Optimizing the Durability of Hydrocarbon-Based Proton Exchange Membranes for Proton Exchange Membrane Fuel Cells

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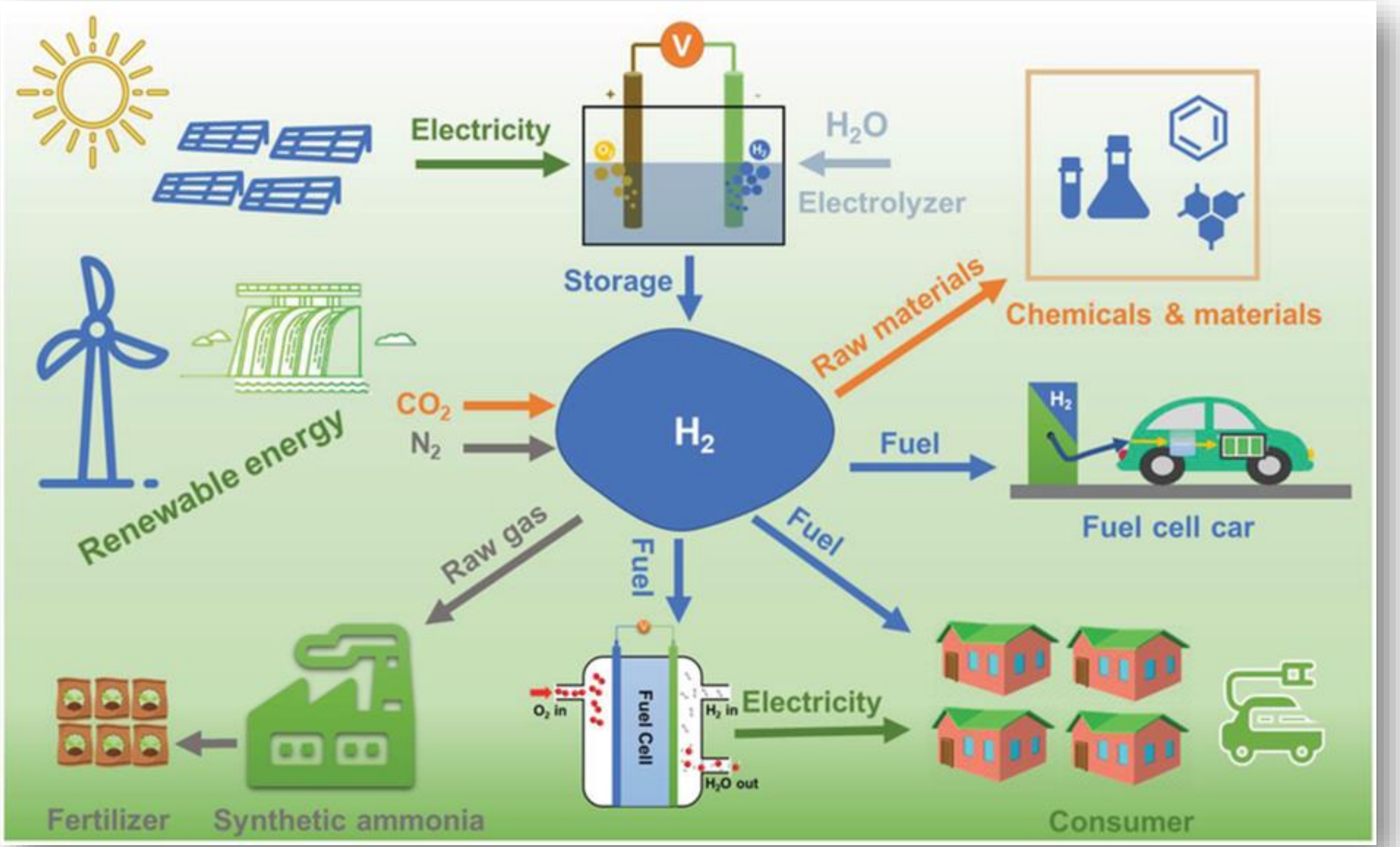
The Potential for a Hydrogen Economy in South Africa



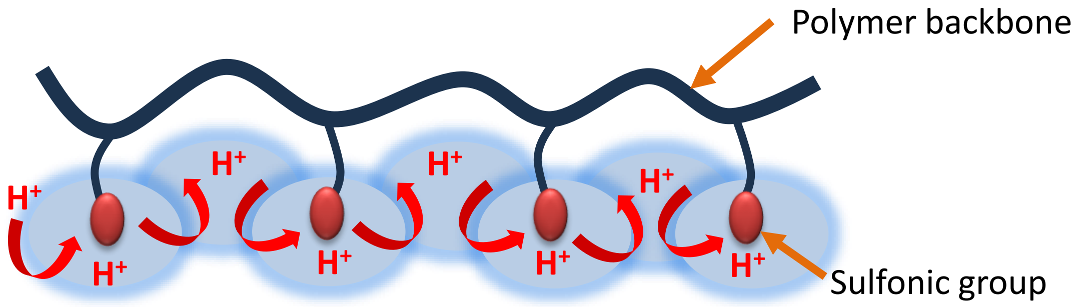
Pathway for a hydrogen economy Figure: Zhang et al., Advanced functional materials, 2020.

- ❑ Beneficiation of SA's resources
- ❑ Energy security and independence
- ❑ Economic growth and industrial development
- ❑ Decarbonization and environmental protection

Introduction to Ion Conductive Polymers or Ionomers

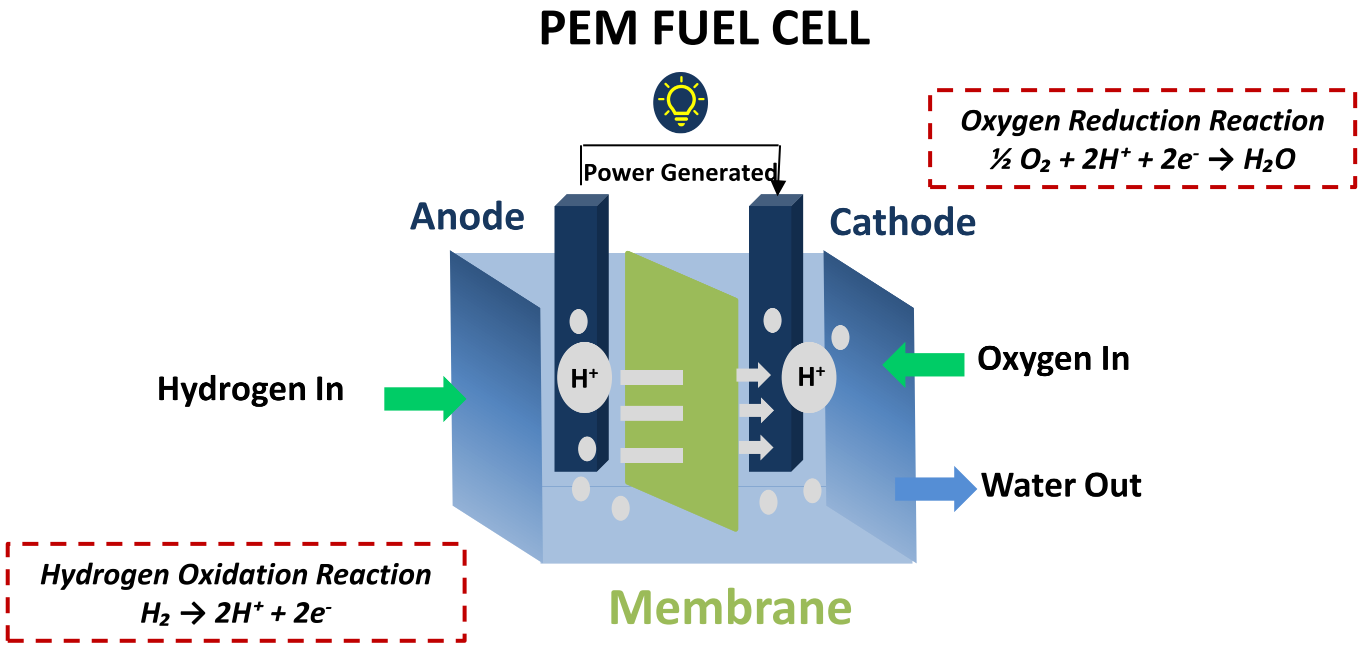
The heart of electrochemical technologies

Ionomers are ion exchange materials that selectively transports ions such as **H^+**.



Ionomers determine a system's:

Performance **Durability** **Efficiency**



State-of-the-Art Ionomer for PEMFC

HySA Catalysis Hydrogen South Africa

Per-fluorosulfonic acid (PFSA) based materials

Advantages

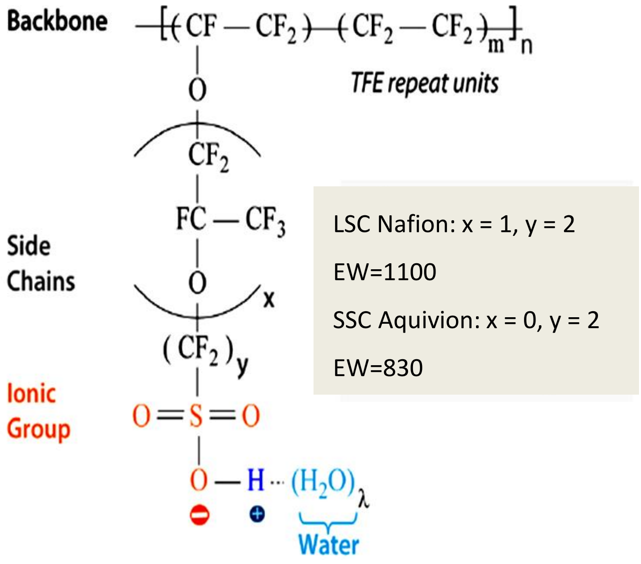
- ✓ Good proton conductivity (0.05 to 0.20 S/cm)
- ✓ Resistant to chemical attack and stability
- ✓ Mechanically strong and can be made into thin films
- ✓ Able to absorb large quantity of water

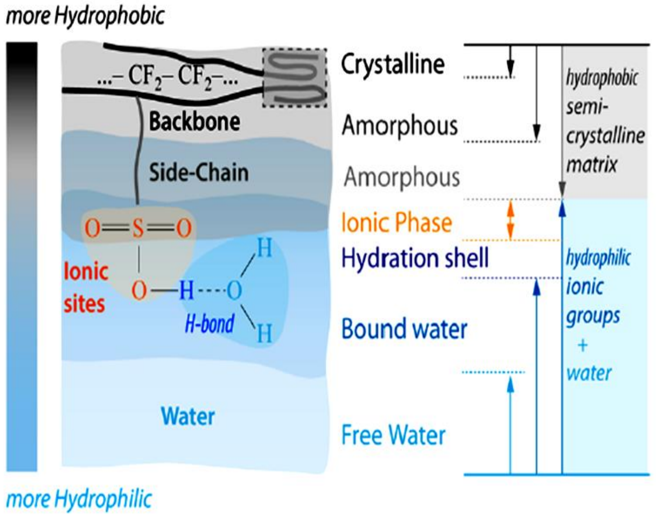
Disadvantages

- x High cost
- x High gas permeability
- x Sensitivity to high temperature (>90°C)
- x Growing environmental concerns

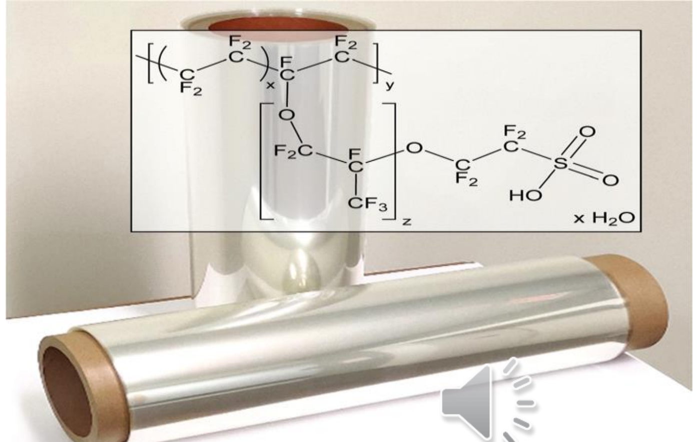
Kusoglu & Weber. Chemical reviews., 2017, 117(3), 987-1104

General chemical structure



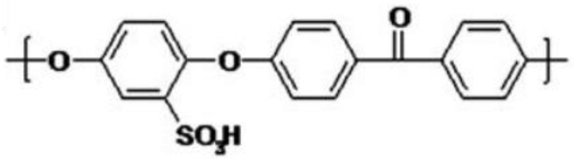


Aquivion Ionomer Dispersion


Nafion Membrane

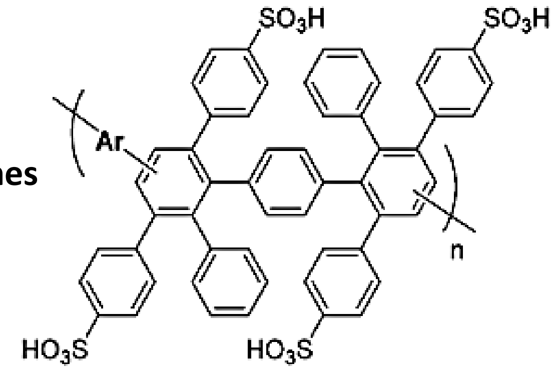
Non-fluorinated Hydrocarbon (HC)-based Ionomers

Structure and Properties



sulfonated polyether ether ketone (SPEEK)

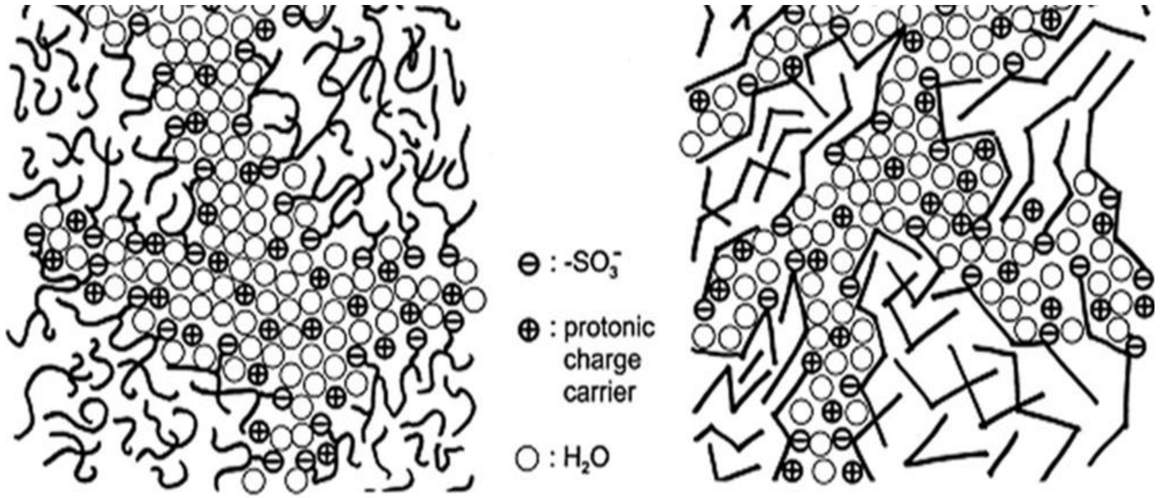
Sulfo-phenylated polyphenylenes (sPPB-H+)



- Aromatic backbone
- Research and development efforts have increasingly focused on sulfonated polyphenylenes (SPPs).
- No side chains.
- Higher glass transition temperatures (>300°C).
- Soluble in polar solvents with high boiling points (excluding water).

Proton Conductivity

PFSA ionomer **Vs** **HC ionomer**



- Generally higher ion-exchange capacity (IEC) than PFSA ionomers, leading to more proton sites.
- Conductivity improves in fully hydrated state.
- Lower conductivity compared to PFSAs under low humidity conditions due to limited water retention.

Balogun et al. Journal of The Electrochemical Society, 2020, 167(8), p.084502
Nguyen et al. Advanced Energy Materials, 2022, 12(12), p.2103559

In-situ Performance and durability of HC-based MEAs

Performance

- Comparable performance to PFSA MEAs at high humidity (> 80%) and under H_2 / O_2.
- Reduced fuel cell performance under targeted automotive conditions (H_2 /Air, T > 90°C, low RH).

PEM Durability

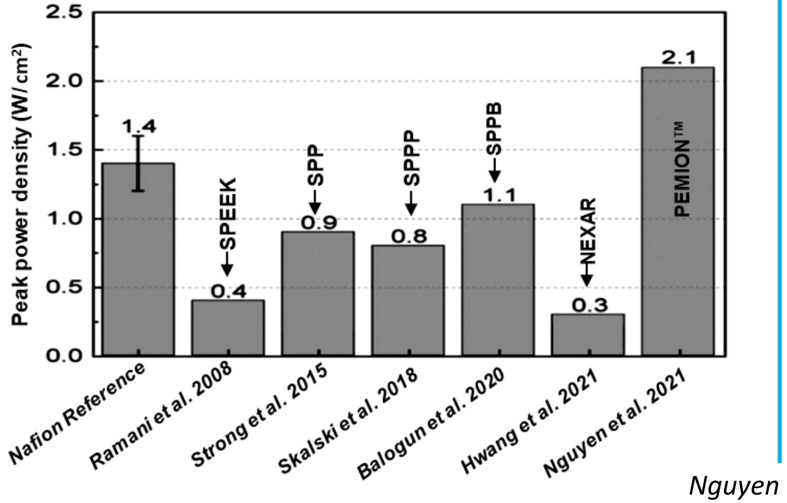
- The high swelling and dimensional instability results in mechanical failure in frequent wet/dry cycles in fuel cell operation.

US DOE target for PEM Durability

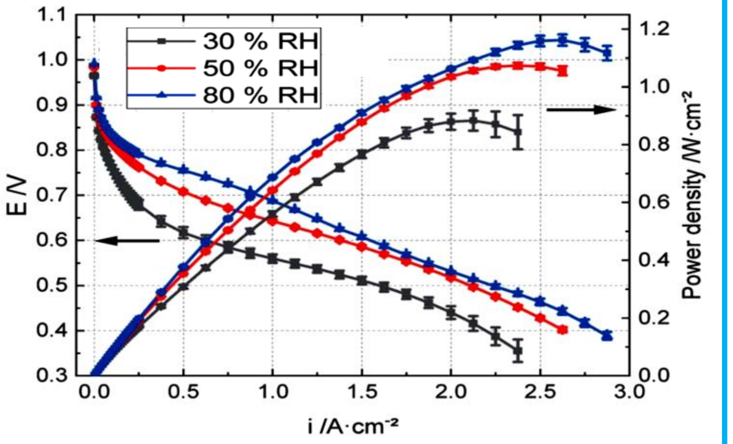
Hydrogen crossover: <15 mA/cm^2
OCV: <20% OCV decrease

After 20,000 cycles

Peak power densities of fully hydrocarbon MEAs over the last decades at 95% RH, 80°C, H_2 / O_2 ambient pressure

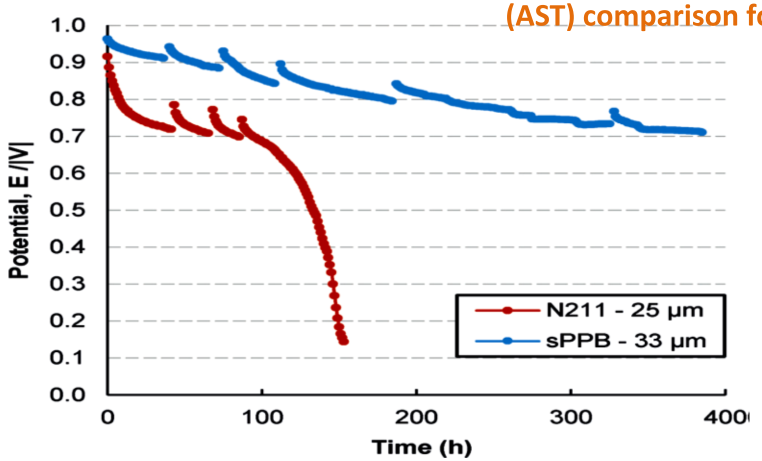


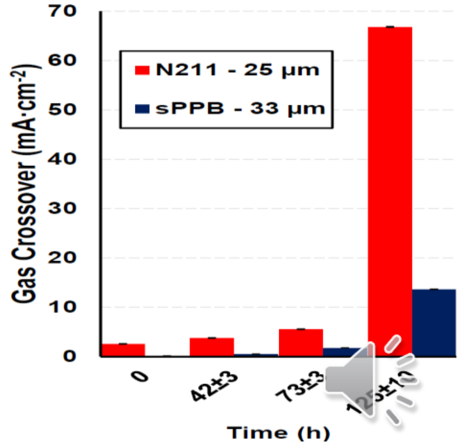
Polarization behaviours of Pemion™ under varied RH levels at 80°C, H_2 /air, 250 kPa abs



Nguyen et al. 2021. Sustainable Energy & Fuels, 5(14), pp.3687-3699.

Combined membrane chemical/mechanical accelerated stress test (AST) comparison for sPPB-H+ vs. N211





Adamski et al. Angew. Chem. 2017, 129, 9186 –9189.

Research Objectives

- To compare the performance of hybrid HC-PFSA based MEAs to that of a fully PFSA-based MEAs under high and low humidity operating conditions.

- To evaluate the durability of HC-based PEMs in comparison to PFSA-based PEMs by subjecting them to accelerated stress testing.

- To evaluate the effect of coating conditions and different solvent systems used in catalyst ink on the durability of HC-based membranes.

WP 1 Establishing Baseline PFSA and Hybrid HC-PFSA MEAs Performance and Durability

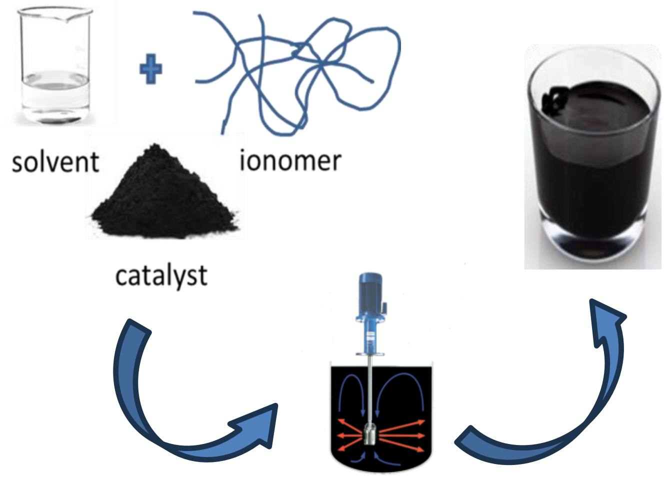
WP 2 Investigating the Impact of Solvent System on PEM Durability

WP 3 Investigating the Impact of Coating Parameters on PEM Durability

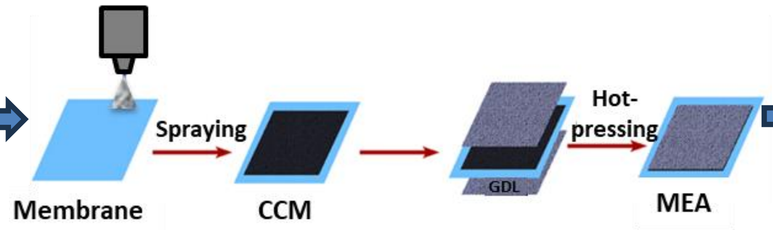
Research Methodology: Work Package 1

Establishing Baseline PFSA and Hybrid HC-PFSA MEAs Performance and Durability

Ink preparation



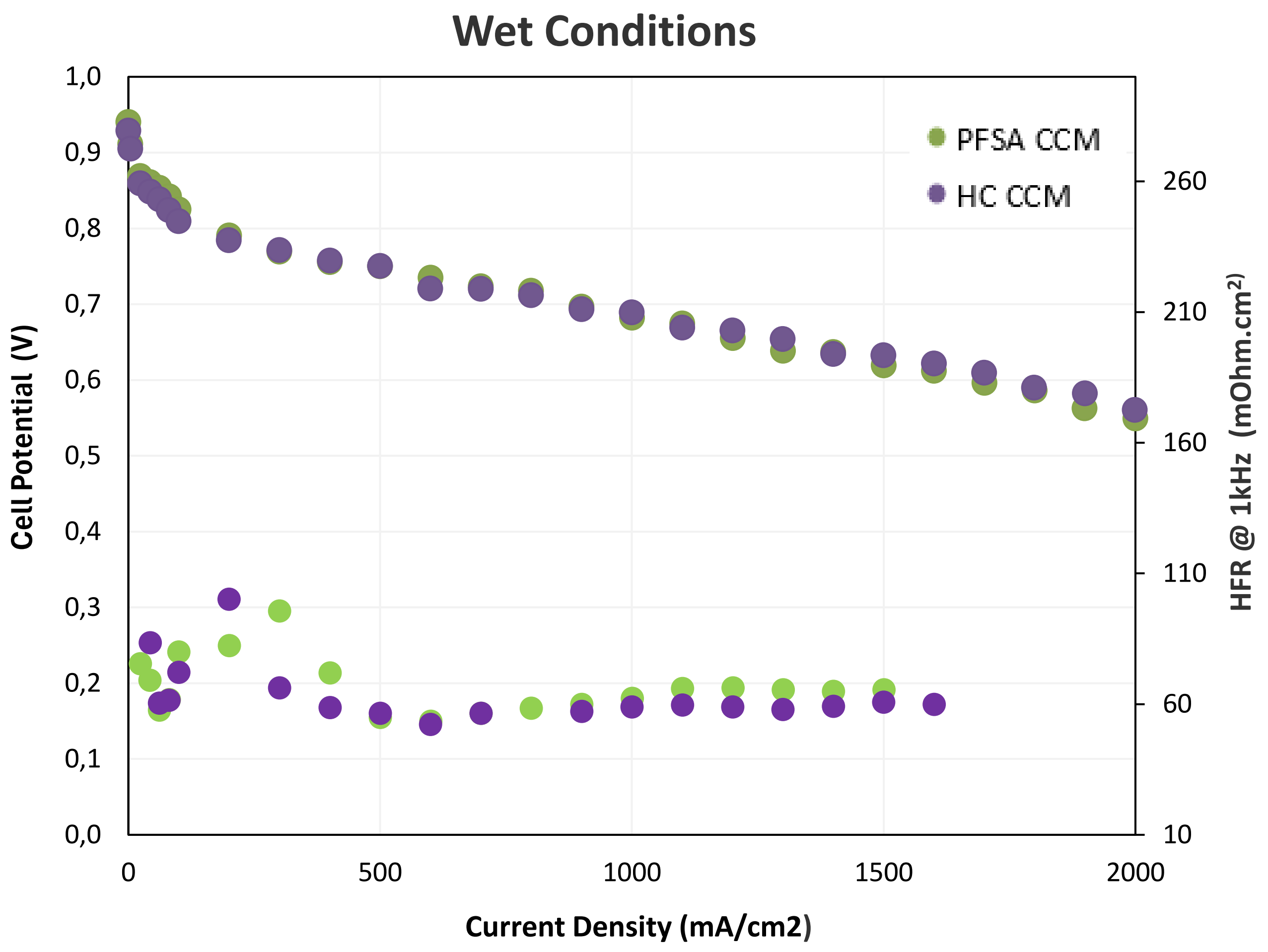
MEA fabrication

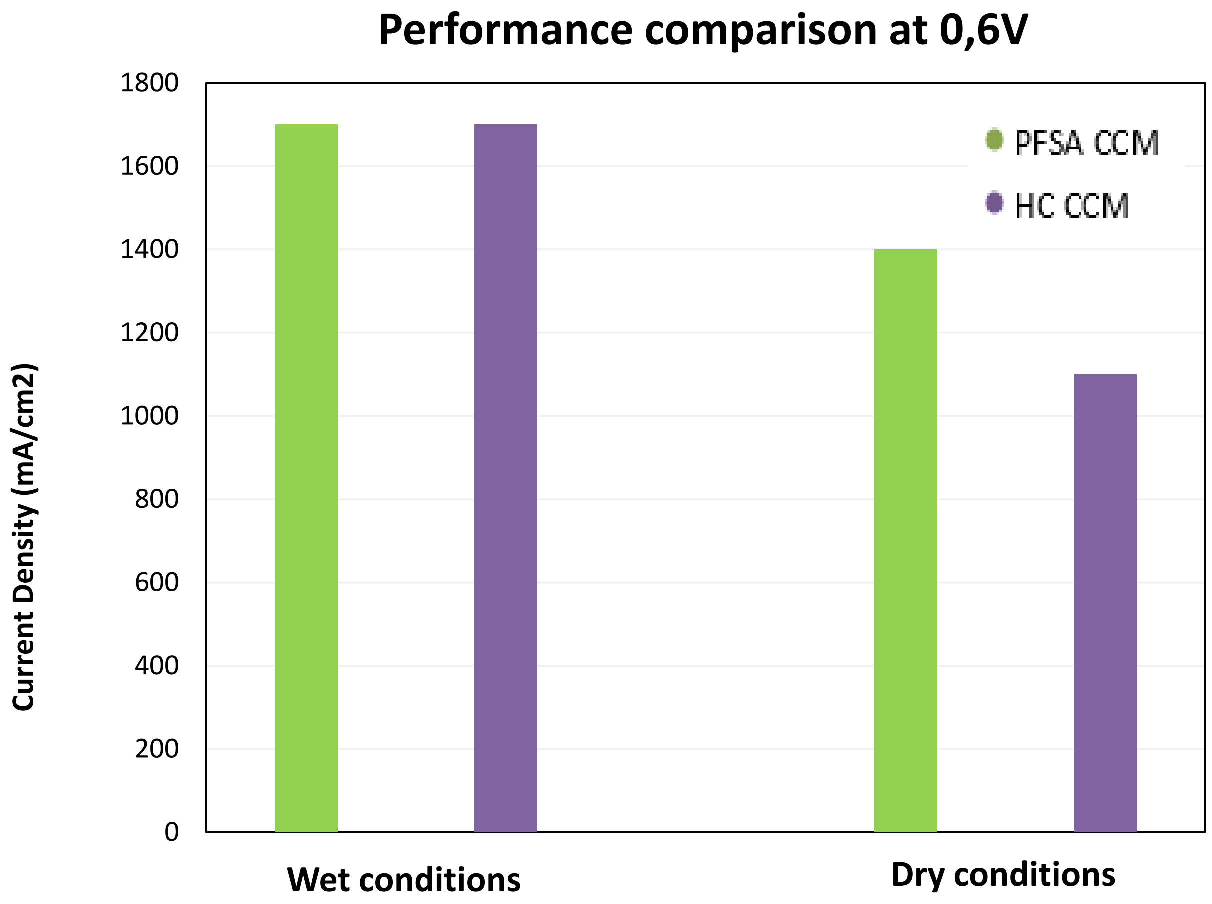


In-situ single cell testing

- Performance under wet and dry conditions.
- Membrane accelerated stress testing (AST) according to US DOE protocol.

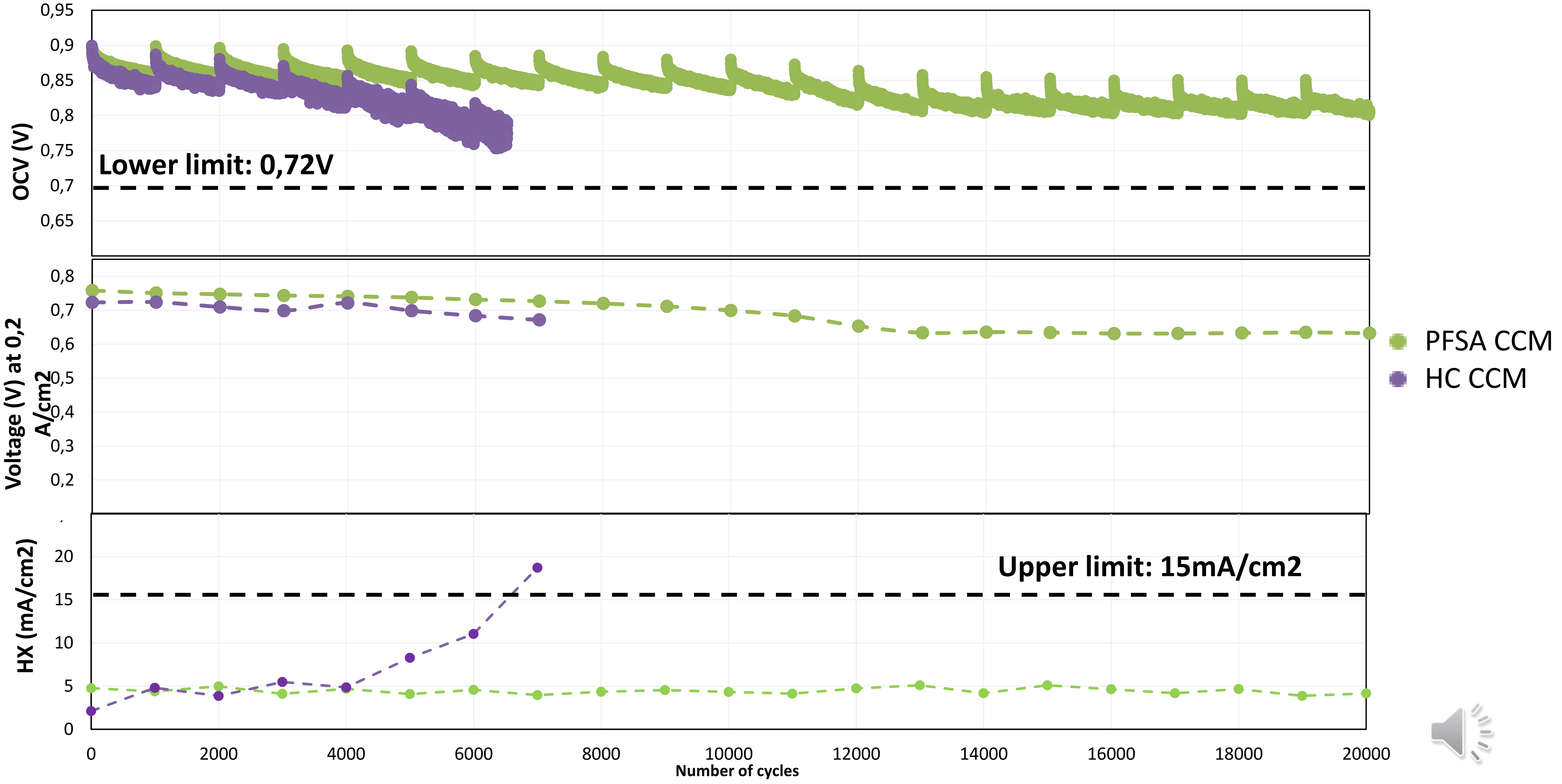
WP1 Results: Performance



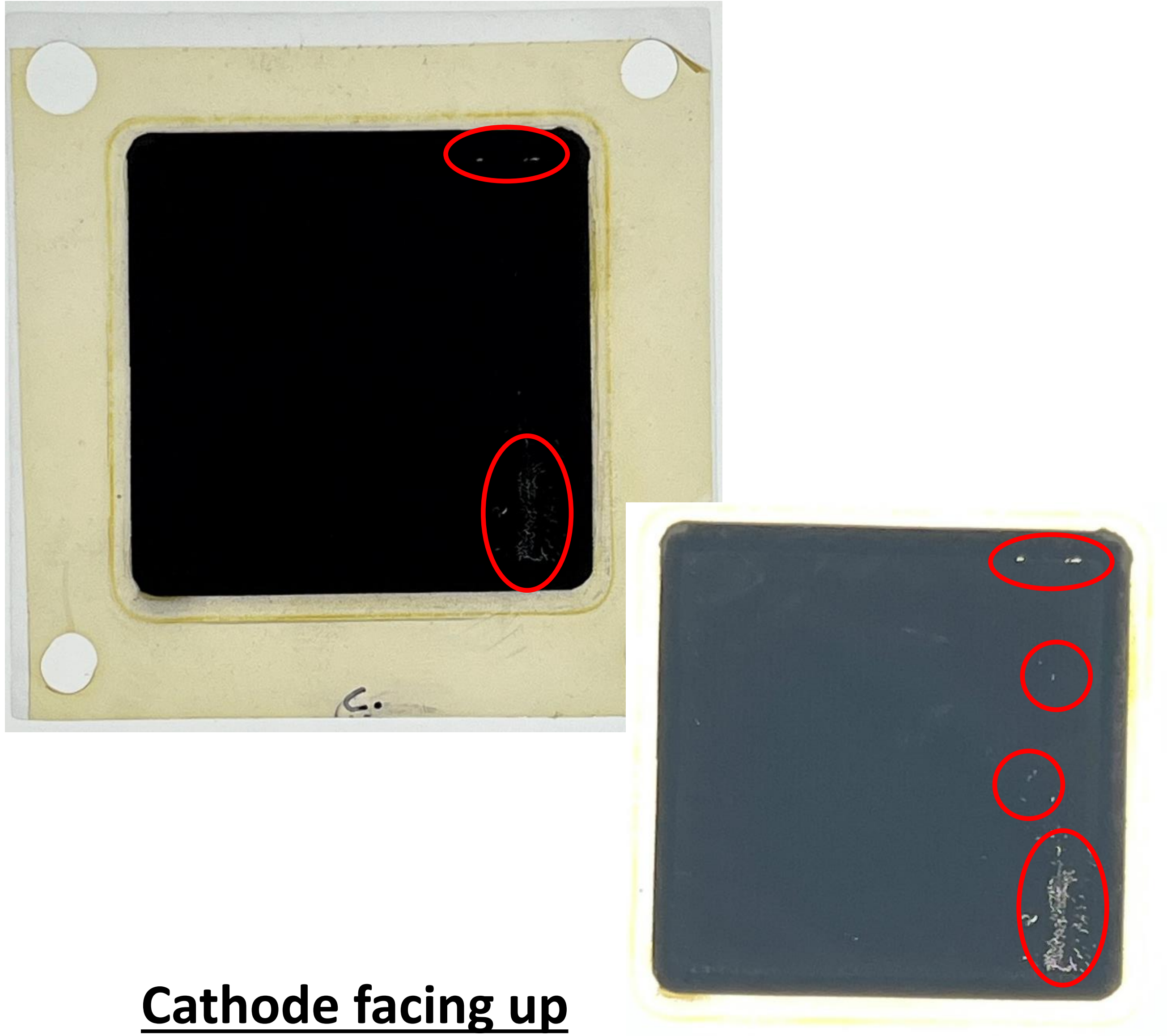


H2/ Air (a/c), Tcell:80 °C, RHan: 80 %, RHcat: 80 %,
s: 1.8 / 2.0, BP: 2barabs / 2barabs (a/c)
FF: Straight channel design

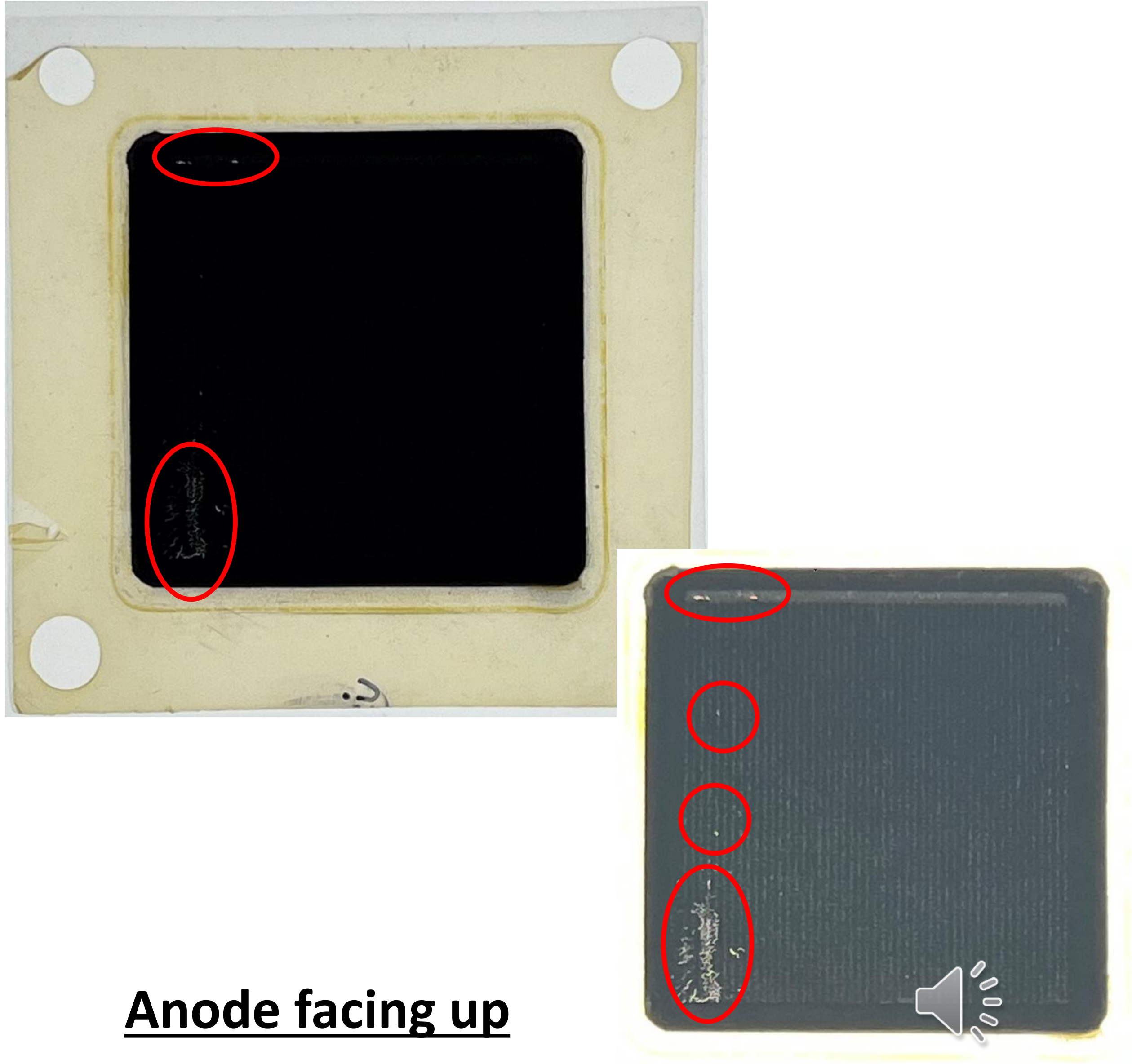
Membrane AST Metrics



Visual Inspection of HC CCM Postmortem

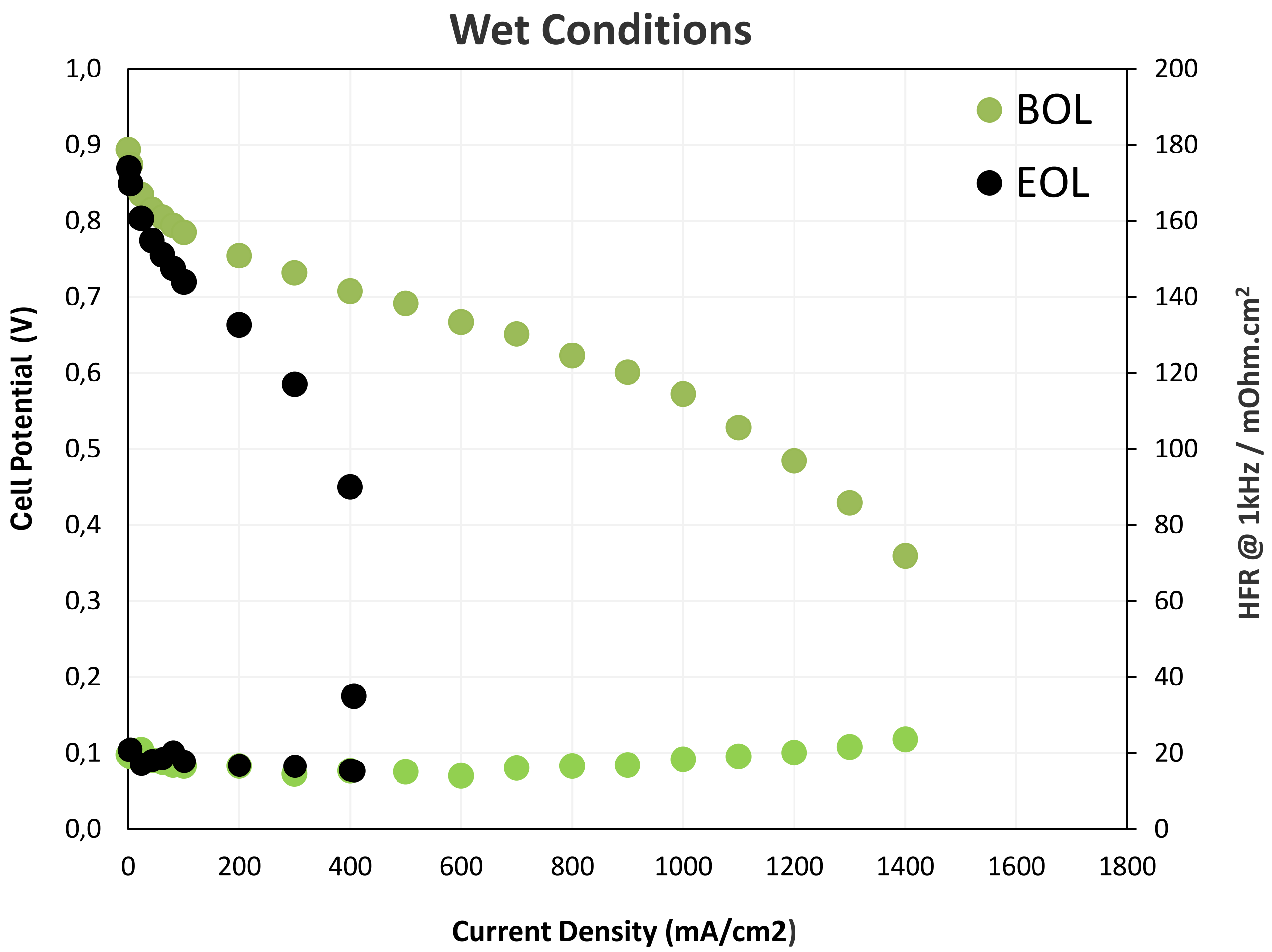


Cathode facing up

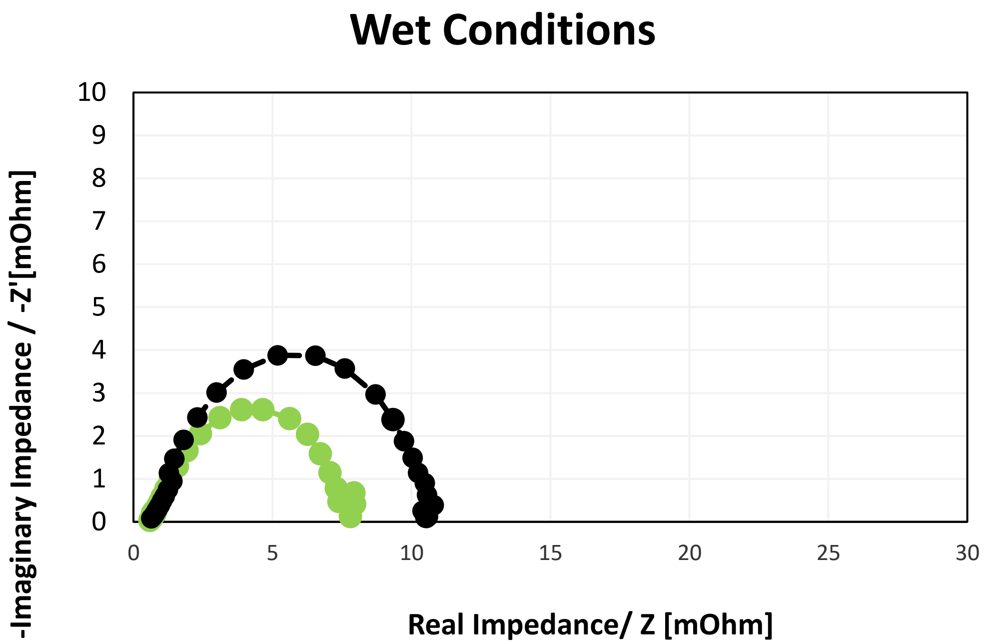


Anode facing up

Performance and Diagnostics: Baseline PFSA MEA

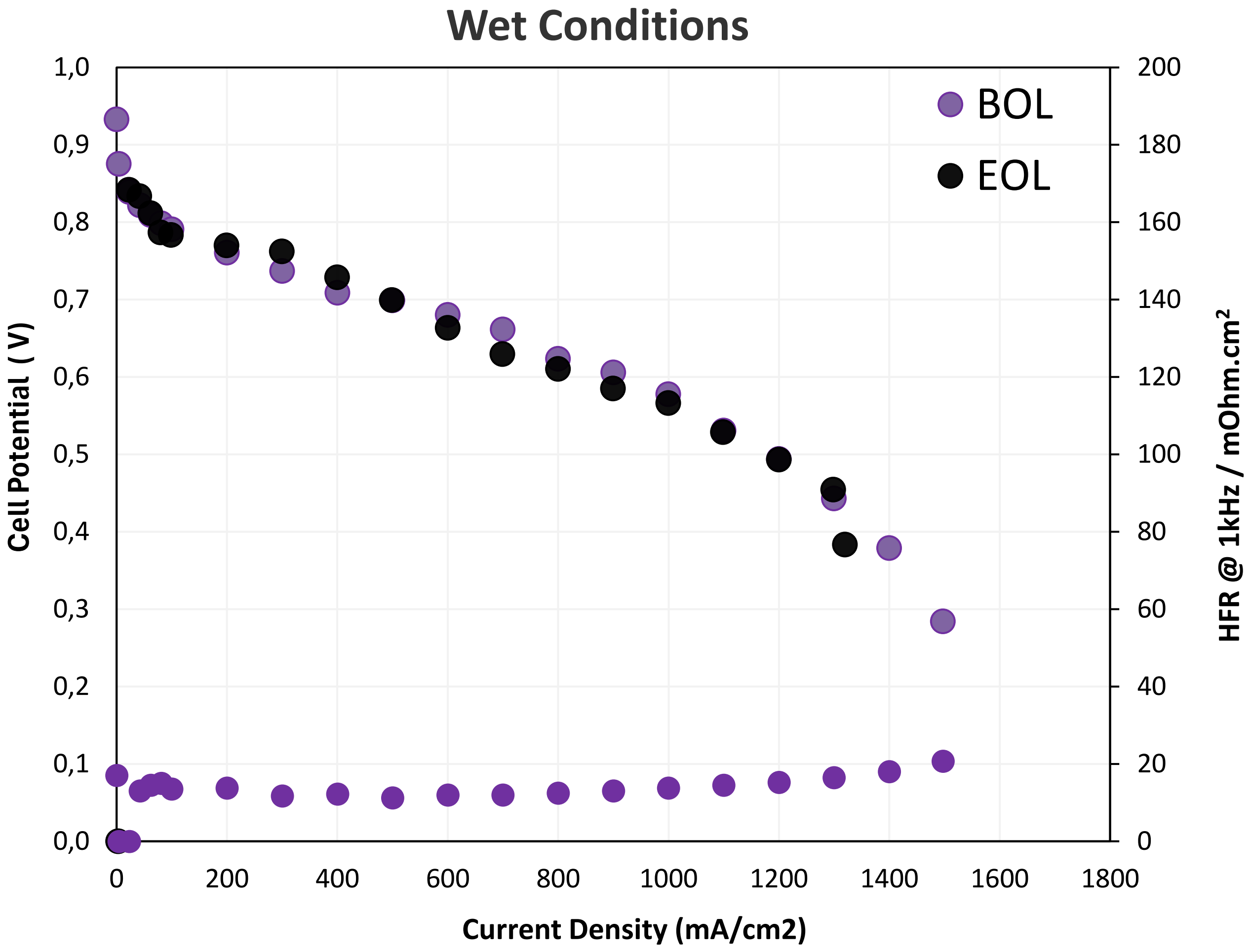


H2/ Air (a/c), Tcell:80 °C, RHan: 80 %, RHcat: 80 %,
s: 1.8 / 2.0, BP: 1barabs / 1barabs (a/c)
FF: Straight channel design

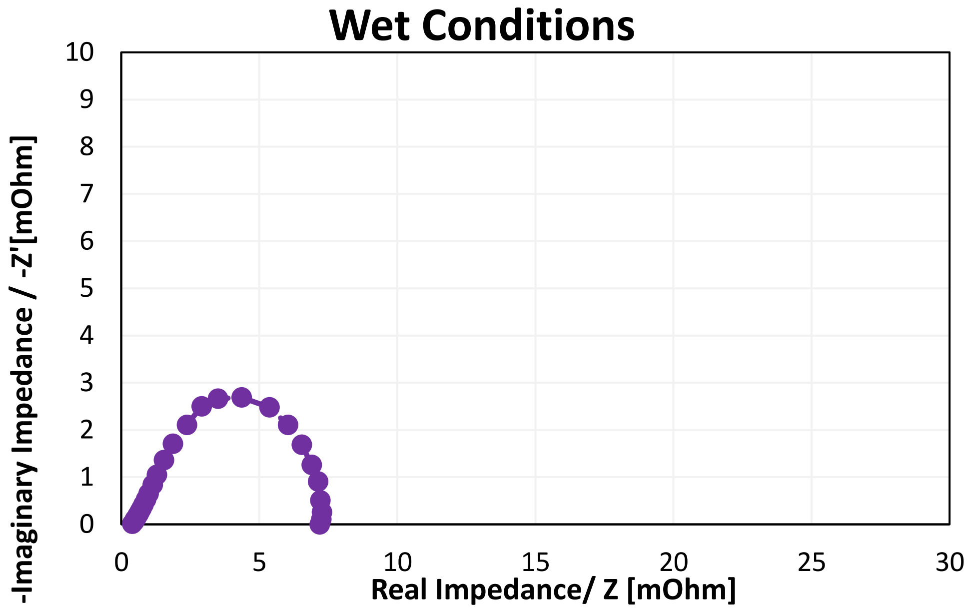


ORR Activity Parameters		
	BOL	EOL
Tafel Slope (mV.dec)	89,2	123,6
Mass Activity @900mV (A.mgPt)	0,038	0,016
Pt SA (m^2.gPt)	40	21
Specific Activity @ 900mV (µA.cm^2 Pt)	94	75
Proton Transport Resistance (mOhm.cm^2)	71	

Performance and Diagnostics: HC MEA



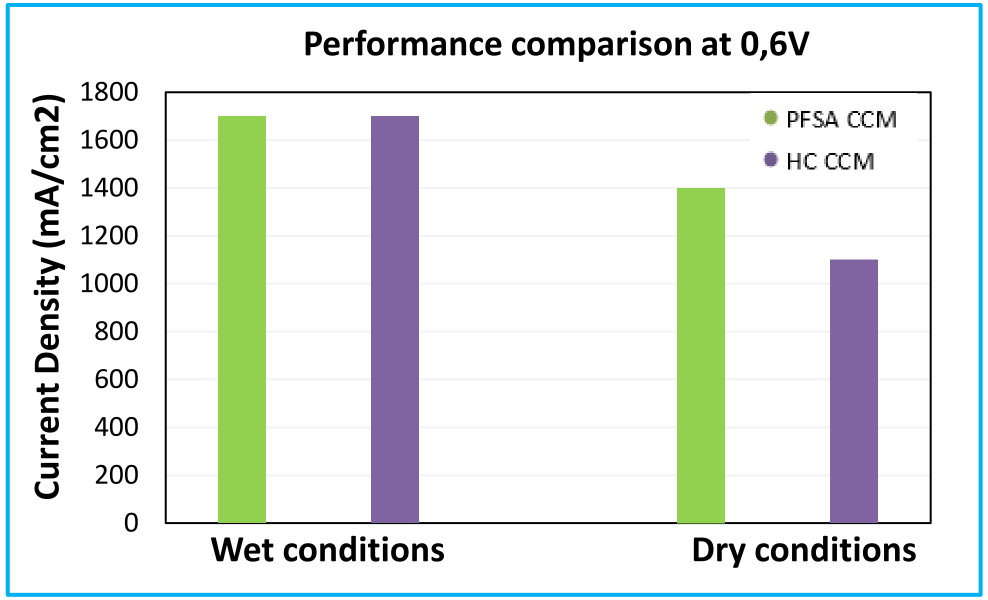
H2/ Air (a/c), Tcell:80 °C, RHan: 80 %, RHcat: 80 %,
s: 1.8 / 2.0, BP: 1barabs / 1barabs (a/c)
FF: Straight channel design

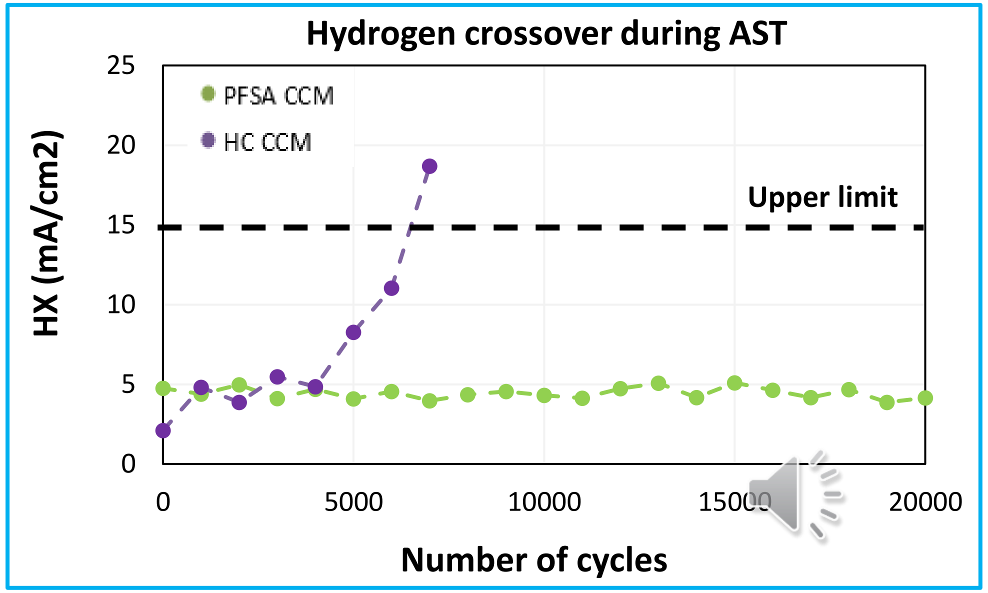


ORR Activity Parameters		
	BOL	EOL
Tafel Slope (mV.dec)	81,7	
Mass Activity @900mV (A.mgPt)	0,043	
Pt SA (m^2.gPt)	49	49
Specific Activity @ 900mV (µA.cm^2 Pt)	88	
Proton Transport Resistance (mOhm.cm^2)	43	

Conclusion and Future work

- HC MEAs perform comparably to PFSA MEAs under high wet conditions, but exhibit higher humidity dependency, leading to significant performance drops under dry conditions.
- HC membrane experience severe membrane degradation after 5000 cycles, with cracks and mechanical failure observed, particularly at the catalyst layer edges.
- PFSA CCMs, while surviving the AST, suffer catalyst layer degradation, ORR kinetic losses, and significant ECSA reductions due to Pt dissolution and/or agglomeration.





Future work:

- More in depth postmortem analysis of the HC based CCMs after AST to identify and understand the mechanisms and stressors responsible for the membrane degradation.
- Investigate how solvent system and coating parameters influence HC membrane integrity and durability.

Acknowledgements

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MINTEK

Thank you for your attention!

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