



Construction of Improved HT-PEM MEAs and
Stacks for Long Term Stable Modular CHP Units



HT-PEM Degradation Aspects

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Peter Wagner



Agenda

■ Introduction NEXT ENERGY

■ Project CISTEM

■ Fuel Switching

■ Oxygen-Enriched Air

■ Start-Stop-Cycling

■ Summary



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 **Introduction NEXT ENERGY**

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Niedersachsen

NEXT ENERGY

EWE-Forschungszentrum für Energietechnologie e.V.



- NEXT ENERGY is an independent research institute at the University of Oldenburg
- Organised as non-profit association with EWE as main sponsor
- Laboratory and research facilities with 4.150 m² floor space
- About 115 employees in R&D and administration





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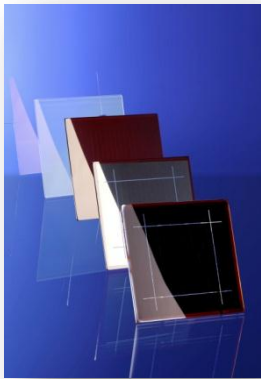




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Photovoltaics

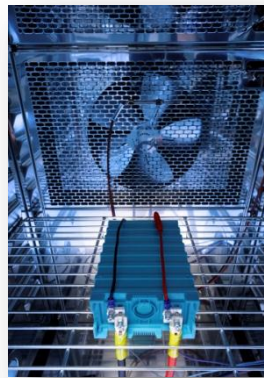
From Thin-Film Technology
to Integrated Energy
Management for Buildings



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Energy Storage

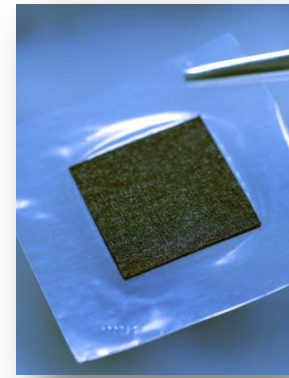
From Electrochemistry
to Grid Integration



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Fuel Cells

Efficient Supply of Power
and Heat

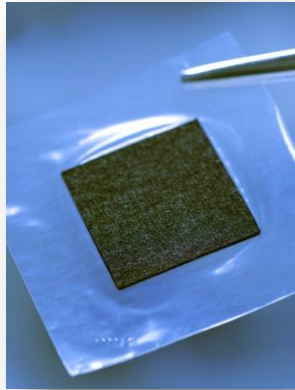


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Fuel Cells Research Topics



Fuel Cells

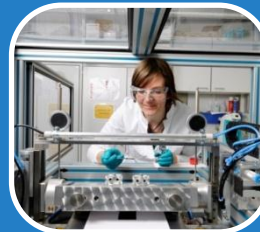
Efficient Supply of
Power and Heat

Head of Division:
Dr. Alexander Dyck



Materials

Catalysts and Membranes for
AEMFC, Electrochemistry



Characterisation

Analytics and Methods,
Coatings, Degradation



Micro-CHP Systems

System Test and Integration,
House Energy Management



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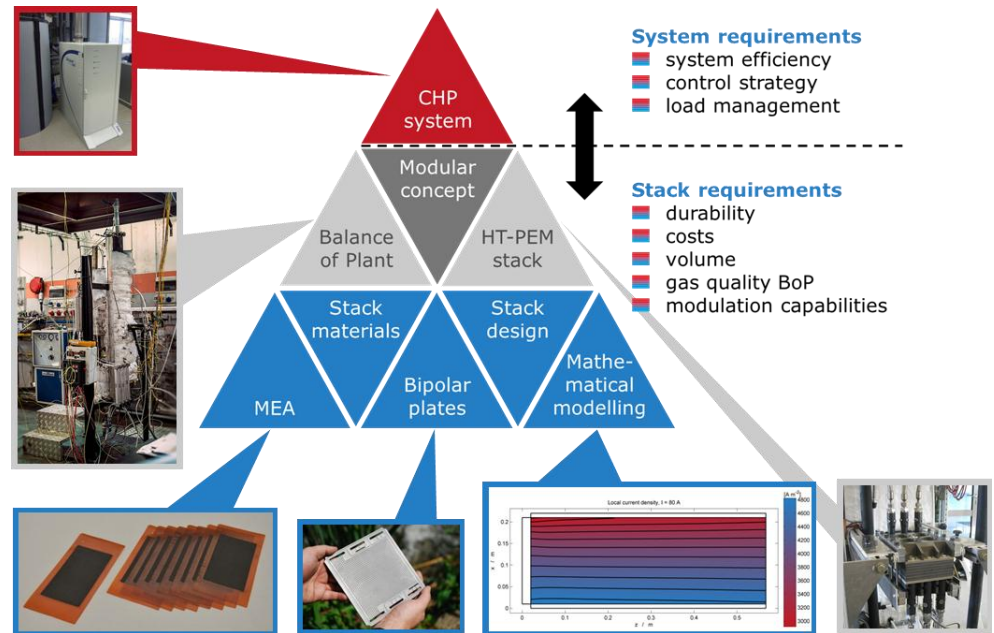


CISTEM

- **CISTEM: Construction of Improved HT-PEM MEAs and Stacks for Long Term Stable Modular CHP Units**
- **Vision:** Development of a new FC based CHP technology with high efficiency and long lifetime
- Fuel flexible operation
- Degradation investigations on all levels (MEAs, single components, stacks, CHP units)



- GA No: 325262
- www.project-cistem.eu



↑ Development Overview



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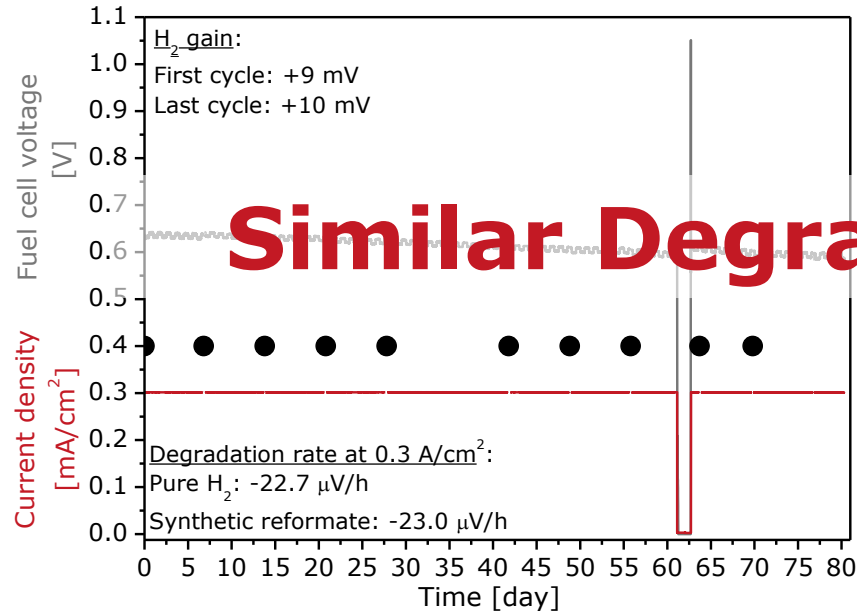
■ Start-Stop-Cycling

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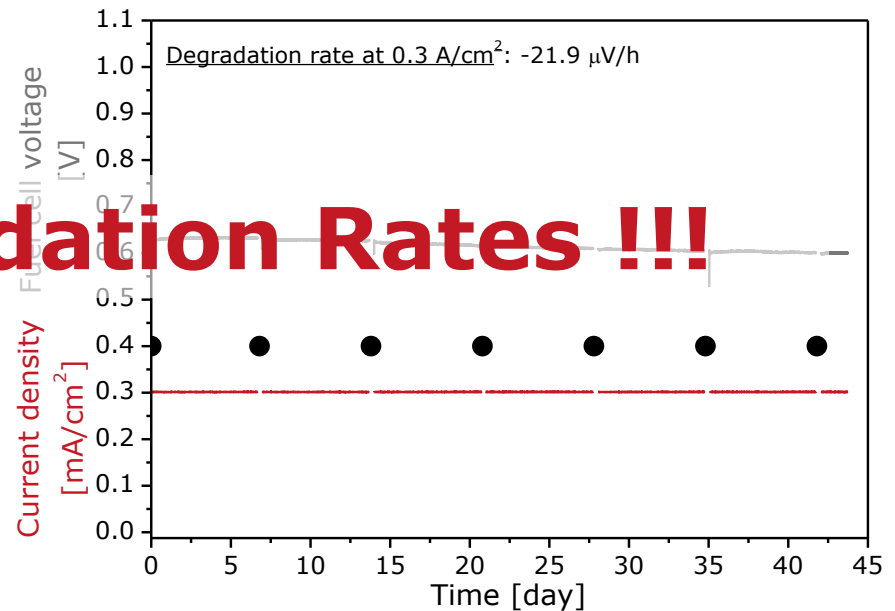
Fuel Switching

Fuel Switching



Similar Degradation Rates !!!

Long Term



- Fuel switching at const. load: 0.3 A/cm²
- Fuel: 12h 78% H₂ + 22% CO₂ operation/12h H₂ operation ($\lambda > 1.5$)
- Oxidant: O₂ enriched Air (30% O₂) ($\lambda > 2.85$) **Still in operation**
- Serpentine flow fields

- 1100h at const. load: 0.3 A/cm²
- Fuel: H₂ ($\lambda > 1.5$)
- Oxidant: O₂ enriched Air (30% O₂) ($\lambda > 2.85$)
- Serpentine flow fields



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■ **Oxygen-Enriched Air**

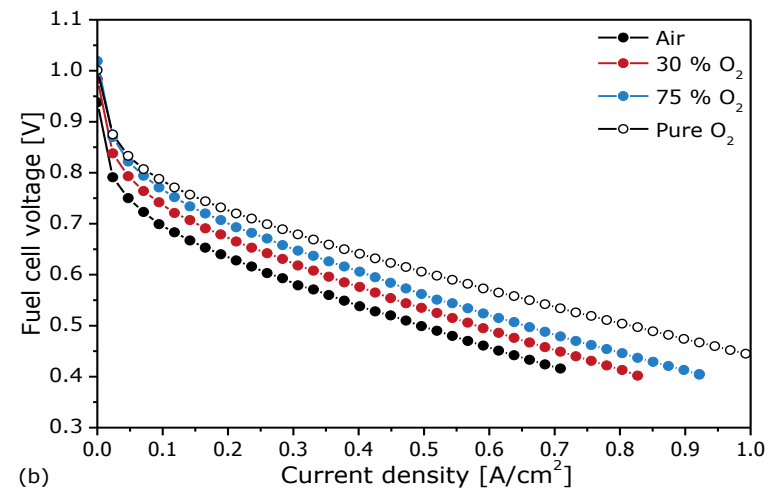
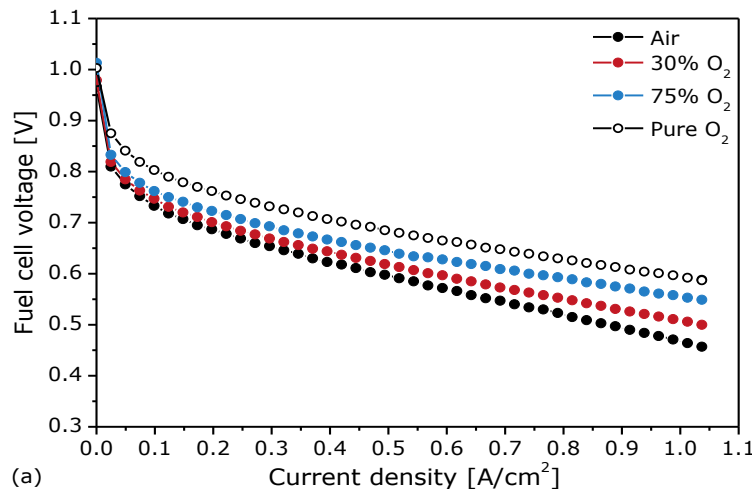
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Fuel and Air/O₂ Optimisation - 1

Effect of O₂-Enrichment on Fuel Cell Performance:



Polarisation curves for the fuel cell operating with H₂/Air* as function of oxygen enriched air. MEA: (a) BASF, (b) DPS. 5-fold serpentine flow field, $P_c=0.75$ MPa, $T=160$ °C, $P=1$ atm. * $\lambda_{H_2}=1.2$; $\lambda_{Air}=2$, $\lambda_{Air-30\% O_2}=2.85$, $\lambda_{Air-75\% O_2}=7.1$, $\lambda_{O_2}=9.5$

- The higher the oxygen concentration, the better the performance of the fuel cell is.
- Mass transport improvement from the gas flow channels to the cathode CL

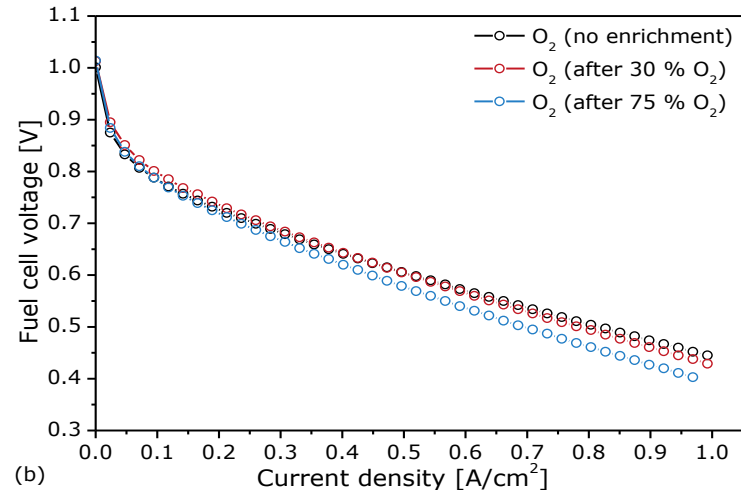
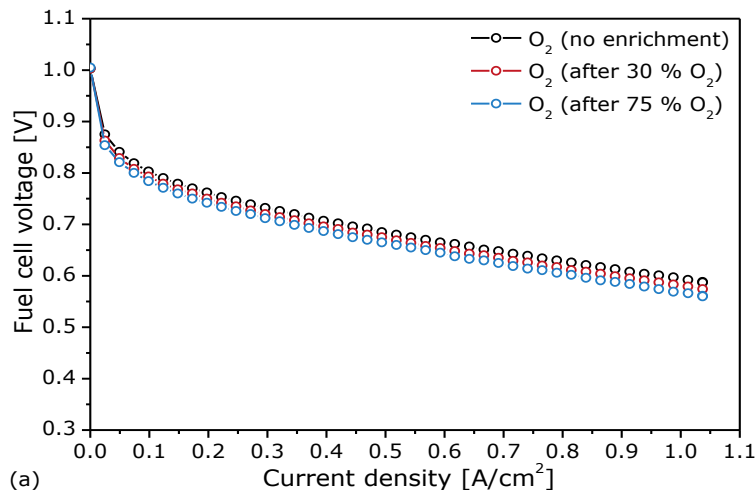
O ₂ [%]	Celtec® η_{el} [%]*	Dapozol® η_{el} [%]*
21 (Air)	43.4	38.5
30	44.4	41.1
75	46.0	43

*At 0.3 A/cm²



Fuel and Air/O₂ Optimisation - 2

Effect of O₂-Enrichment on Fuel Cell Performance:



Polarization curves for the fuel cell operating with H₂/ O₂ after oxygen enriched operation. MEA: (a) BASF, (b) DPS. 5-fold serpentine flow field, P_c=0.75 MPa, T=160 °C, p=1 atm. λ_{H2}=1.2; λ_{O2}=9.5

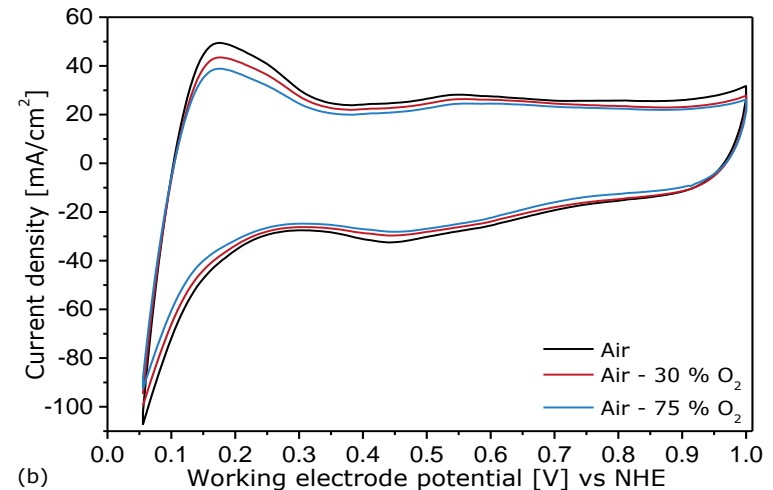
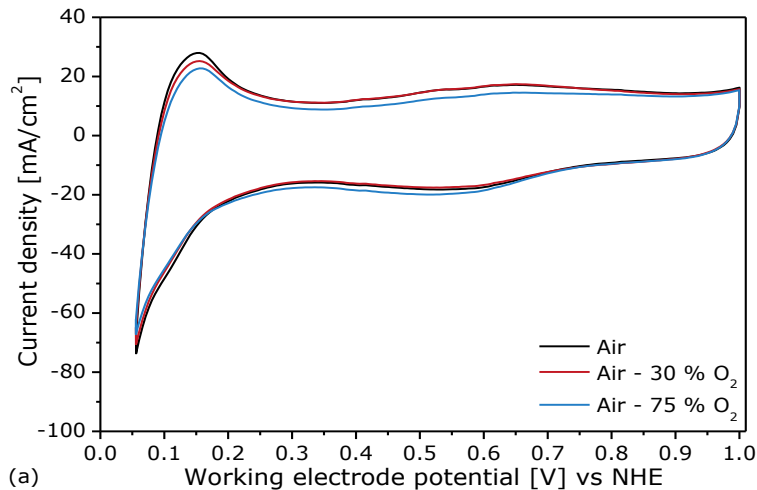
Operation with pure O₂:

- Celtec®: FC performance cannot reach the initial performance anymore after operating with the oxygen-enriched air → slight degradation.
- Dapozol®: FC performance has been reduced after operation with the oxygen-enriched air but not after operation with 30% oxygen.



Fuel and Air/O₂ Optimisation - 3

Effect of O₂-Enrichment on CV:



Cyclic voltammograms with electrical short correction after fuel cell operation with oxygen enriched air. MEA: (a) BASF, (b) DPS. 5-fold serpentine flow field, $P_c=0.75$ MPa, $T=160$ °C, $p=1$ atm. $H_2/N_2=100/100$ ml/min, sweep rate=100 mV/s

Reduction of H₂ desorption area after O₂-enrichment

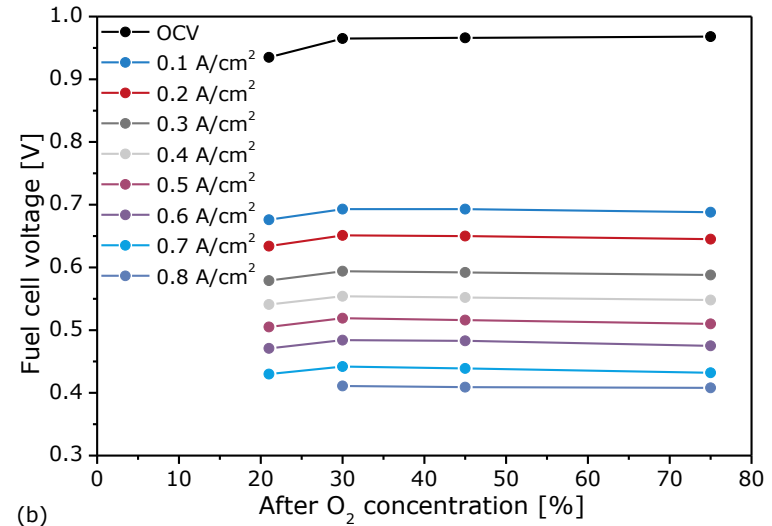
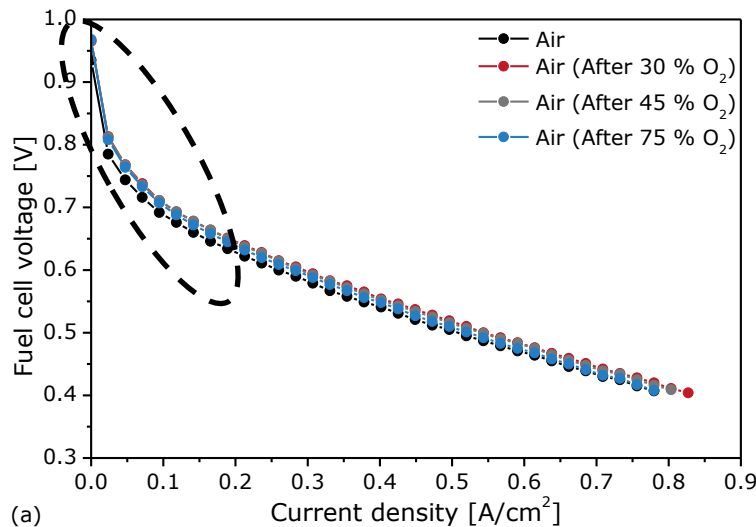
- Higher O₂ availability during FC operation → C corrosion (reduction CL support):
 - Pt detachment, Pt agglomeration, Pt ripening ...



Fuel and Air/O₂ Optimisation - 4

Effect of O₂-Enrichment (Fuel: synthetic reformat):

- MEA Characterisation: O₂ enrichment → Air

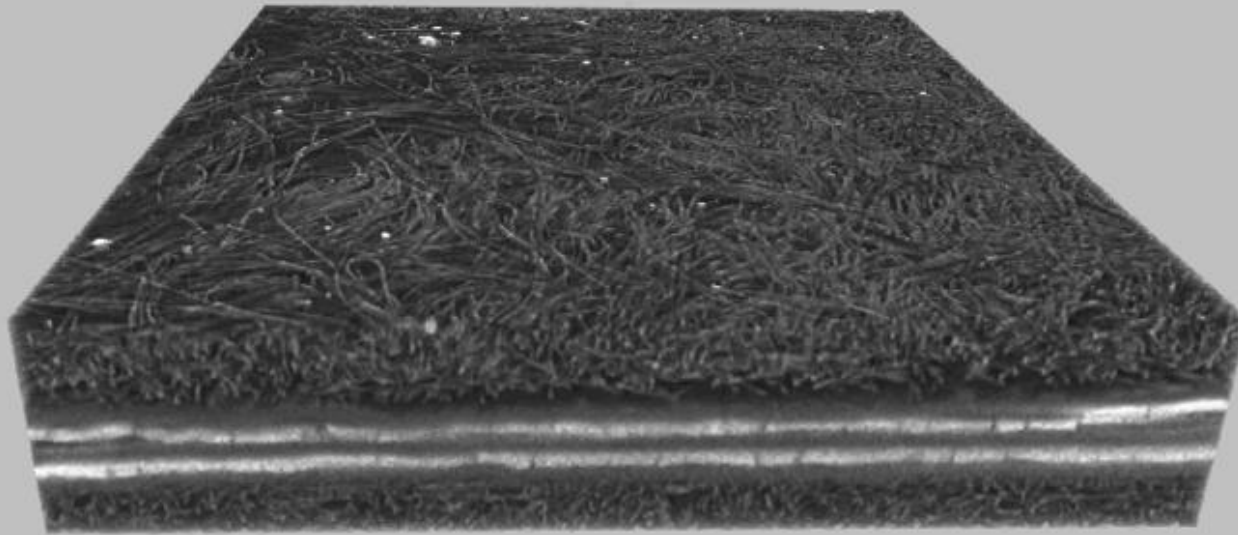


(a) Polarisation curves and (b) selected points of polarisation curves for the fuel cell operating with 78% H₂ + 22% CO₂/Air ($\lambda_{H_2}/\lambda_{Air}=1.5/2$) after oxygen enrichment. T=160 °C, p=1 atm, serpentine flow fields, P_c=0.75 MPa

- Polarisation curves: ↑ performance after [O₂] = 30 %
- Selected points: [O₂] = 45 - 75 % → ↓ performance at j>0.5 A/cm² ≈ Air
- After O₂-enrichment “activation region” is improved.



Fuel and Air/O₂ Optimisation - 5





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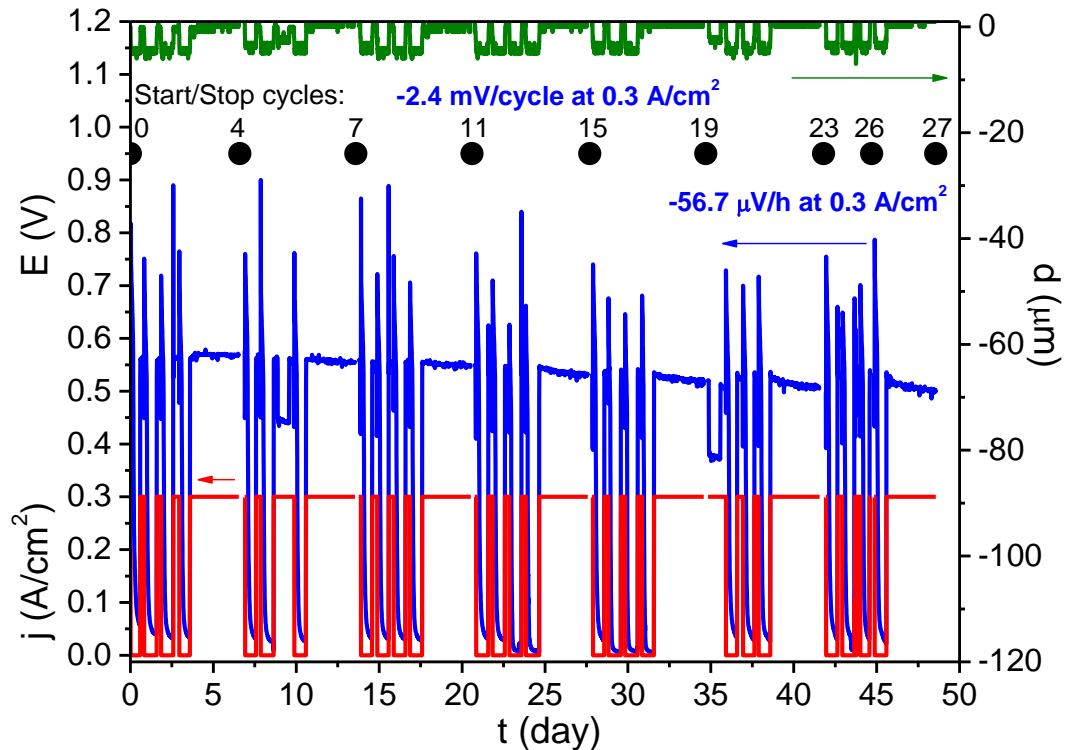
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Start-Stop-Cycling - 1

Test Procedure


- Duration of start/stop cycle: 1 day
- Standard break-in
- 0.3 A/cm^2 for 6h between cycles
- Shut-down with N_2 and OCV to T_{idle} and equilibration overnight
- T_{idle} : 100°C
- Weekly: IV and EIS with air/ O_2
- Monthly: full characterisation
- Weekend: 0.3 A/cm^2 / $160^\circ\text{C}/\text{H}_2/\text{air}$
- 4 cycles per week

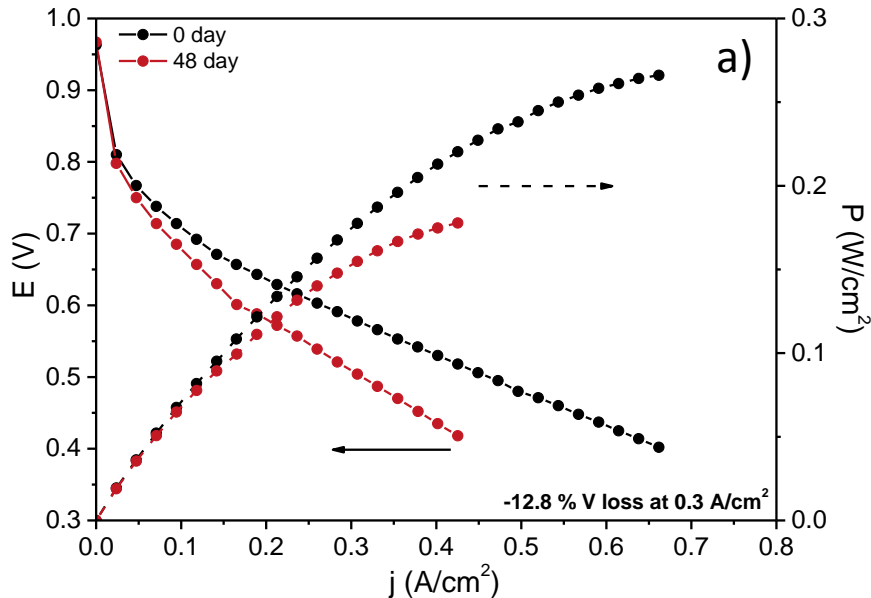



Current density, voltage and thickness changes as function of time, start-stop-cycling, $T=160^\circ\text{C}$, $p=1 \text{ atm}$, serpentine flow fields, $P_c=0.75 \text{ MPa}$

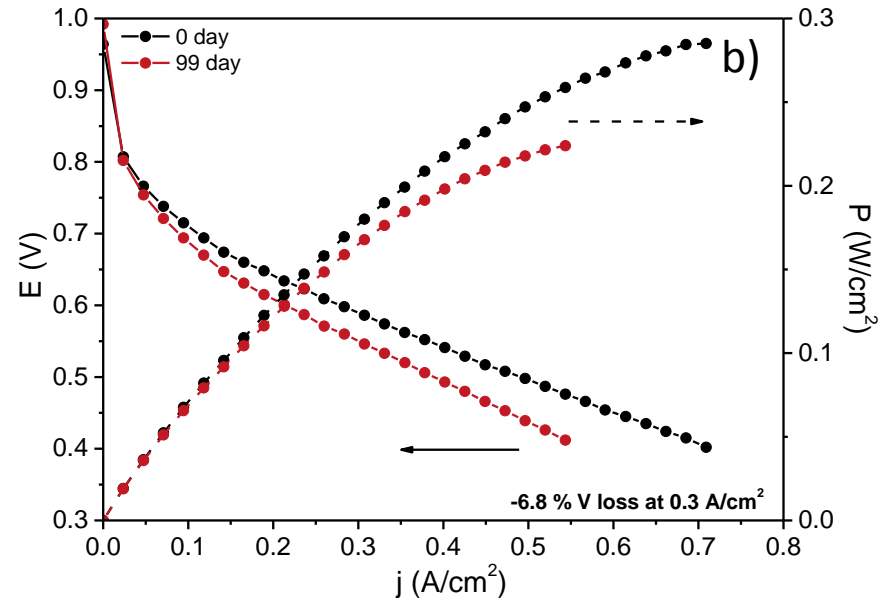


Start-Stop-Cycling - 2

 $T_{idle} = 100^{\circ}\text{C}$



 $T_{idle} = 25^{\circ}\text{C}$



Polarisation and power density curves for the fuel cell operating with $\text{H}_2 + \text{Air}$ ($\lambda_{\text{H}_2}/\lambda_{\text{Air}} = 1.5/2$), start-stop-cycling-procedure, a) $T_{idle} = 100^{\circ}\text{C}$ and b) $T_{idle} = 25^{\circ}\text{C}$, $T = 160^{\circ}\text{C}$, $p = 1 \text{ atm}$, serpentine flow fields, $P_c = 0.75 \text{ MPa}$

 27 cycles until EoL (at day 48)
 >1100h

 50 cycles until now; >2300h
 Test is still running.

→ Lower degradation rates for lower T_{idling}



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Summary

- Similar degradation rates for long term tests at constant current densities and for **fuel switching**
- Improvement of fuel cell performance after operating with **oxygen-enriched air** ($O_2=30\%$)
- Lower degradation rates for **start-stop-cycling** with lower idling temperature ($T_{idle}=25^\circ C$)



Thank you for your attention!

