Durable Membrane Electrode Assemblies for Proton Exchange Membrane Electrolyzer Systems Operating at High Current Densities

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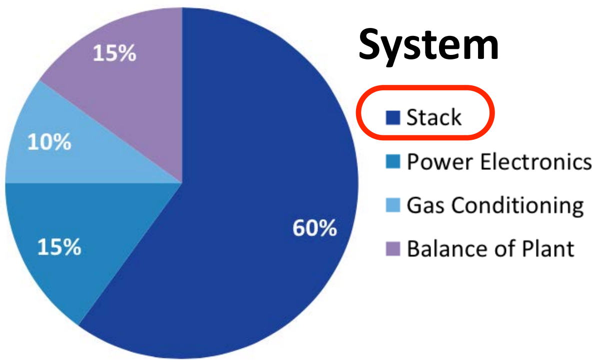
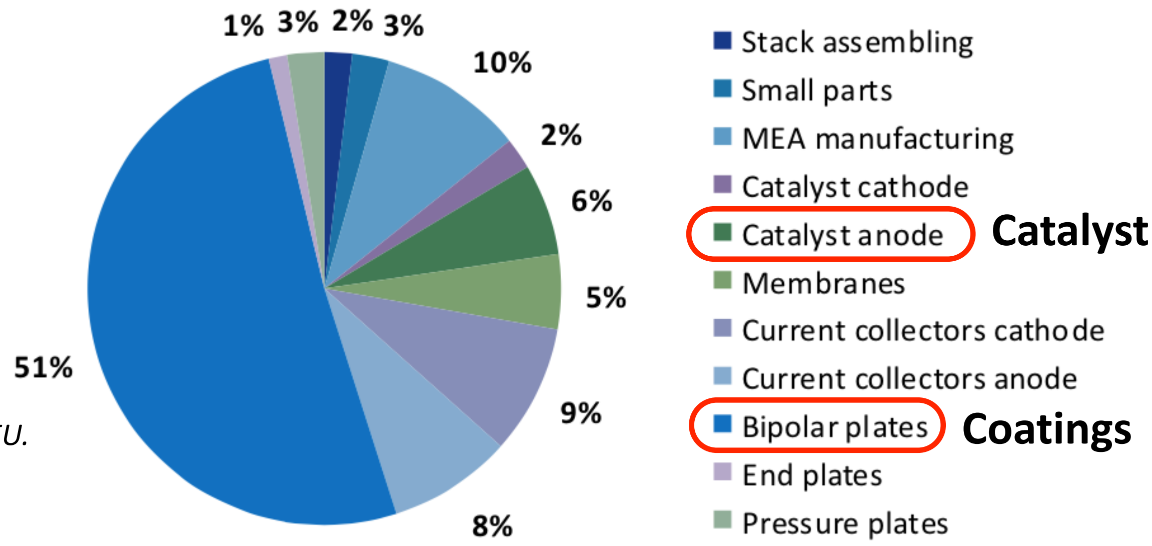
Outline

- Cost reduction of the PEM electrolyzer stack
- MEA tests in a 20 kW_{el} PEM electrolyzer system
- Protocol of measurements
- Benchmark MEA with Ir-black catalyst
- Electrochmical analysis of deagradation mechanisms
- *Post mortem* analysis of the MEAs and water resin
- Summary

Cost breakdown of PEM electrolyzer system and stack



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



How to reduce the stack cost?

- Substitute titanium based components (bipolar plates, current collectors, PTLs, GDLs) by coated stainless stee, steel, copper or aluminium.
- Use thin hydrocarbon based membranes and highly conductivenon precious metal coatings. Reduce ohmic losses.
- Develop more effcient anode and cathode catalysts with low loading and improved stability. Use ceramic supports or increase activity surface area ratio
- **<u>Operate at high current densities</u>.** Extend operation range from 2 (nominal) to 4 A cm^{-2}.

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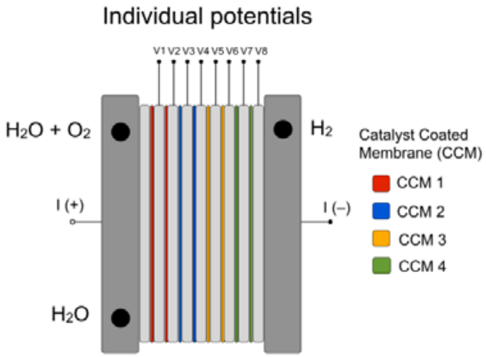
Project on degradation phenomena in PEM electrolyzer systems operating at high current densities

Partner	Tasks in the project
DLR Deutsches Zentrum für Luft- und Raumfahrt e.V. in der Helmholtz-Gemeinschaft	▪ Testing of MEAs with different catalysts in a 12 kW_{el} PEM electrolyzer system ▪ Assessment of results and post-mortem analysis
HYDROGENICS SHIFT POWER | ENERGIZE YOUR WORLD	▪ Construction a 12 kW_{el} PEM electrolyzer system ▪ Stack assembly and evaluation of the degradation tests



Rainbow stack with different MEA configuration

8 Cell - 120 cm^2 – 20 kW_{el} PEM electrolyzer stack

12 kW_{el} PEM electrolyzer

Goal of the project: Gain knowledge about degradation mechanism of PEM electrolyzer MEAs

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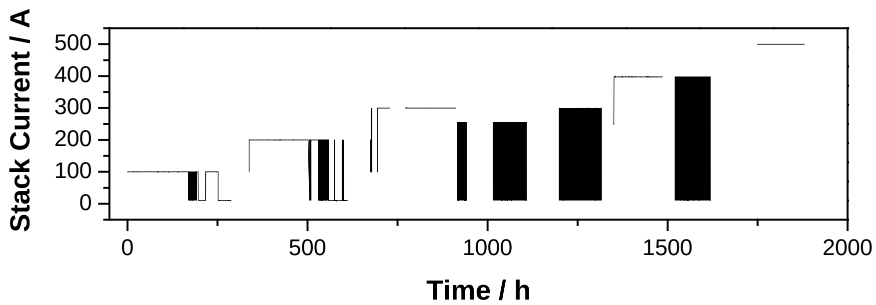
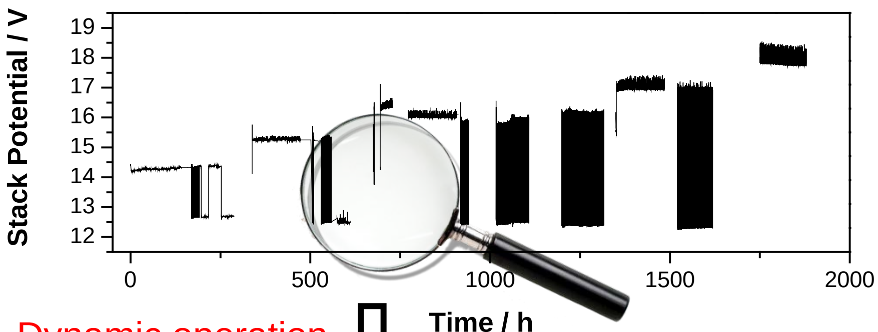
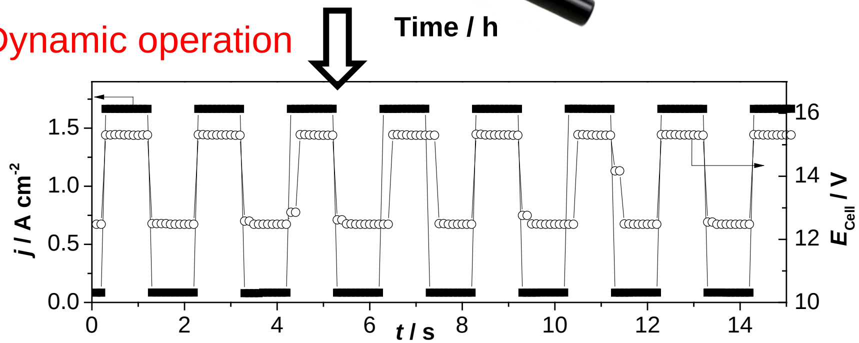
Protocol of measurements

Stack 1: Different catalyst loadings

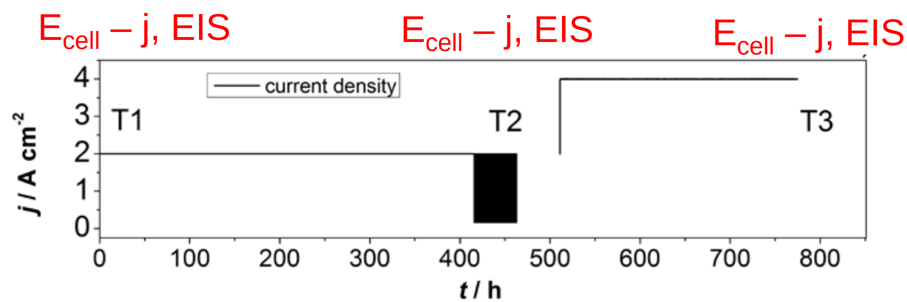


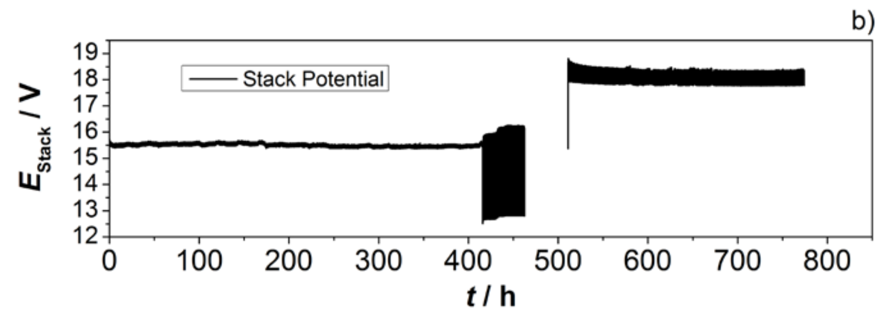


Dynamic operation



Stack 2: MEAs from different providers





- There is an urgent need for accelerated stress test (AST) protocols for PEM electrolyzers
- Degradation caused by operation time, current densities, voltage, temperature, water quality, etc. is not well understood

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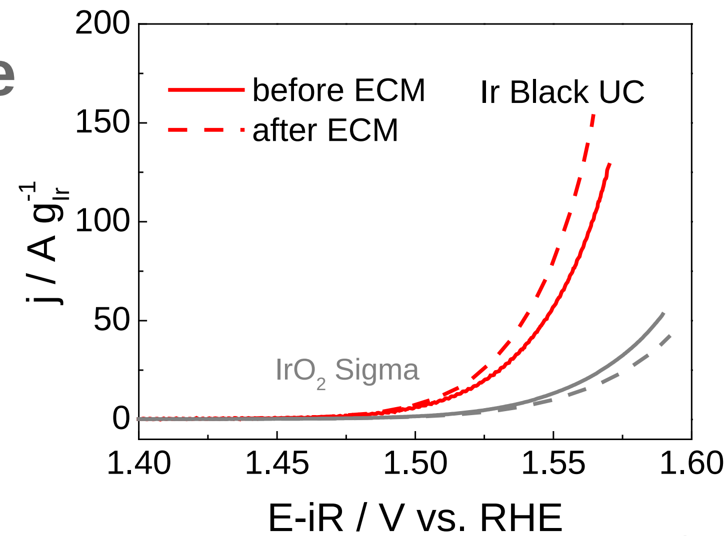
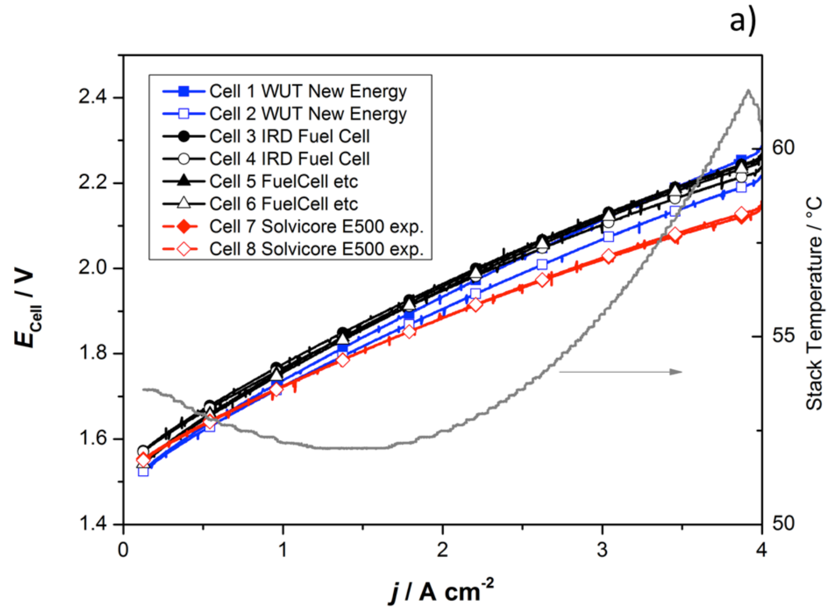
Benchmark PEM electrolyzer anode

- 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





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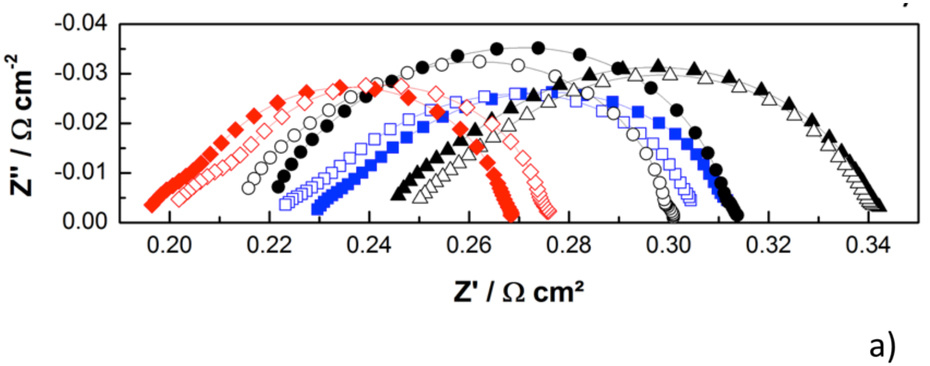
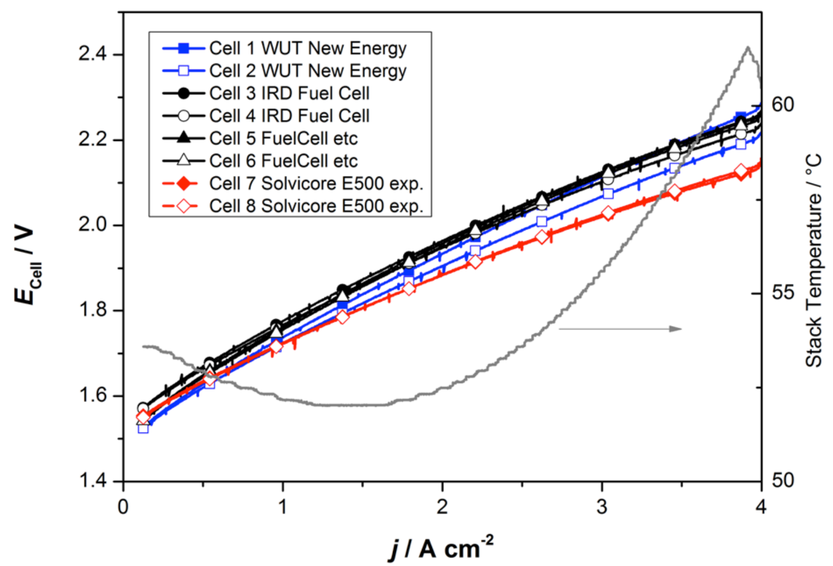
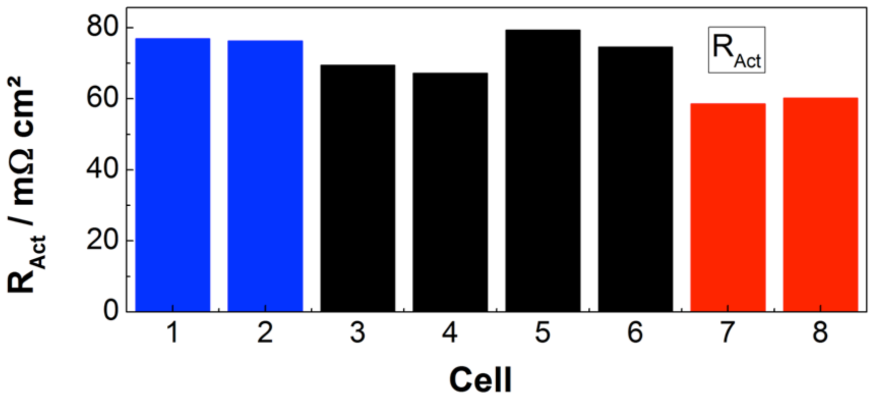
Electrochemical impedance spectroscopy (EIS)

- EIS was performed before and after 500 h (T1) at 2 A cm², and before and after 250 h (T2) at 4 A cm²
- MEA with Ir-black (1 mg cm^{-2}) showed the lowest activation and ohmic resistances
- EIS results correlate well with E_{cell} - j characteristics
- At high current densities the ohmic resistance has the largest impact
- No mass transport was observed







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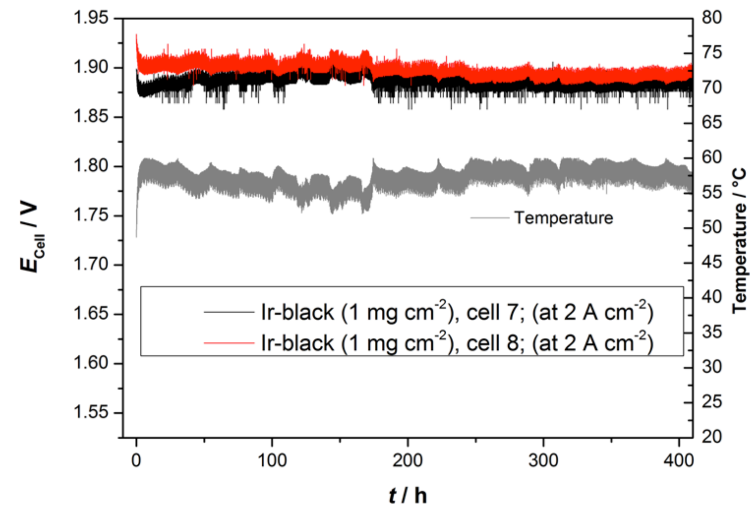
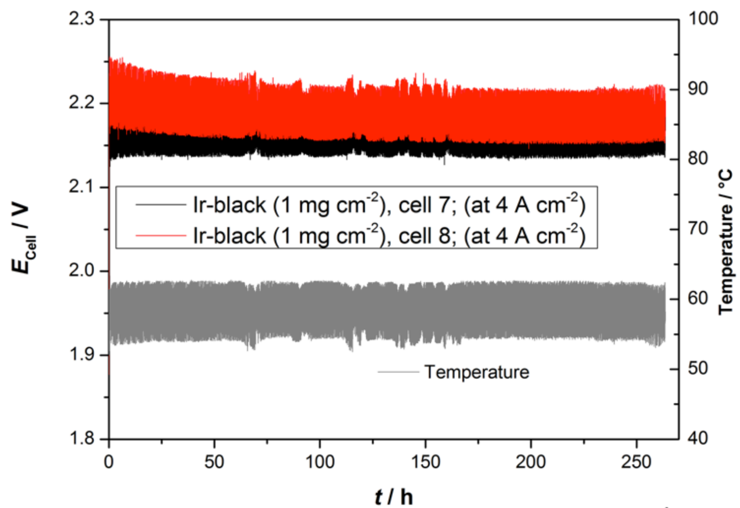
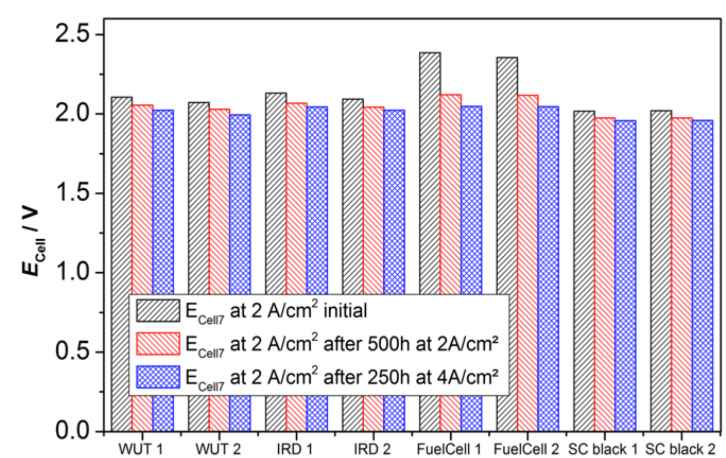
Evolution of E_{cell} through the time and current density

- Difficult analysis of degradation rate because of temperature fluctuation.
  At j = 2 A cm^{-2}, **$\Delta T = \pm 1.5$ °C** caused by the addition of fresh water into the stack.
  At j = 4 A cm^{-2} **$\Delta T = \pm 4$ °C** caused by the periodic turn on-off of the fan that cools down the entire system enclosure
- No increase in Ecell after 4 A cm^{-2} test for all cells
- No increase of E_{cell} over time for all cells







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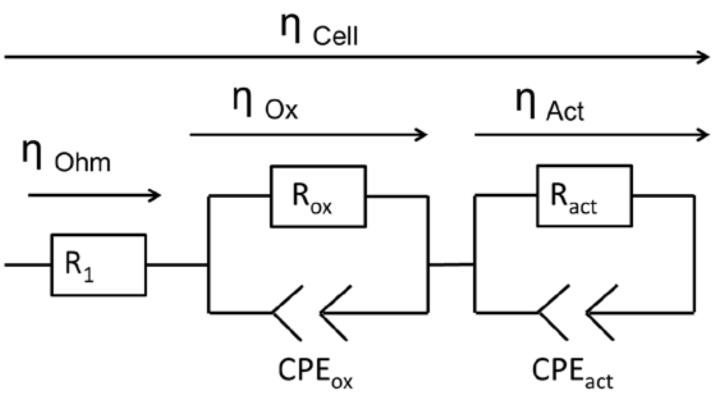
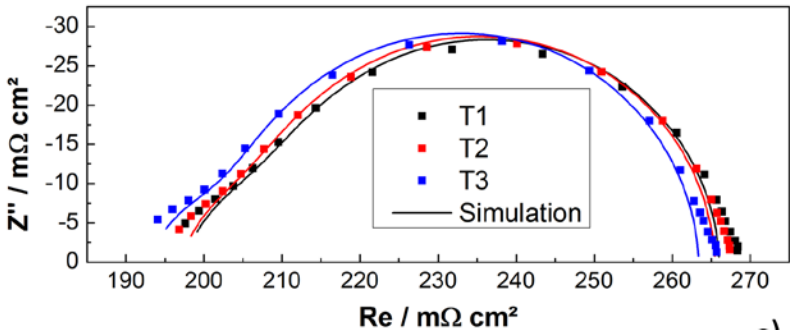
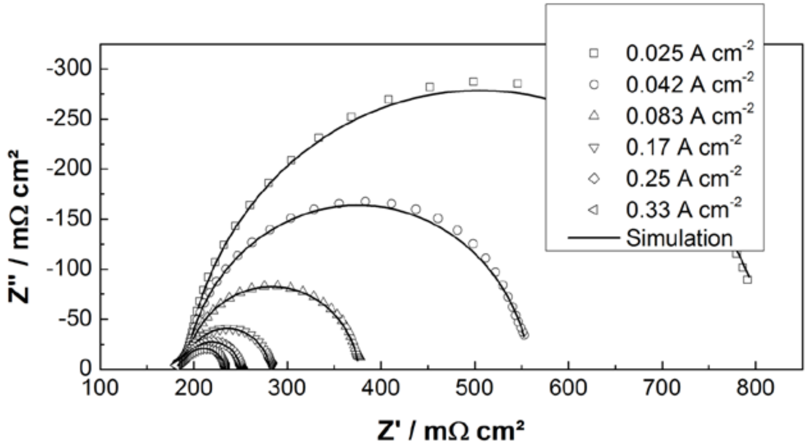
Determination of ohmic losses from EIS

- Temperature of the stack was strickly controlled at **29 ± 0.5 °C** by shutting off completely the H_2-generator. An external pump with low flow rates was used.
- The EIS were simulated using an equivalent circut
- The EIS spectra at a given current density changed over time and when the current was increased
- The cell resistance (**η_{Ohm}**) and kinetics (**R_{act}**) were analysed







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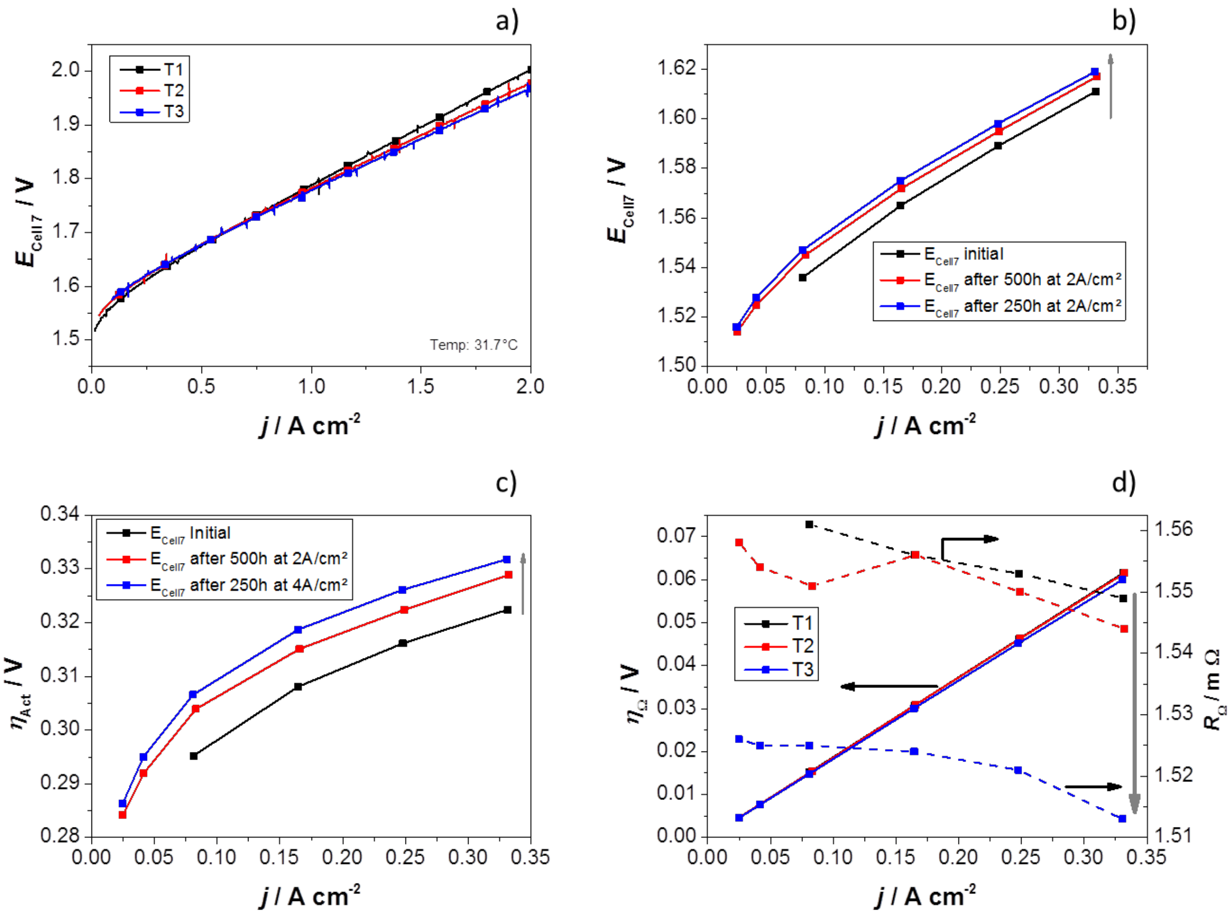
Degradation mechanism from EIS analysis

- The degradation was analyzed through changes in ohmic loses and potential over time.
- The kinetic resistance (**R_{act}**) increased over time
- The ohmic resistance (**η_{Ohm}**) decreased at high current densities

Potential	Change at 0.33 A cm^{-2}
E_{cell}	**↑ +10µV/h**
η_{ohm}	**↓ -2µV/h**
η_{Ox}	**→**
η_{Act}	**↑ +13µV/h**



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Degradation analysis and XPS on DI water resin

- Nafion degradation:
  1. Presence of F in the DI water resin
- Degradation of intrinsic properties:
  1. Significant decrease of exchange current density during time of measurement. Deactivation of the anode
  2. Presence of Ir in the DI water resin

Elem.	Fresh [wt%]	Used [wt%]
Fe	0.0	2.6
F	0.0	2.9
O	10.9	21.4
Ti	0.0	2.7
N	2.4	3
C	79.6	52.9
S	7.2	9.9
Si	0.0	3.3
Ir	0.0	1.3

	T / °C	β /mV dec^{-1}	j_o / 10^{-9}A mg_{Ir}^{-1}
Ir-Black (Umicore)	25	43.1	2.5
(Half Cell, kinetic analysis)	30	43.1	3
	40	43.2	5.8
	50	43.6	12.0
	60	43.9	22.8
	70	44.6	46.2
Before 2A/cm²	30	44.3	18.1
After 2A/cm²	30	41.1	3.5
After 4A/cm²	30	41.1	2.8

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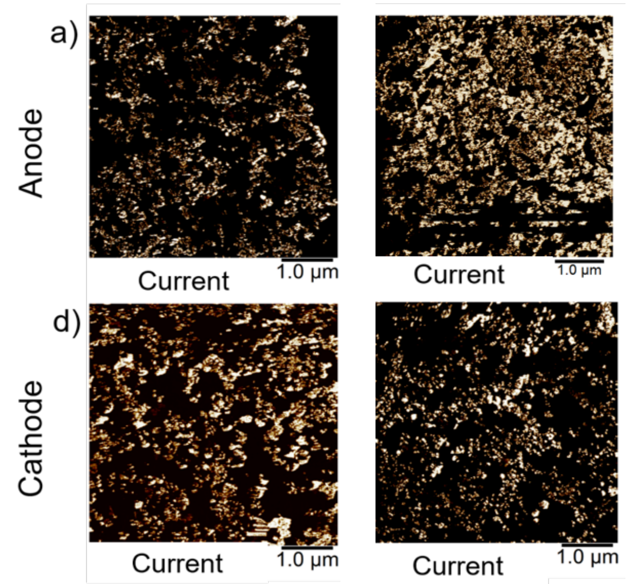
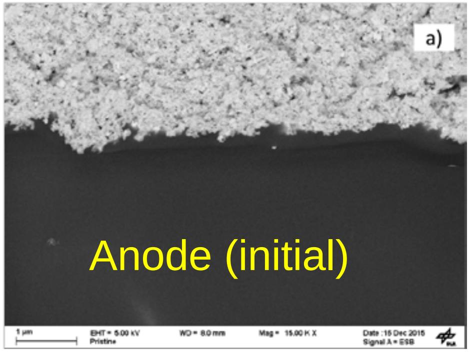
Post mortem analysis of the MEAs

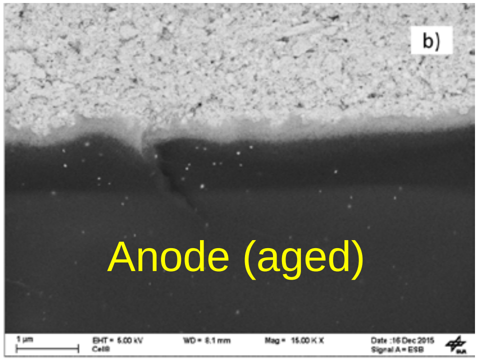
- No decrease of membrane thickness was observed from cross-section SEM images.
- Release and diffusion of Ir catalyst into the membrane.
- After operation, the conductive area of the anode increased by approximately 50% while the conductive area of the cathode remained the same.
- Surface conductivity of the catalyst layer changed due to ionomer loss.

AFM



SEM





	Conductive area (%)		Average Thickness / µm	
	unused	Cell 8 (used)	unused	Cell 8 (used)
Anode	30 ± 4	45 ± 5	5 ± 0.4	4.3 ± 0.6
Cathode	37 ± 2	39 ± 5	16.1 ± 0.6	16.7 ± 1
Membrane			121.5 ± 1.5	137.4 ± 2.9

Summary

- Investment cost can be reduced by operating the PEM electrolyzer at high current densities
- The lowest Ir catalyst loading (1 mg cm^{-2}) showed the lowest E_{cell} at any current density.
- Aging of the PEM electrolyzer MEAs depends on current density and operation time, but the associated degradation mechanisms are different in each case.
- EIS shows a progressive decrease in the specific exchange current, while the ohmic resistance decreases when doubling the nominal current density.
- *Post mortem* analysis of the MEAs (SEM and AFM) and water resin (XPS) revealed a current dependent loss of ionomer and catalyst material in the anode, which resulted in an unexpected enhancement of cell performance at high current densities.
- A first step towards developing an acelereted stress test protocol (AST) for PEM electrolyzers has been given

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Grand Challenges in Energy Conversion and Storage 2

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Novel Components for PEM Electrolysis: Status and Challenges

A. S. Gago, P. Lettenmeier, L. Wang, S. Kolb, F. Burggraf, and K. A. Friedrich

Thank you for your attention

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