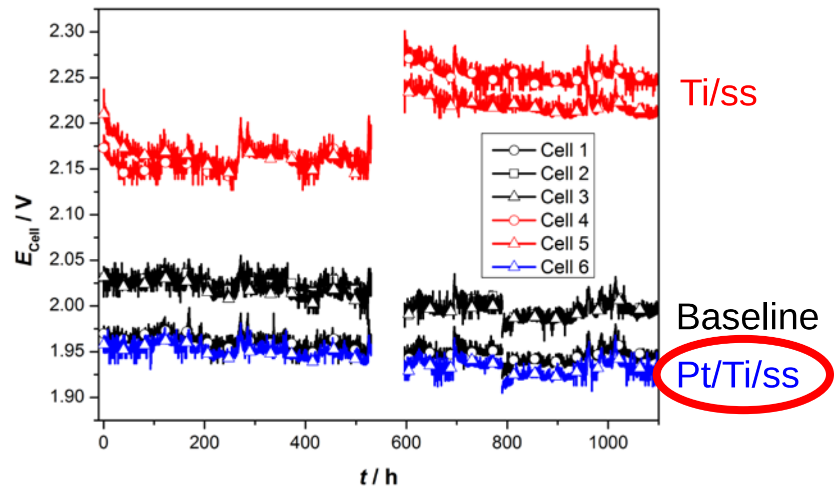
Hochschule Esslingen
University of Applied Sciences

Durability of coated stainless steel bipolar plates in commercial PEM electrolyzer

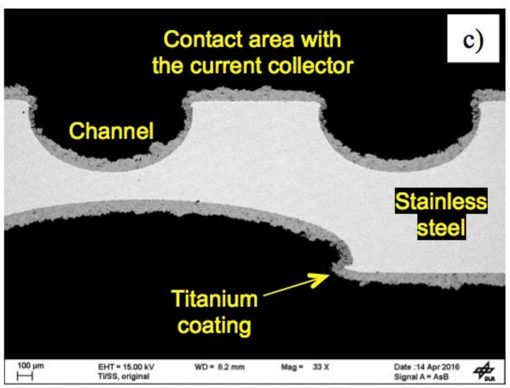
- No degradation of stainless steel after more than 1000 h. Validated by SIEMENS and HYDROGENICS
- Performance of cells with Pt/Ti/ss are comparable to proprietary bipolar plates of
- HYDROGENICS
- Contact resistance of Pt/Ti/ss (anode and cathode) did not increase

J. Electrochem. Soc. **2016**, *163*, F3119–F3124

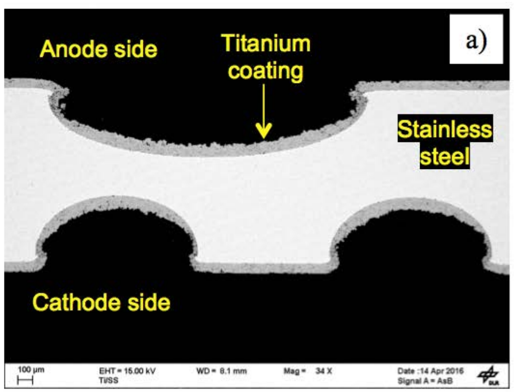
j_{const}= 1 A cm^{-2}, T = 38 °C , P = 8 bar



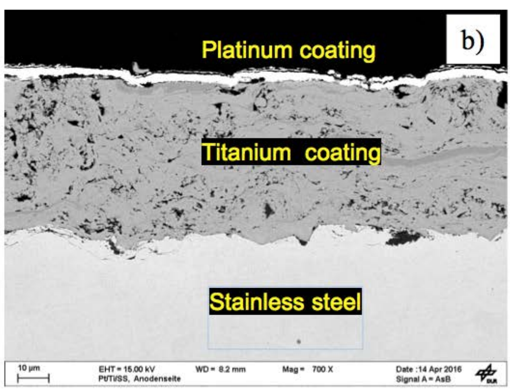
Ti/ss Initial



Ti/ss after 1000 h test



Pt/Ti/ss after 1000 h test



50 µm

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Cost of the thermally sprayed Ti coating

- Thermal spraying coating technology is well stablished in the industry
- Surfaces up to 2 m^2 can be coated
- Non-deposited Ti powder can be recycled
- Coating process last a few minutes
- Cheaper stainless steels, Cu or Al can be used

Cost of possible stack base materials and their respective electrical conductivities

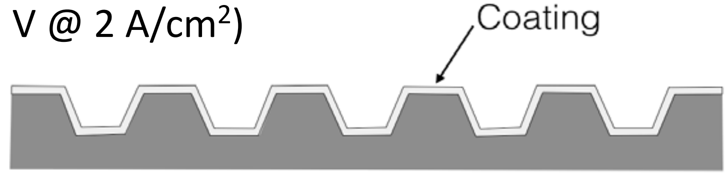
Metal	Cost (30 x 30 x 0,3 cm3) / USD[a]	Electrical conductivity (S/m) at 20 °C
Titanium (99.6+)	614	2.38×10^6
Fe/Cr18/Ni10 (ss 304)	268	1.45×10^6
Copper (99.9%)	242	5.96×10^7
Aluminium (99%)	161	3.5×10^7

[a] http://www.goodfellow.com/catalogue/GFCatalogue.php?Language=E

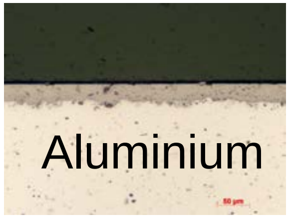
J. Power Sources, **2016**, *307*, 815–825

Cost of coating BPPs for 1 MW PEM electrolyzer:

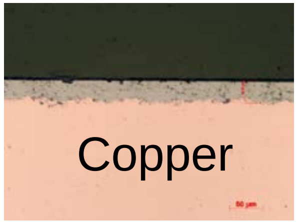
(2 V @ 2 A/cm^2)



After corrosion at Constant 2 V *vs.* RHE



250 x 1000 cm^2



3 EUR / bipolar plate (considering only consumables, feedstock powder and working hours)

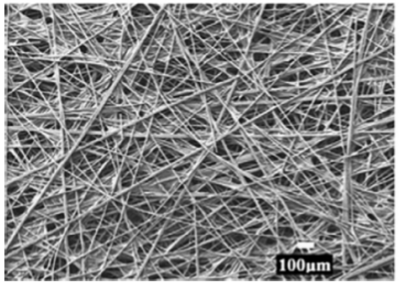
Coatings for gas diffusion layers (GDL)

Porous titanium layers or GDLs of PEM electrolyzers

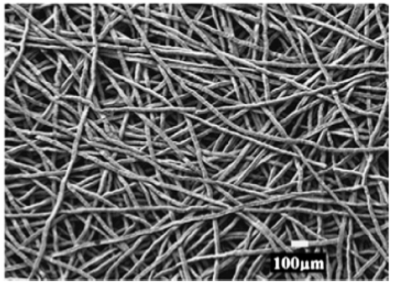
Current collector	Features
Ti felts	Widely used in URFC. Reduced contact with catalyst layers. Require Pt coatings. Expensive
Sintered Ti filters	Good contact with catalyst. Good performances without Pt coatings. Difficulties for reducing thickness and controlling porosity. Very expensive (200 € / 25 cm^2)
Ti expanded meshes	Low cost solution for manufacturing flow field on Ti (Fraunhofer ISE / Sintef). Disadvantages?

Felts

A Carbon



B Titanium L

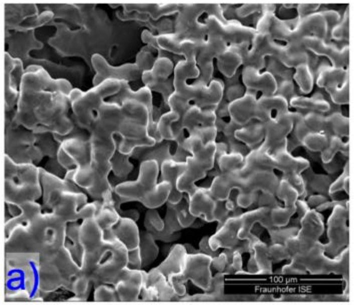


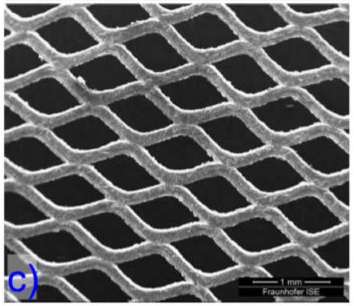
C. M. Hwang et al. Int. J. Hydrogen Energy **2011**, *36*, 1740–1753.

Sintered Ti

Carbon paper (GDL)

Sintered Ti

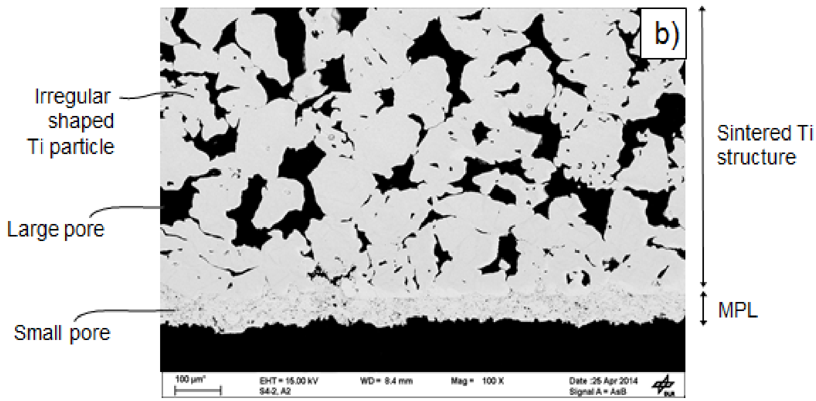


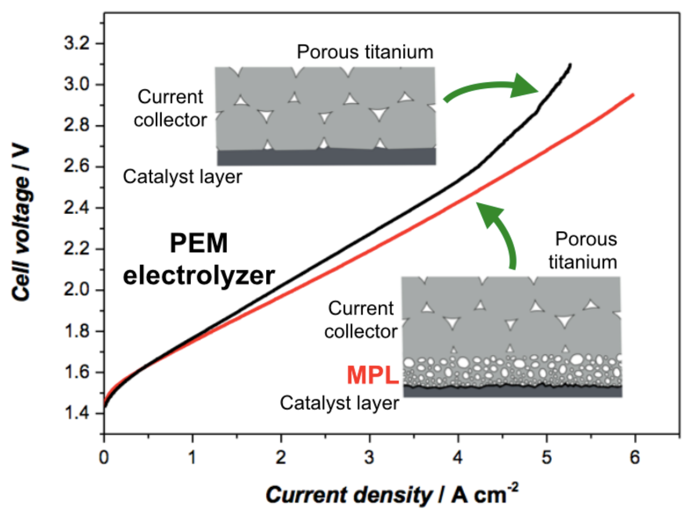


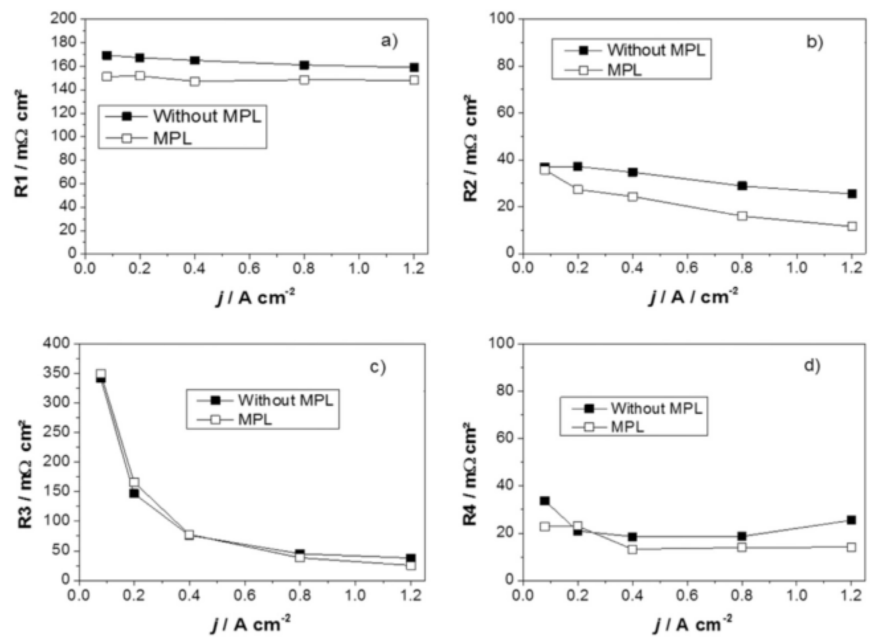
Ti mesh

Development of a backing layer or MPL by plasma spraying for PEM electrolyzers

- The MPL reduces contact resistance by ca. 20 mΩ cm^2
- The improvement in the PEM electrolyzer has been confirmed by EIS
- The MPL enhances significantly the performance at high current densities







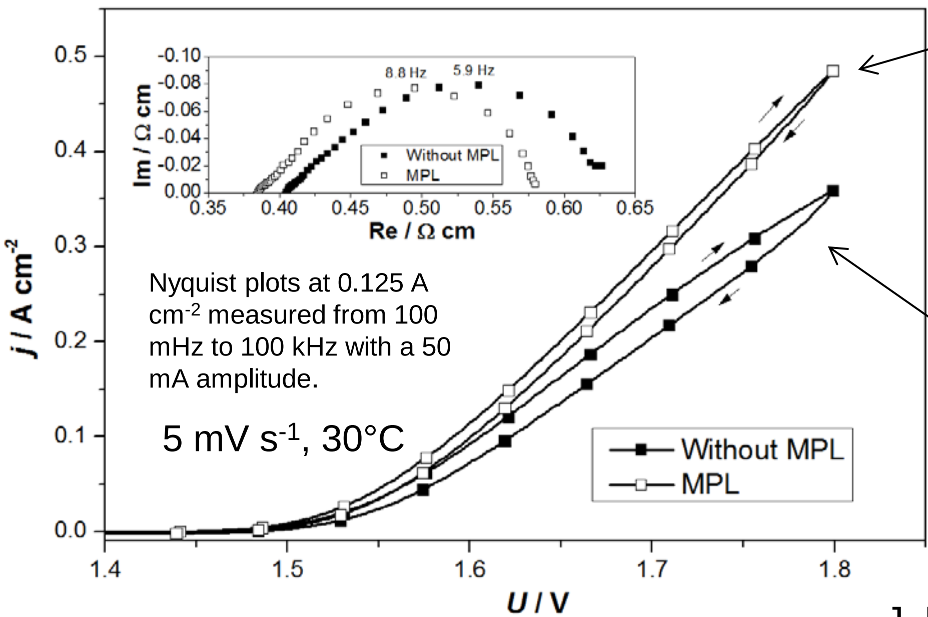
J. Power Sources, **2016**, *311*, 153–158.

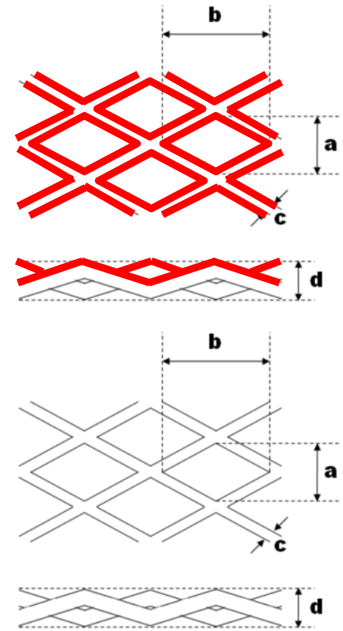
Coated expanded Ti meshes

- The improvement in performance of the PEM electrolyzer with coated current collectors is exclusively attributed to coating on the current collector, and the effect does neither depend on the nature of MEA nor the cell design

Ti meshes as current collectors, with and without **porous Ti coating**

Measurements were carried out in potentiostatic mode





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Summary

Catalysts

- Cost-effective and environmentally friendly synthesis on IrO_x-Ir catalyst
- Up to 5 times more active for OER than commercial Ir-black
- Better utilization of Ir by using a Ti_4O_7 support
- New stability of $Ir_{0.7}Ru_{0.3}O_2$ and OER mechanisms were uncovered with near ambient pressure X-ray photoelectron spectroscopy (NAP-XPS)

Coatings

- Coatings of Ti on low cost substrates (ss, Cu, Al) by vacuum plasma spraying (VPS). Ti. Stable in PEM electrolyzer anode environment for more than 1000 h
- Surface modification of the Ti coating with Au and Pt reduces passivation
- Thermally sprayed MPL improves the contact of the current collectors with the catalyst layers, increasing significantly the efficiency of the device at high current densities

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