FURTHER-FC

Further **U**nderstanding **R**elated to **T**ransport limitations at **H**igh current density towards future **E**lect**R**odes for **F**uel **C**ells

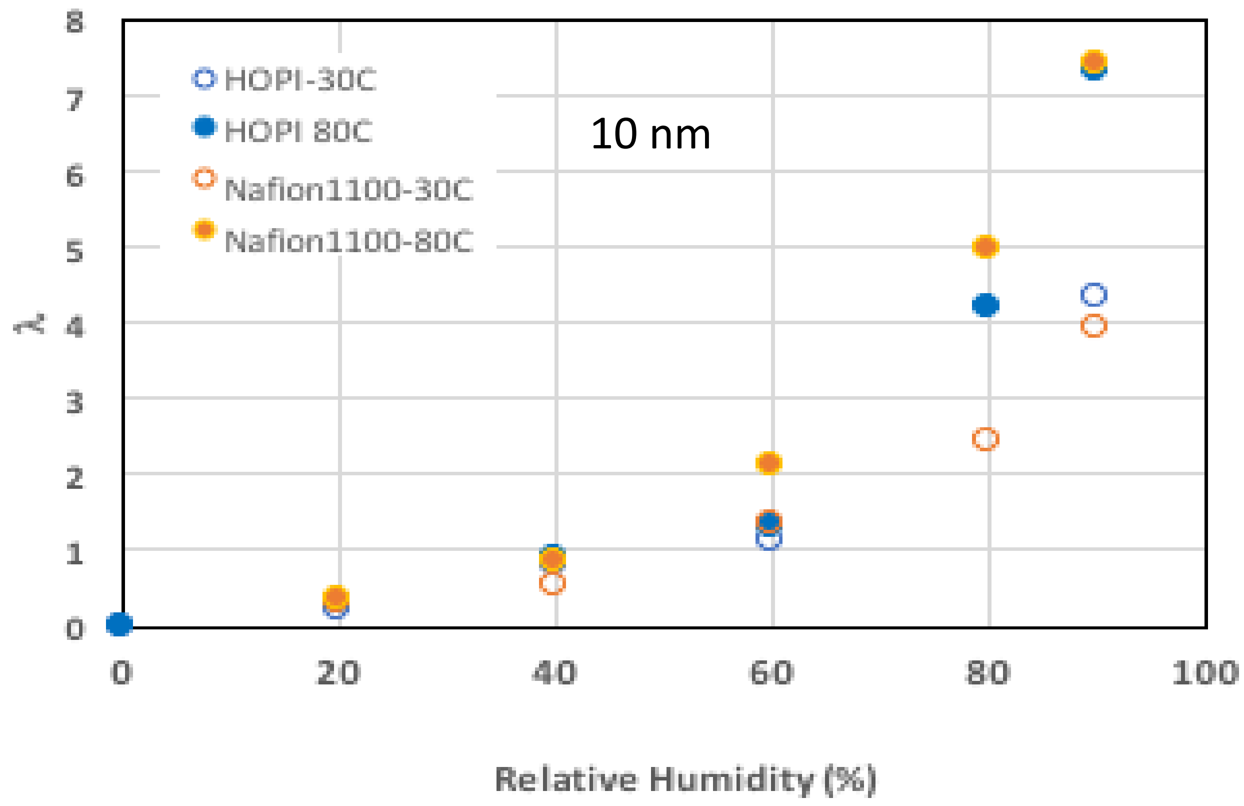
Characterization of transport properties: thin film and CCL

Final Workshop

Ionomer ultra-thin film hydration

Quartz Crystal Microbalance

Average number of water molecule per SO_3^-



Wate uptake increases with RH and T

Very similar behaviour for HOPI and D2020

OUTLINE

Ionomer thin films properties

- Swelling
- H^+ conductivity
- O_2 transport properties

CCL properties

- Hydrophilicity/solvophilicity
- H^+ conductivity
- e^- conductivity

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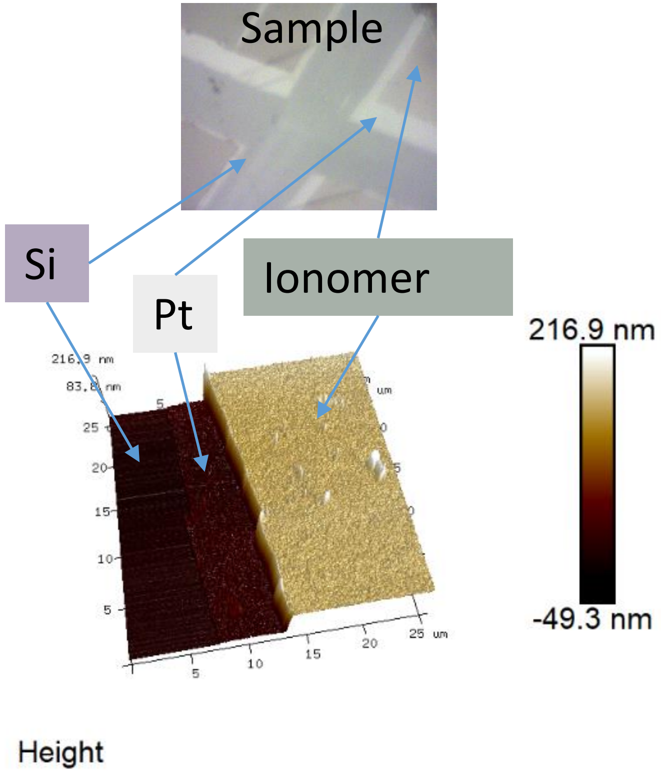
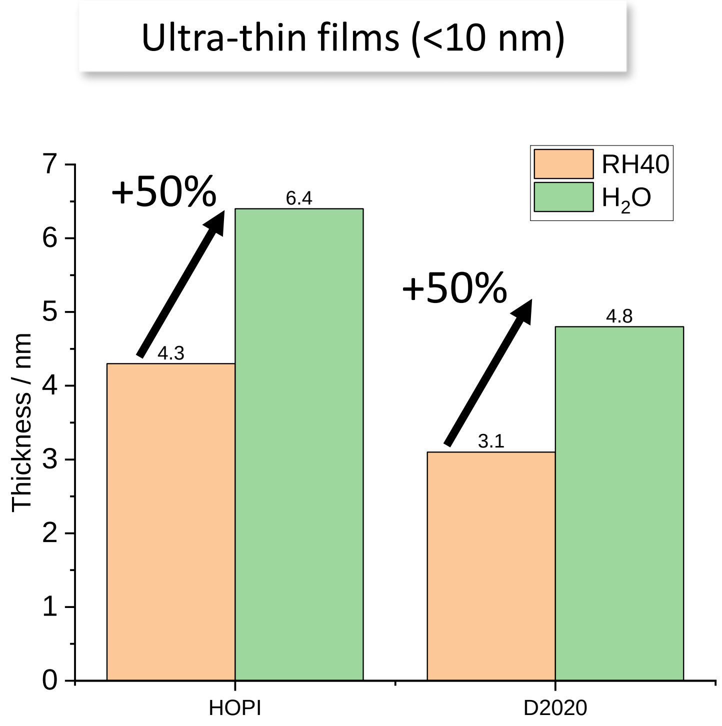
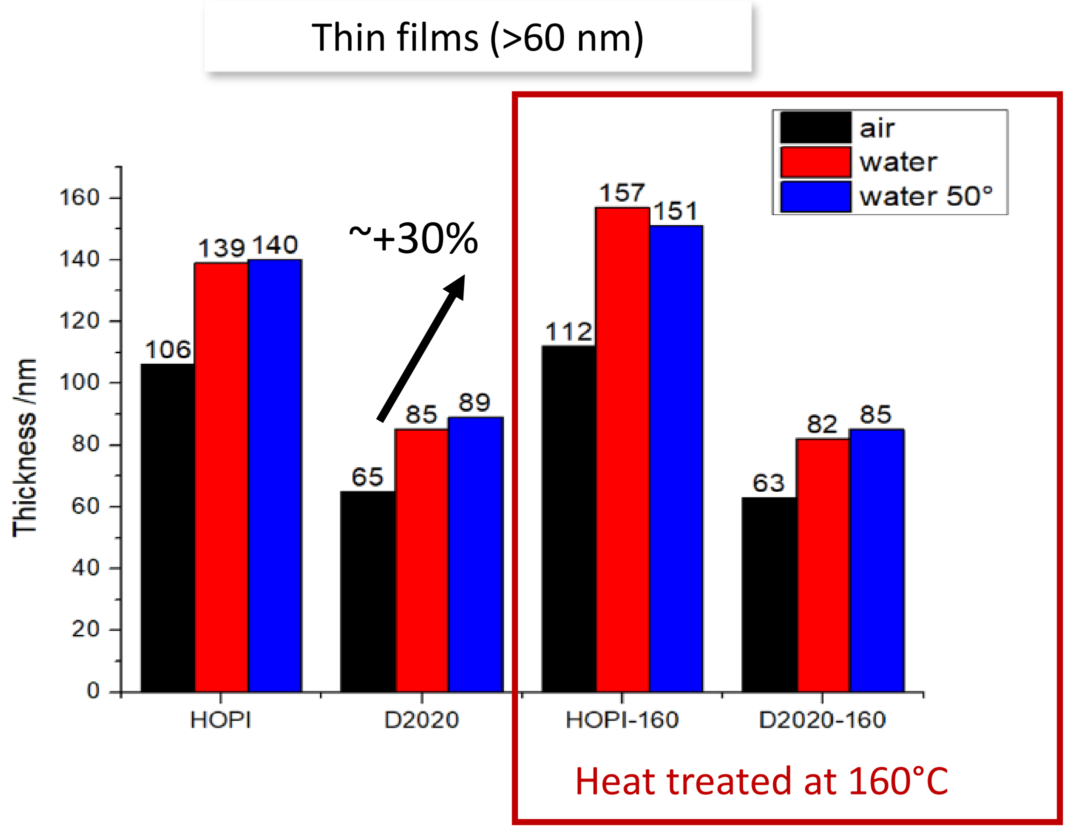
Ionomer thin film swelling

Atomic Force Microscopy







Measurement of ionomer swelling with AFM in liquid cell:

- Ultra-thin layers (< 10 nm) and thin fims produced via self assembly from IPA diluted dispersion
- Measurement of HOPI/D2020 thickness in air then adding of water, measurement at exact same position in liquid
- For thicker layers additional measurements: water at 50 °C then heating to 160 °C and measuring again in air, water and water at 50 °C
- +50 % thickness for ultra-thin layers and +30 % for thin layers in water. Same for HOPI and D2020.

Ionomer ultra-thin film proton conductivity

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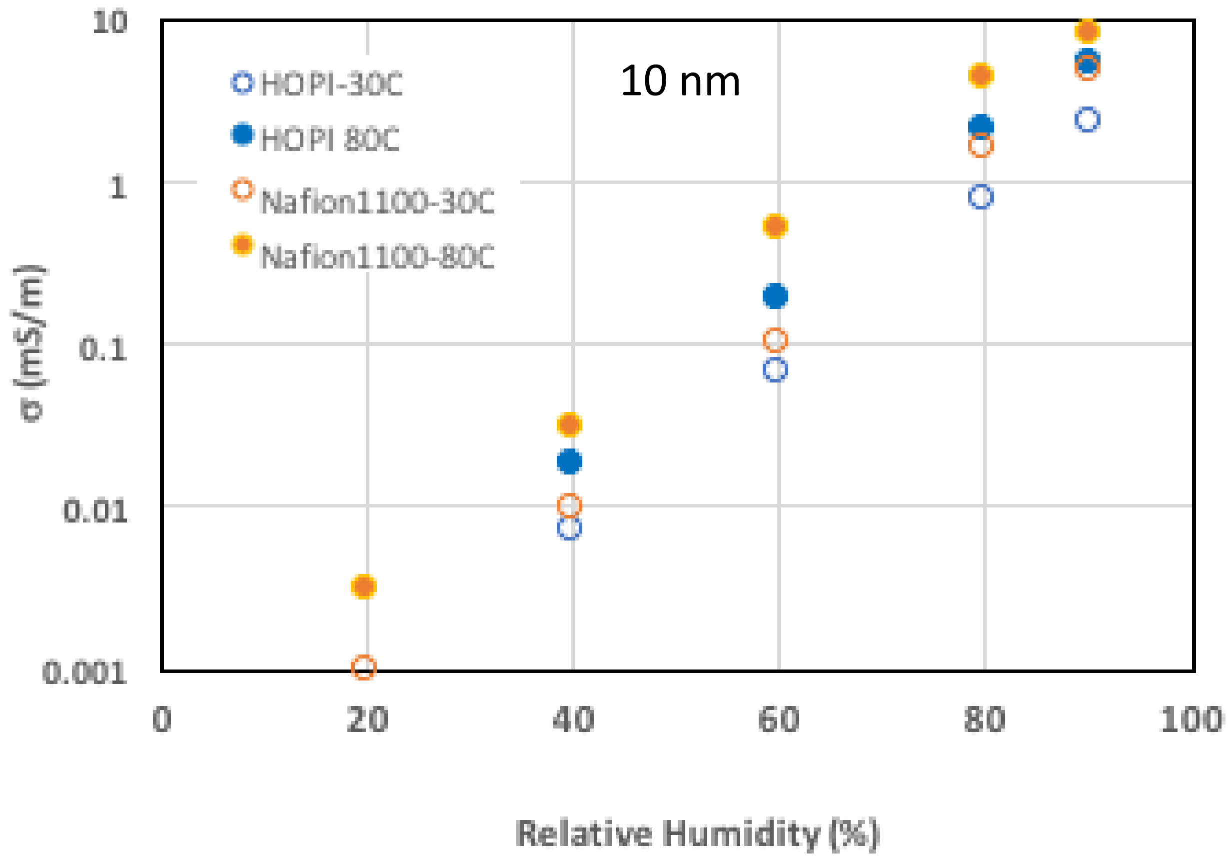
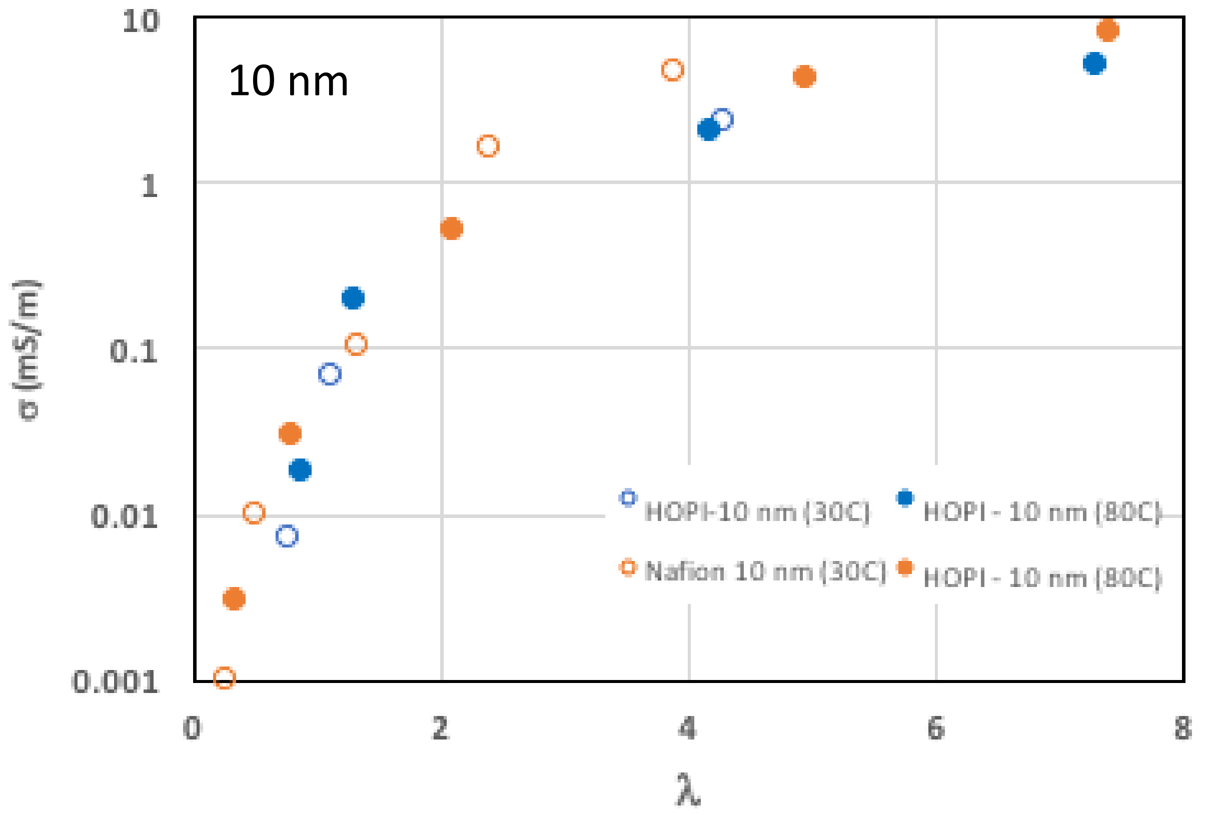
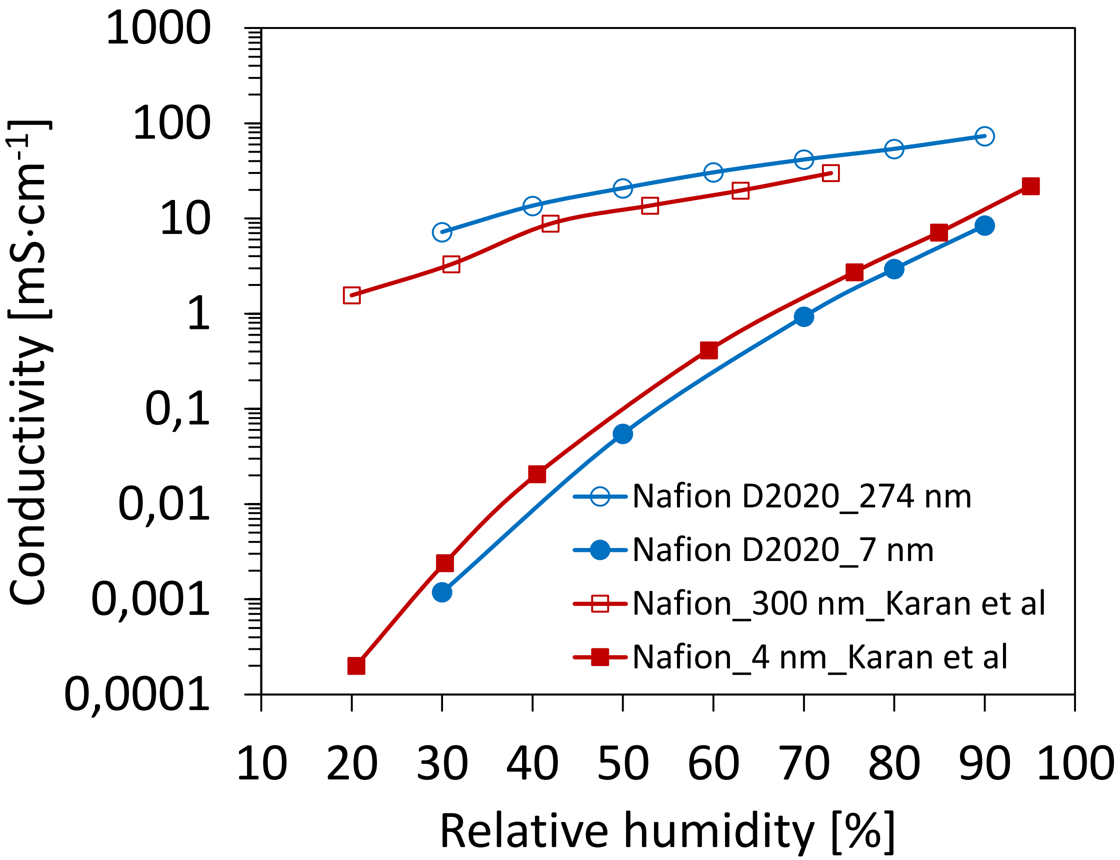




Conductivity of HOPI and Nafion thin film similar, possibly slightly lower conductivity for HOPI

Ionomer thin film proton conductivity



- Significant decrease in conductivity with the thickness of the film
- Good agreement between CEA results and results from Karan *et al.*

Ionomer thin film ionic current by AFM

Hochschule Esslingen
University of Applied Sciences

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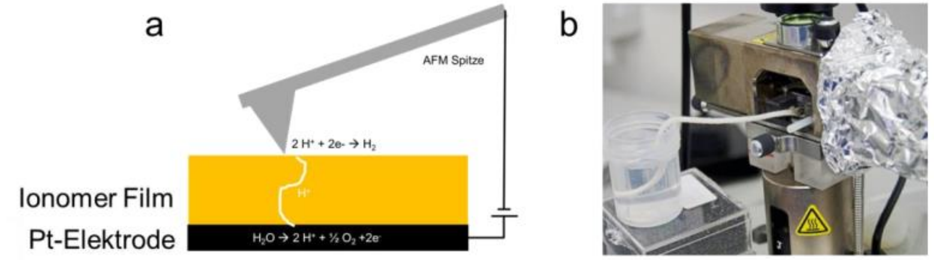
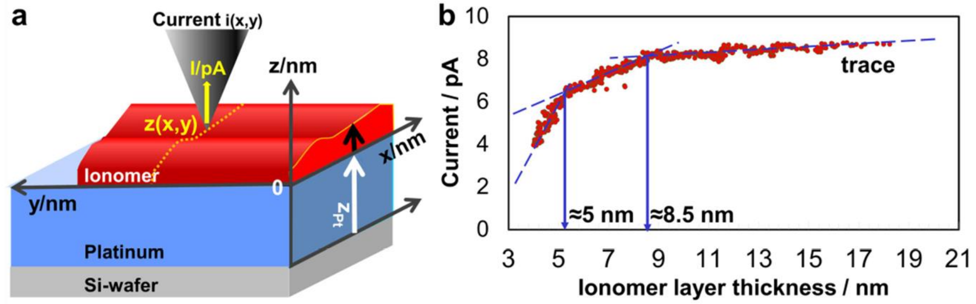
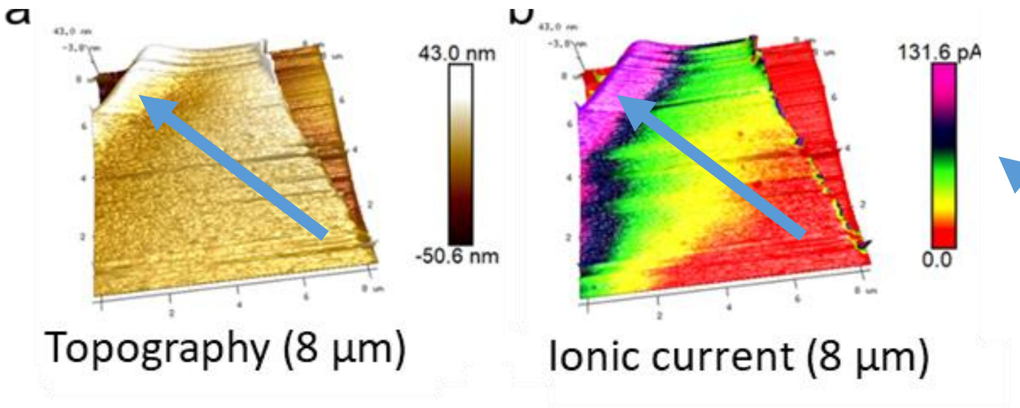






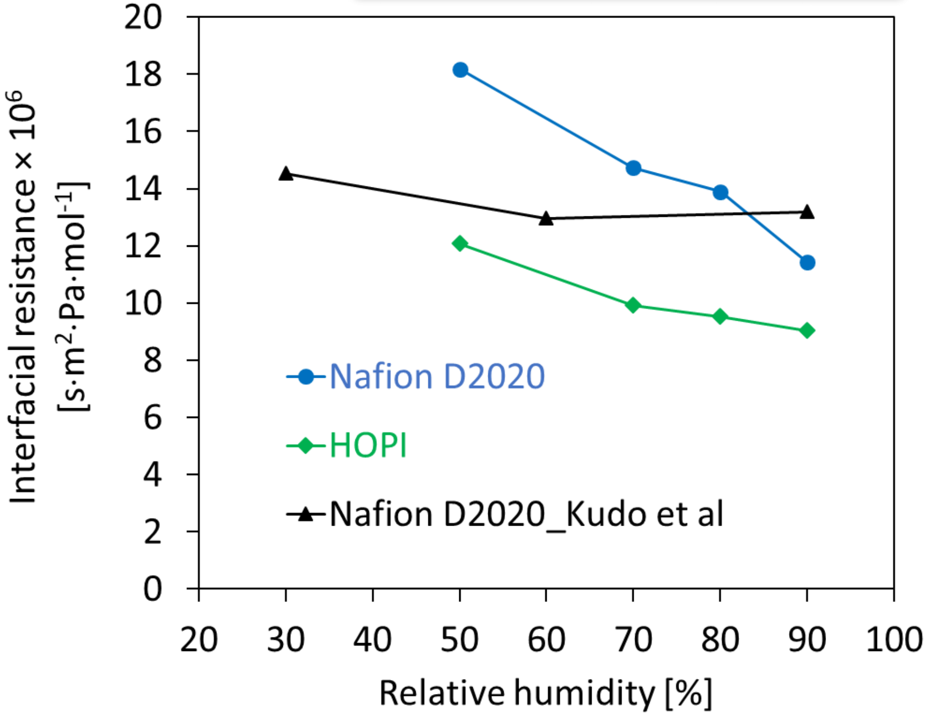
Increasing thickness and ionic current

Ionic current at different ionomer layer thickness

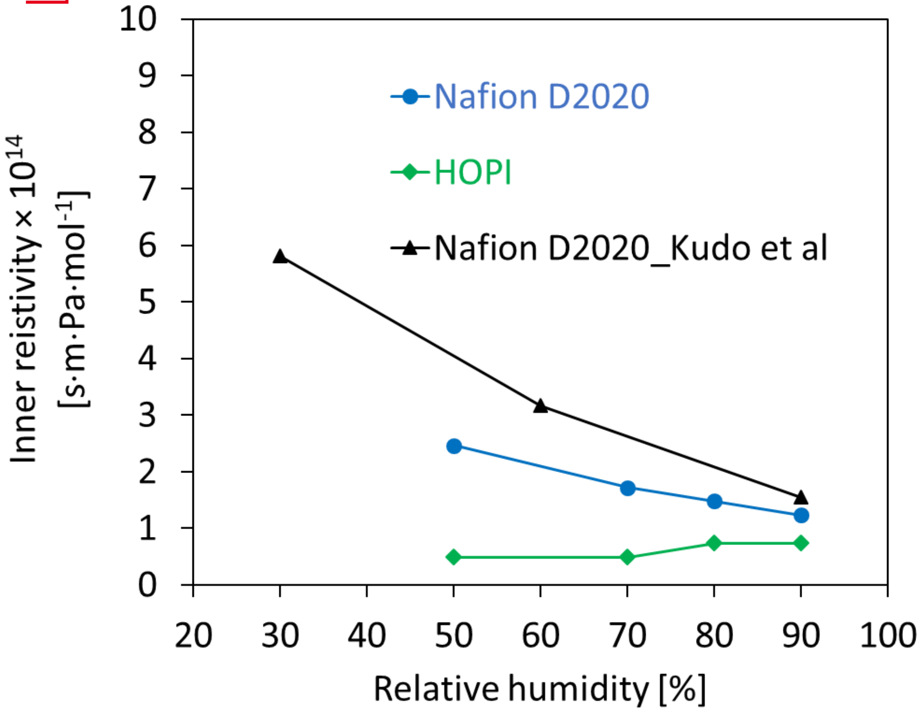
- Ultra-thin ionomer films (Nafion 1100) y on sputtered Pt layers
- Measurement of ionic current via Pt coated tips (H^+ on back-electrode)
- Ionic current correlates with layer thickness
  - → **Thin layers**: equals lower conductivity
  - → **Utra-thin layers**: lamellar and parallel to surface, no 3D-network

Ionomer ultra-thin film O_2 transport properties

Interfacial resistance



Inner resistivity



- New setup developped at CEA to measure in-plane proton conductivity and through-plane O_2 transport resistance (Patent in progress)
- HOPI shows lower interfacial and inner O_2 transport limitations

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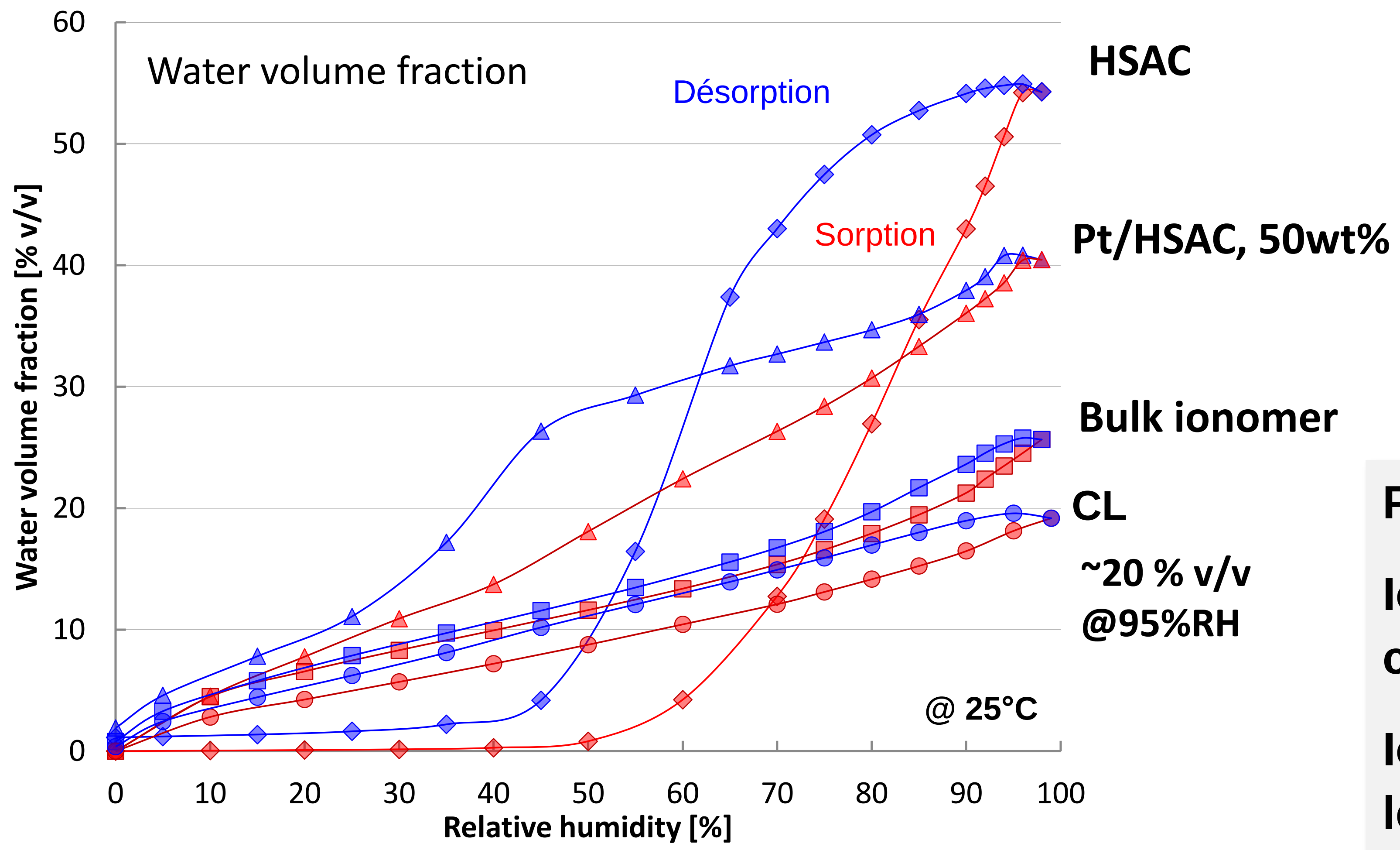
CCL Hydrophilicity

Water vapor sorption isotherm



Water uptake:

CL < Ionomer < Pt/HSAC

Less water in the **CL than** in the **« individual » components**

Less hysteresis between **sorption** and **desorption**

Pt/C takes water, not only ionomer

Ionomer reduces water uptake by catalyst (may block/fill nano pores)

Ionomer in CL is likely to absorb less water than bulk ionomer

CCL Hydrophilicity/Solvophilicity

Imperial College London

Clean Hydrogen Partnership

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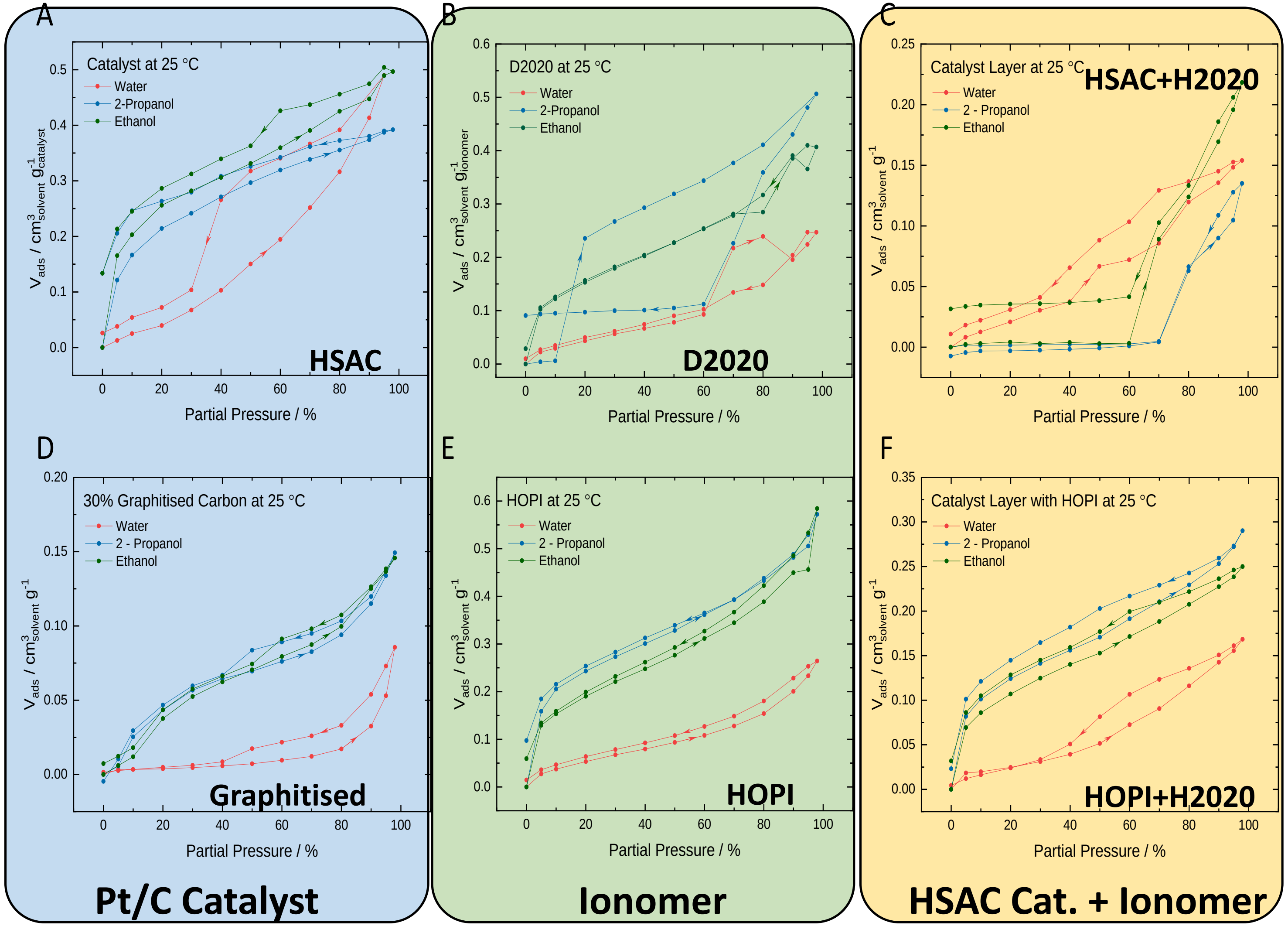
FURTHER-FC Understand to improve

Water and Solvent Uptake



25°C

Catalyst

HSAC: Less hydrophilic solvents wet catalyst more quickly: Hydrophobicity of pores

Graphitic catalyst: Less solvent adsorption (lower SA, only 20% as much water). Much more hydrophobic.

Ionomer

D2020 ionomer: 2-fold more solvent adsorption (swelling/free space filling) using alcohols compared to water

HOPI: Similar to D2020 for water, but even more alcohol adsorbed

CCL Effective proton conductivity

Imperial College London

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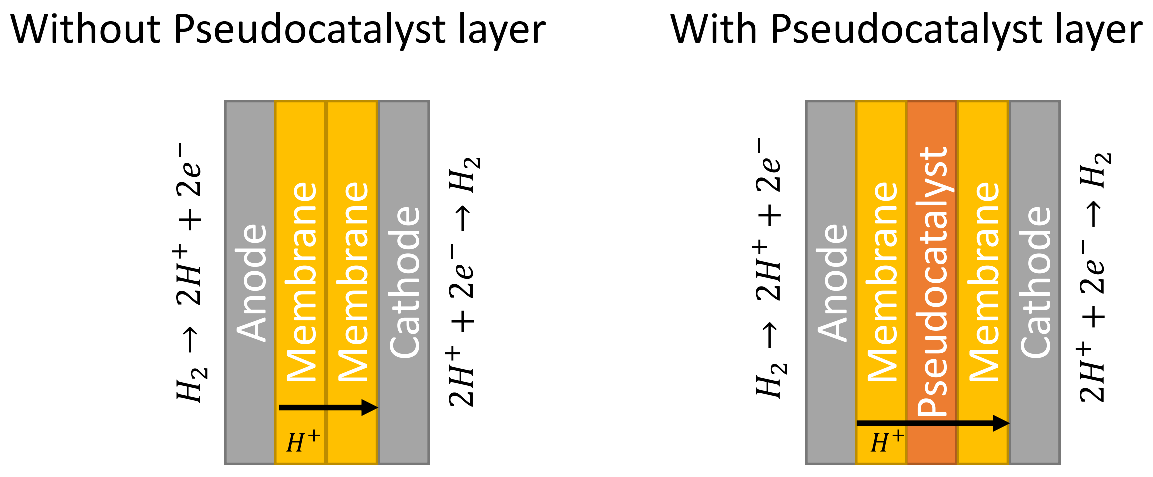
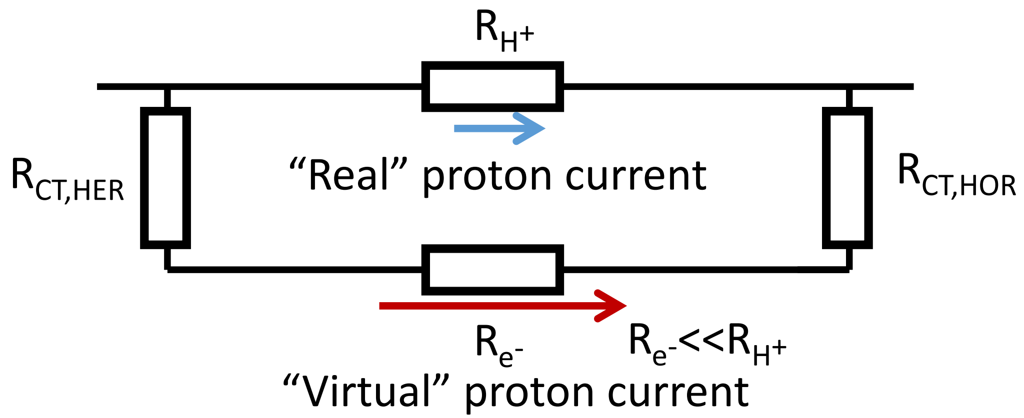


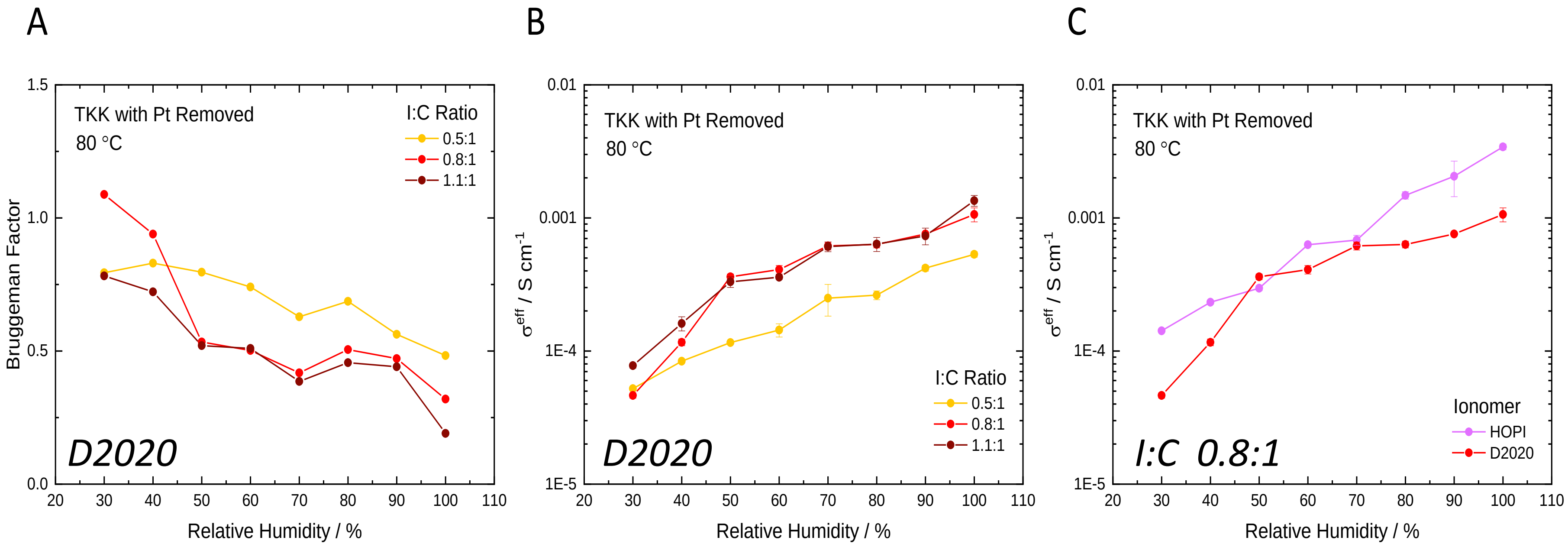
- Proton pump configuration used to measure the proton conductivity of the catalyst layer
- Thickness of Pseudocatalyst layer estimated by SEM after measurement
- Through-plane proton conduction is performed using the demetallated catalyst to establish only proton conduction aspect (avoid « virtual proton » current).
- Calibrated against same configuration without catalyst layer



$R_{CT,HER}$ and $R_{CT,HOR}$ small with Pt present

Remove Pt from carbon so $R_{CT,HER}$ and $R_{CT,HOR}$ become large

CCL Effective proton conductivity



Bruggerman factor gives estimate of tortuosity, $\sigma^{\text{eff}} = \sigma^{\text{bulk}}\varepsilon_{\text{ion}}^{\gamma}$

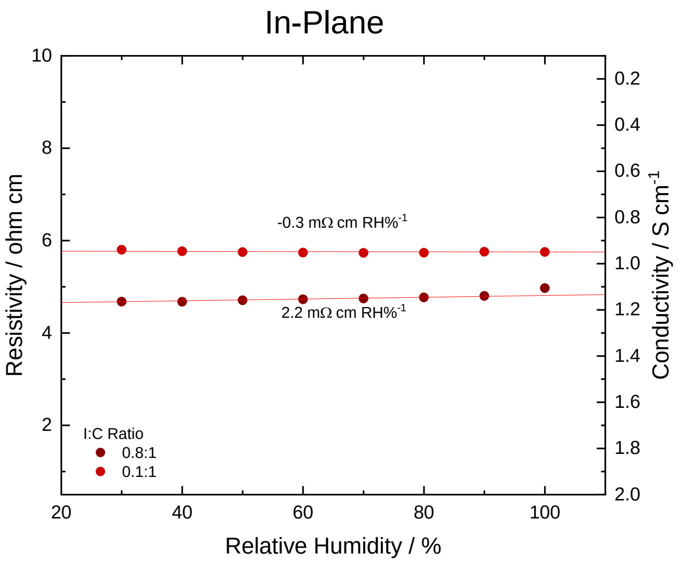
- ➢ Decreases with relative humidity and ionomer content as would be expected

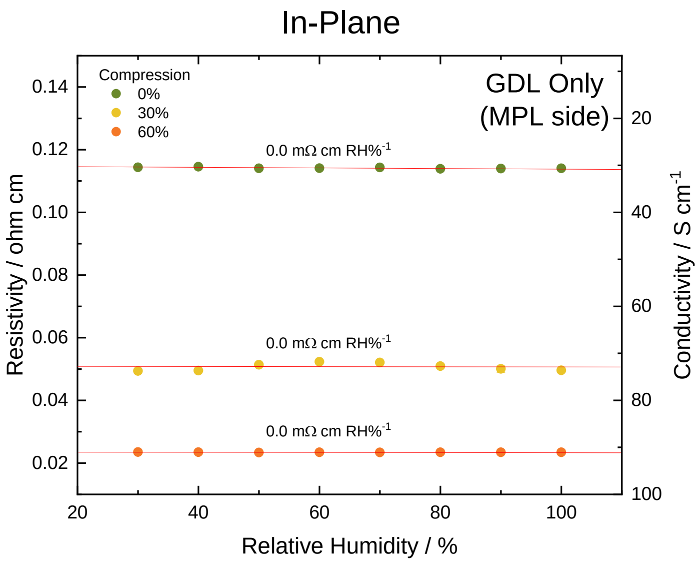
Effective conductive, improves by an order of magnitudye between RH30-100% for all systems

- ➢ ~2-fold improvement between 0.5 and 0.8 I:C but little benefit above that

HOPI shows statistically significant ~2-fold improved proton conduction especially under v.dry and wet conditions

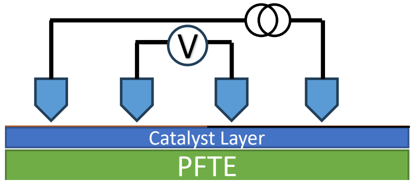
CCL Effective Electronic Conductivity – In plane

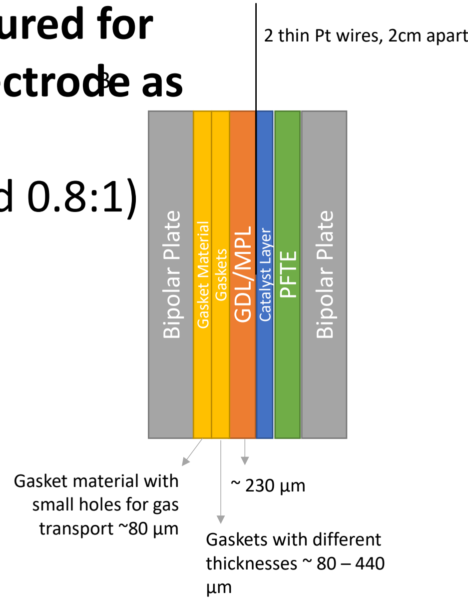


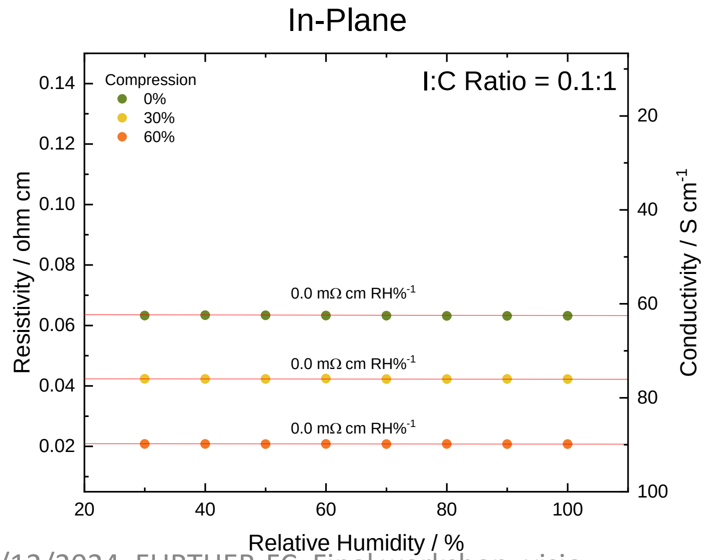


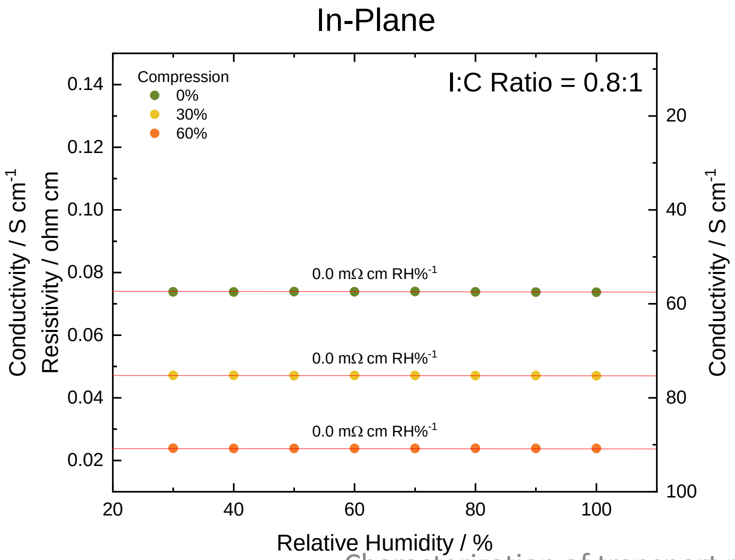
Electronic resistivity measured for Catalyst layer, GDL and Electrode as function of

- Ionomer ratio (0.1:1 and 0.8:1)
- Compression
- Relative humidity









Catalyst layer:

- Ionomer improves electrical conductivity (more particle-particle contacts)
- Electronic conduction little affected by RH

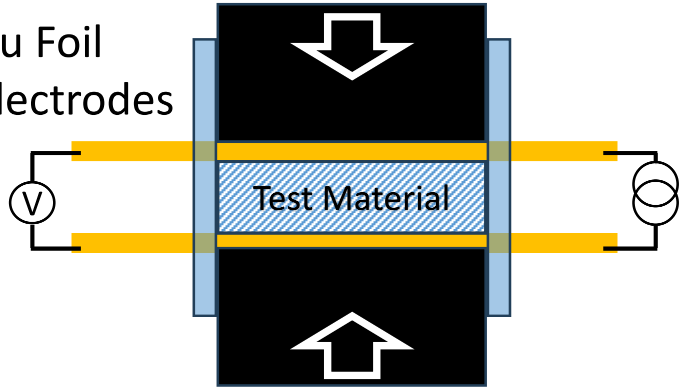
GDL: Large difference in values due to compression

Complete Electrode:

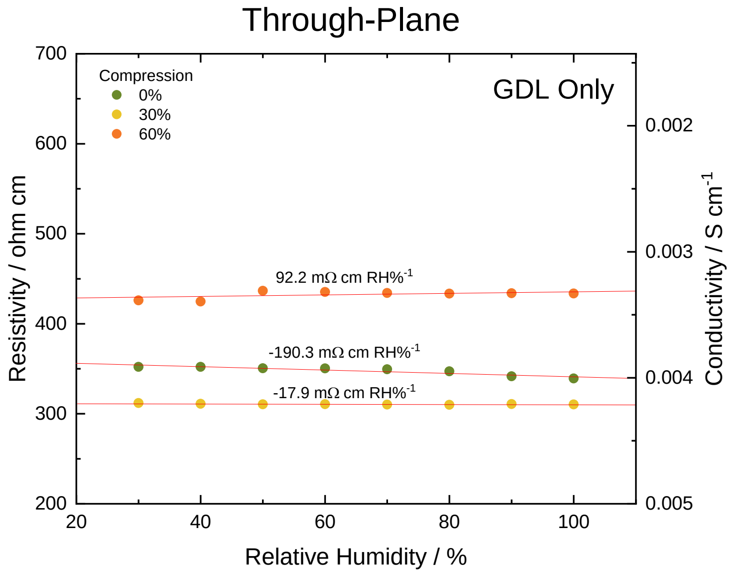
- Compression effect is significantly reduced
- Results dominated by GDL

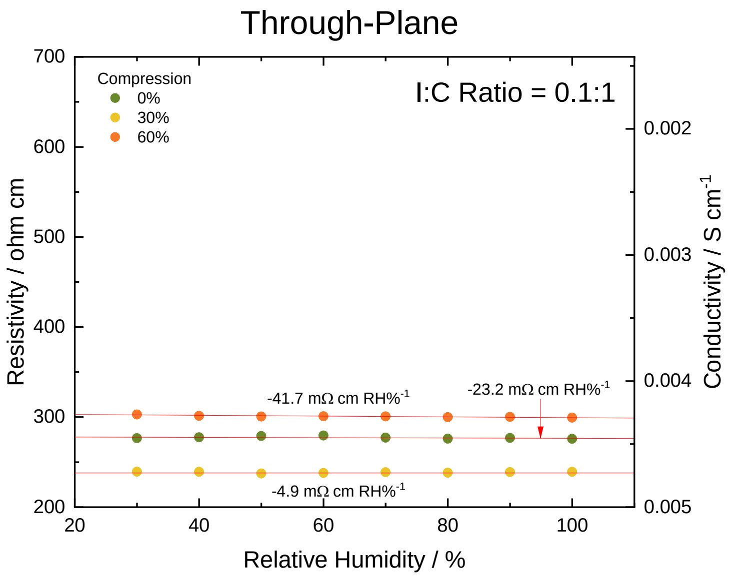
Effective Electronic Conductivity – Through plane

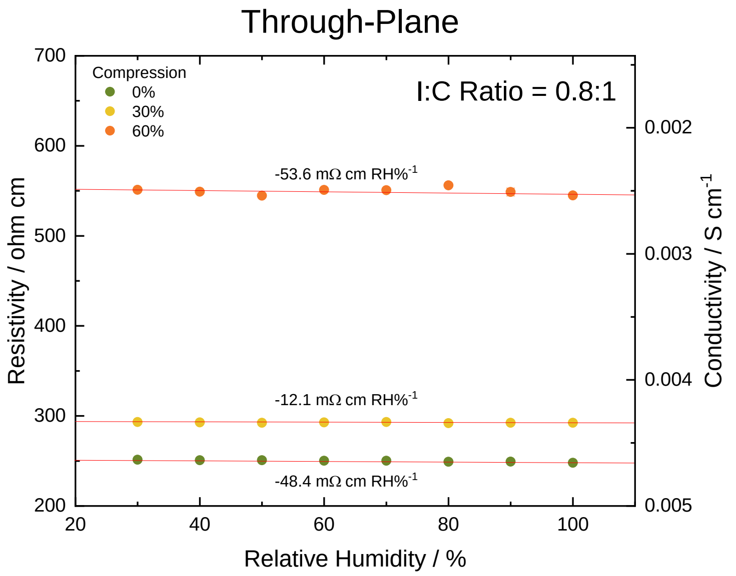
Au Foil Electrodes



- Maximum compression consistently gives higher resistivity (damage?)
- Catalyst layer reduces magnitude of this effect (more points of contact)
- Increased RH fives decreased resistance by small amount in all cases (lubrication effect?)







FURTHER-FC
Understand to improve

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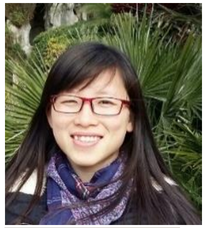


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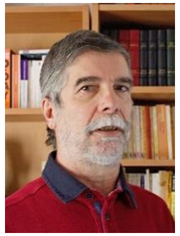

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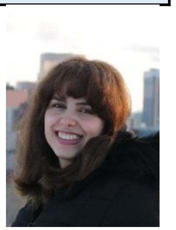
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