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Understand to improve

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Clean Hydrogen Partnership

Co-funded by the European Union

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

Characterisation of CCL materials - local transport properties and transport-free electrocatalysis

Anthony Kucernak, Imperial College

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Université Montpellier iem	PAUL SCHERRER INSTITUT PSI	ESSLINGEN UNIVERSITY	Chemours™	UNIVERSITY OF CALGARY

Overview

- Motivation is to measure important parameters in model systems under conditions as close as possible to those which exist in the fuel cell electrode
- The parameters studied are:

Parameter	System components	Conditions	Limiting conditions
Solvent sorption isotherms and wetting properties (water, ethanol, 2-propoanol)	Catalyst, ionomer, catalyst layer	Temperature; Solvent activity;	Steady-state Atmospheric pressure
Electrical conductivity	Catalyst and catalyst layer; in-plane and through-plane;	I:C ratio; Relative humidity; Compression	Steady state; Ionic effects assumed negligible
Proton conductivity	Catalyst layer	I:C ratio; Relative humidity; Ionomer	Platinum removed
ORR electrocatalyst performance ex-situ	Catalyst	½-cell reaction, potential, p_{O2}, T	1 M $HClO_4$ electrolyte, Atmospheric pressure
ORR electrocatalyst performance in-situ	Catalyst layer	Potential, p_{O2}, T	HOR assumed negligible

Solvent sorption isotherms

Dynamic Vapour Sorption

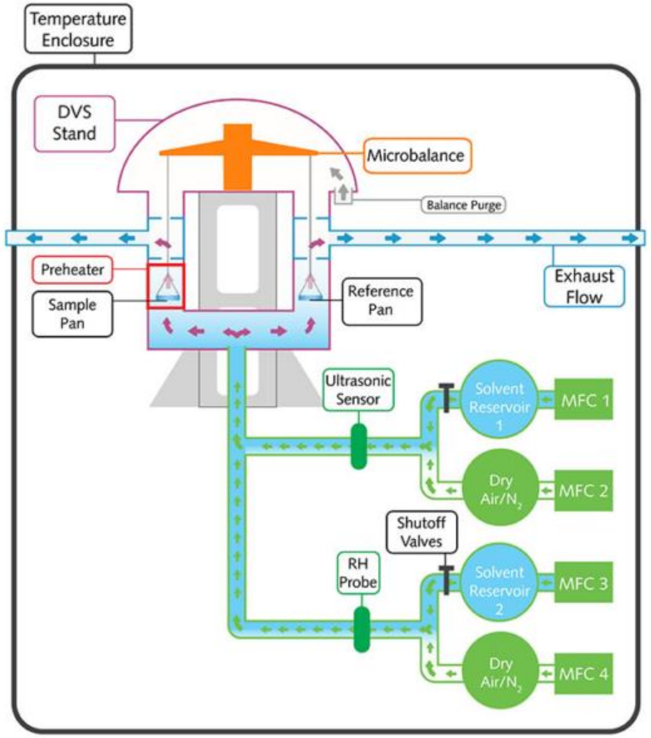
- Multiple solvents (not just water)
- Determination of both polar and dispersive components of surface tension
- Calculation of spreading pressure

$$\pi_e = \frac{RT}{MS}\int_{P}^{P'} \frac{Q}{P}\, dP$$

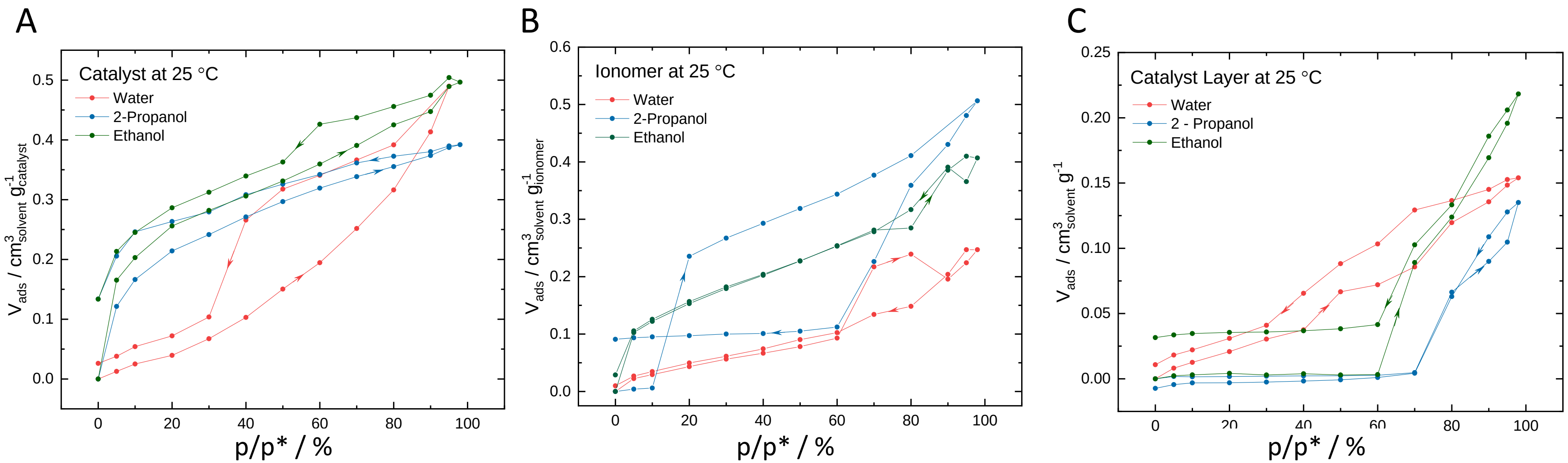
$$W_{s-l} = 2\gamma_L + \pi_e = 2\sqrt{\gamma_L^d \times \gamma_s^d} + 2\sqrt{\gamma_L^p \times \gamma_s^p}$$

$$\gamma_s = \gamma_s^p + \gamma_s^d$$

$\boldsymbol{\gamma_s}$ = surface tension of the catalyst
γ_s^d = dispersive component of catalyst surface tension,
γ_s^p = polar component of catalyst surface tension,
$\boldsymbol{\gamma_L}$ = surface tension of the liquid,
π_e = spreading pressure (θ=0°),
W_{s-l} = Work of adhesion,
M = molar mass of liquid, S = specific surface area, T = temperature and R = gas constant and Q = total amount adsorbed.



Solvent sorption isotherms and analysis



- The catalyst layers did not adsorb IPA or ethanol until partial pressures of above 60%.
- Hydrophilicity of the catalyst layer is 37% of what is expected from simple addition of components, while IPA is 30% and ethanol is 46%.
- Similar polar components of the surface tension for the catalyst powder and layers, but the dispersive component, the van der Waals influence, of the surface tension on the catalyst layer is 10x lower than on the catalyst powders, similarly, the spreading pressure is ~5x lower on the catalyst layers.

Calculated parameters	Catalyst Powder	Catalyst Layer
γ_s / mJ m^{-2}	117 ± 3	105 ± 1
γ_s^d / mJ m^{-2}	19.4 ± 6.3	2.5 ± 0.3
γ_s^p / mJ m^{-2}	97.8 ± 9.4	103 ± 1
π_e / mJ m^{-2}	29.2 ± 8.7	6.1 ± 7.0
W_{s-l} / mJ m^{-2}	105 ± 67	85 ± 64

Large change $\longleftrightarrow$

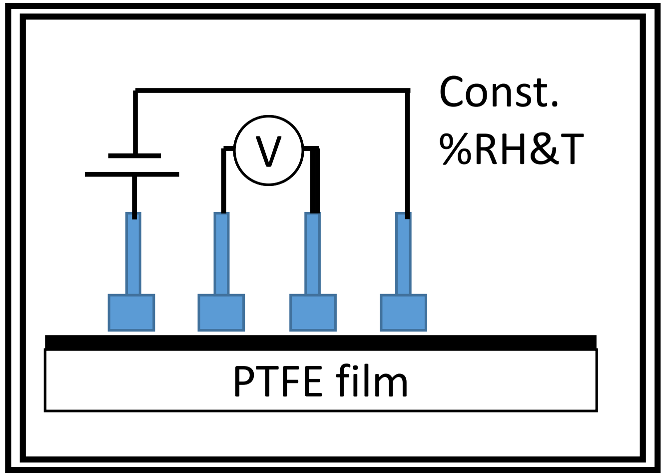
Small change $\longleftrightarrow$

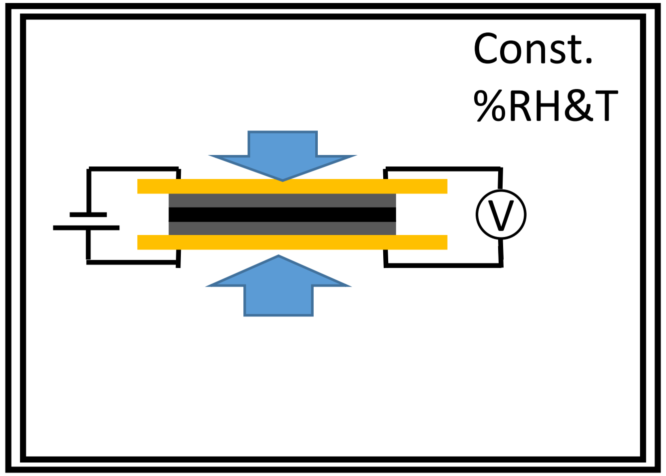
γ_s = surface tension of the catalyst
γ_s^d = dispersive component of catalyst surface tension,
γ_s^p = polar component of catalyst surface tension,
γ_L = surface tension of the liquid,

π_e = spreading pressure (θ=0°),
W_{s-l} = Work of adhesion,
M = molar mass of liquid, S = specific surface area, T = temperature and R = gas constant and Q = total amount adsorbed.

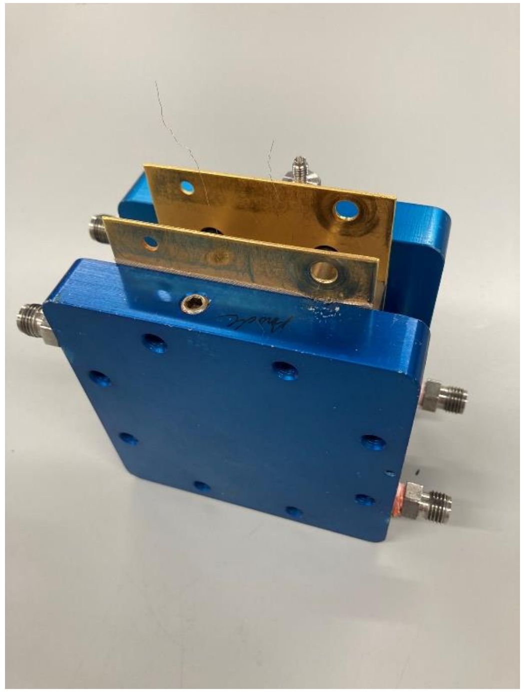
Catalyst layer wetting properties does not seem to be a simple combination of the individual components

Electronic conductivity





- Electronic conductivity measured under environmental control (T, RH%)
- 4-probe contact measurement on appropriate samples
- Controlled compression
- High performance/accuracy system DMM (1$\mu\Omega$ resolution)
- “Dry circuit resistance” 4-probe resistance measurements (20mV)
  - Avoid driving electrochemical reactions



Keithley 3706A System Switch/Multimeter

Electronic conductivity

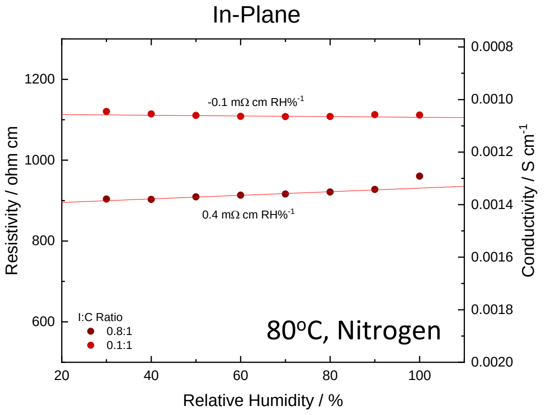
Catalyst Layer + GDL

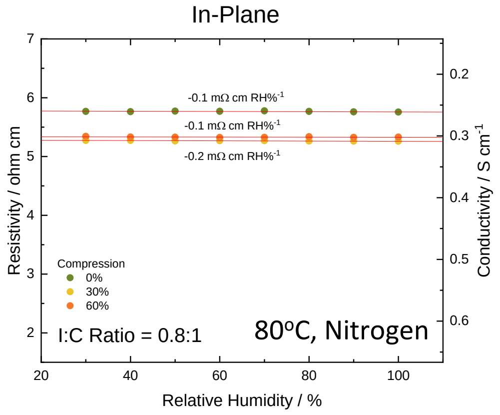
Catalyst Layer Only

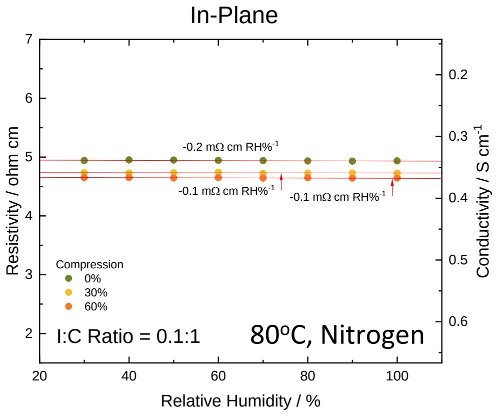
Normal I:C Ratio (0.8:1)

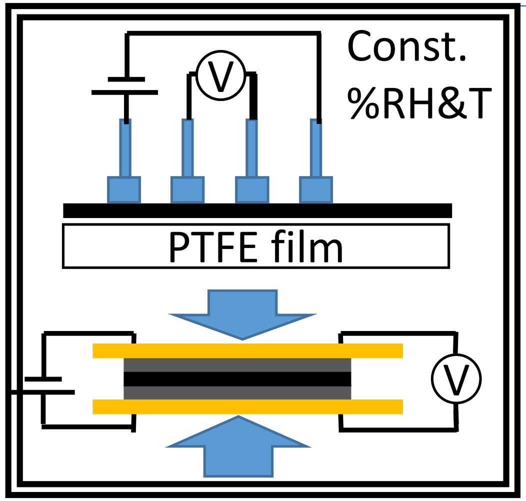
Low I:C Ratio (0.1:1)

In-Plane Conductivity



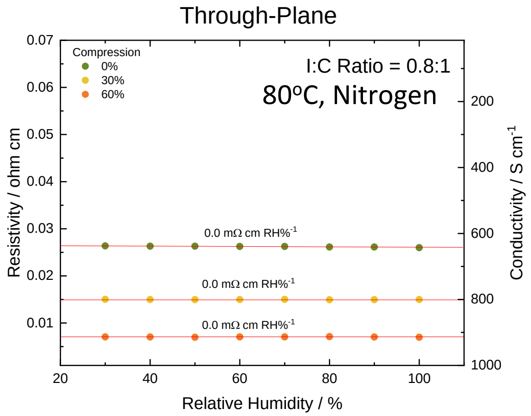


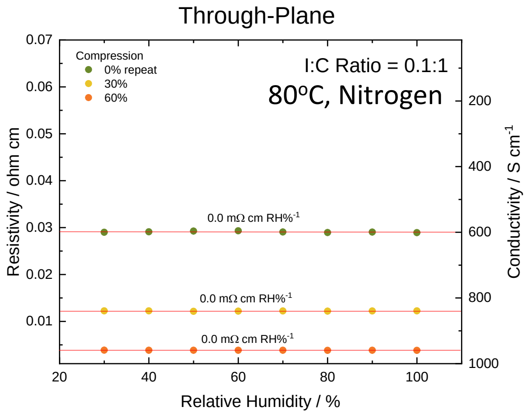




Low overburden potential (20 mV)

Through-Plane Conductivity



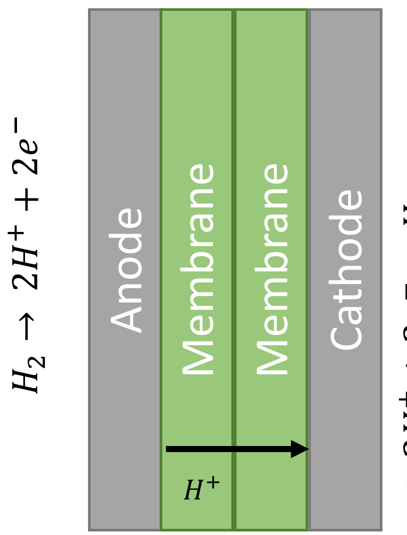


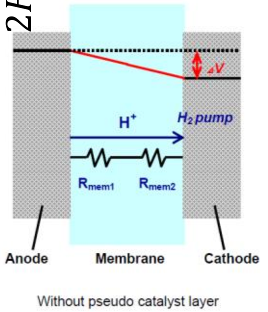
- Increase in electronic conductivity as compression is increased
- Little change in conductivity as relative humidity is increased
- Two orders of magnitude lower conductivity in catalyst layer only for in-plane conductivity
- Increase in conductivity as I:C ratio is decreased
- Two orders of magnitude higher conductivity in through-plane vs in-plane

RH has little effect on electronic conductivity ➔ swelling of ionomer does not affect particle-particle contact

Proton conductivity

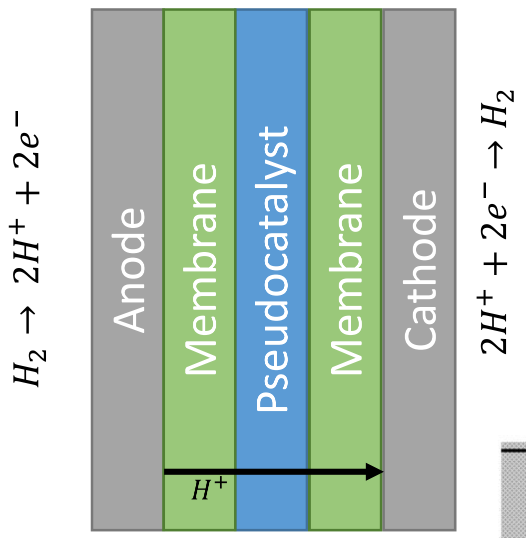
Without Pseudocatalyst layer

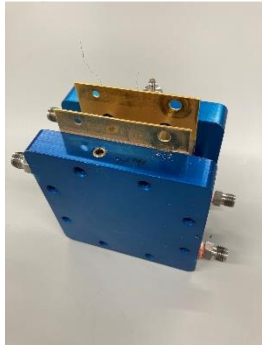


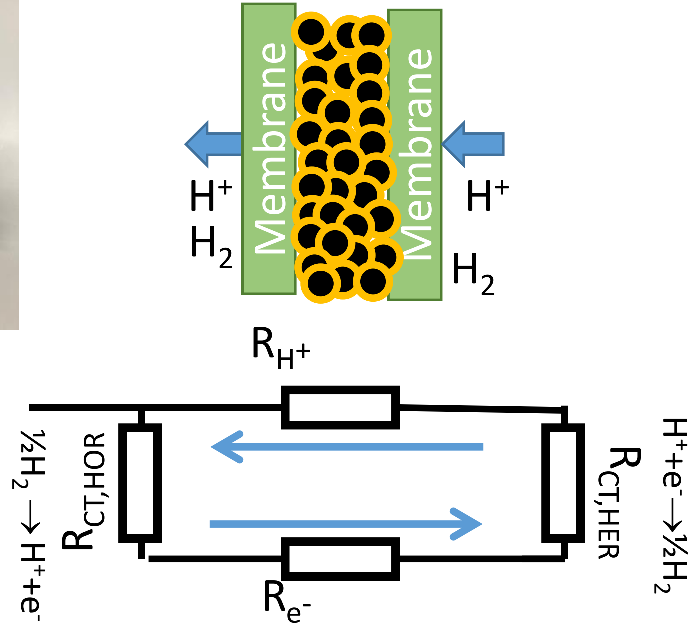


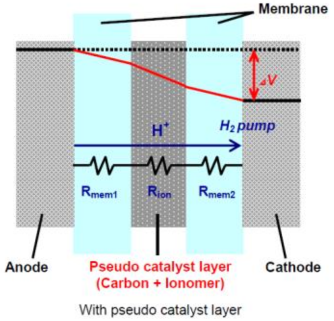
Without pseudo catalyst layer

With Pseudocatalyst layer





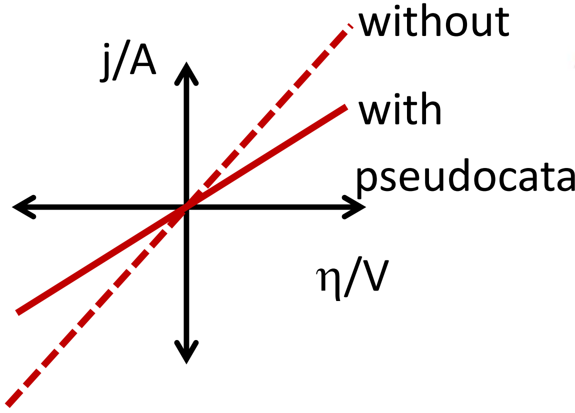




With pseudo catalyst layer

$$\sigma^{eff} = \sigma^{bulk}\varepsilon_{ion}^{\gamma}$$

σ^{eff}: proton conductivity of catalyst layer
σ^{bulk}: proton conductivity of bulk ionomer
ε_{ion}: Volume fraction ionomer in layer (corrected for swelling)
γ : Bruggeman correction factor

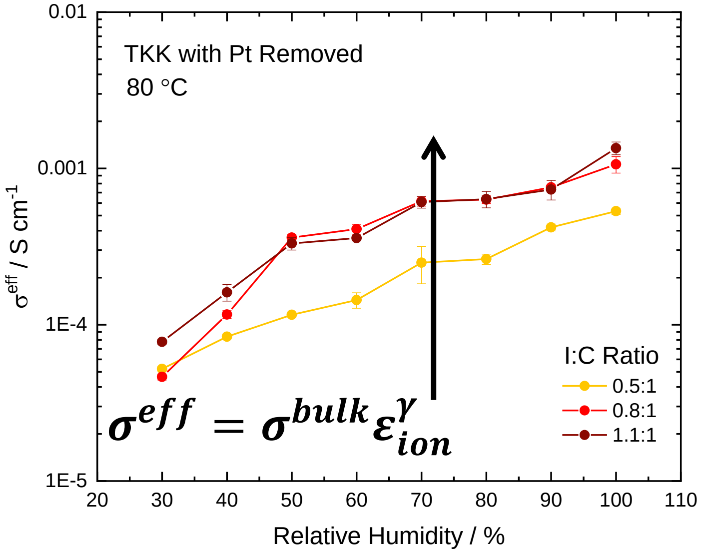


"Virtual" proton current

Pseudocatalyst: actual catalyst with Pt removed

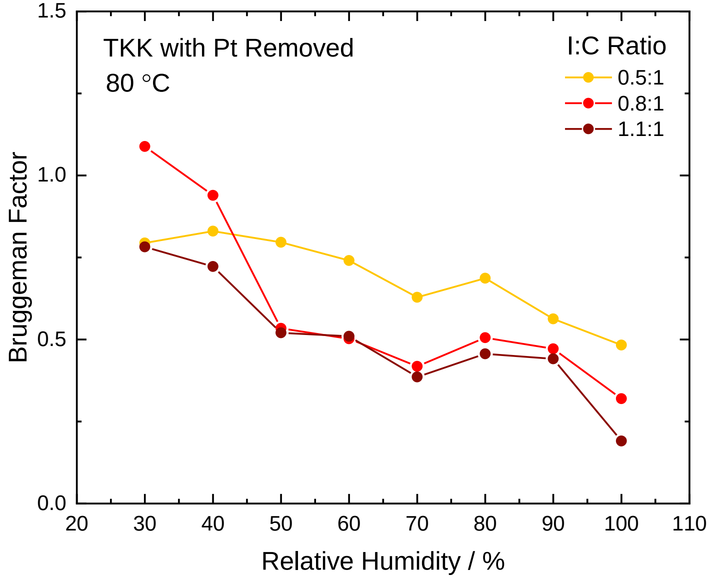
Hiroshi Iden et al 2008 ECS Trans. 16 1751
Hiroshi Iden et al 2009 J. Electrochem. Soc. 156 B1078

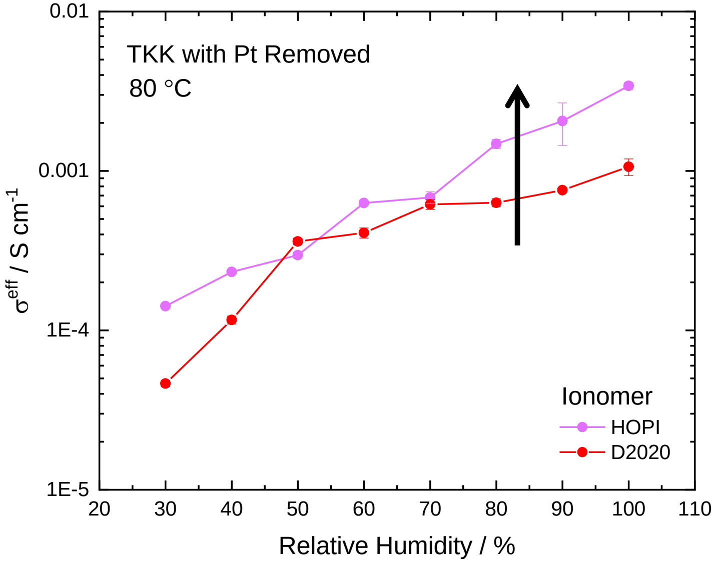
Proton conductivity



$$\sigma^{eff} = \sigma^{bulk} \varepsilon_{ion}^{\gamma}$$

- Increase in proton conductivity as RH increases
- Increase in proton conductivity as I:C ratio increases
- Increase in proton conductivity when using HOPI ionomer
- Decrease in Bruggeman Factor as RH increases
- Little change in Bruggeman Factor with different I:C ratios
- As Bruggeman Factor <1, conductivity is less strongly affected by increases in ionomer

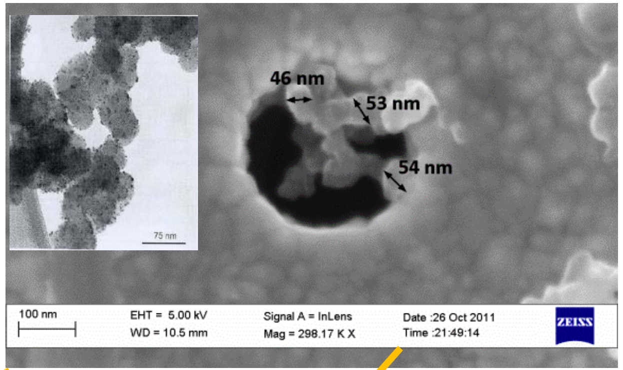


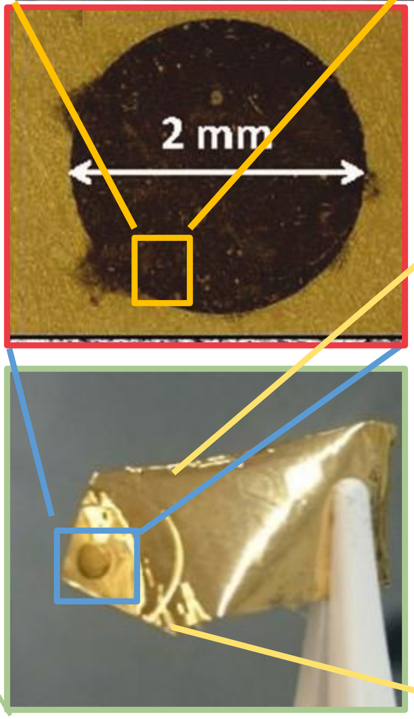


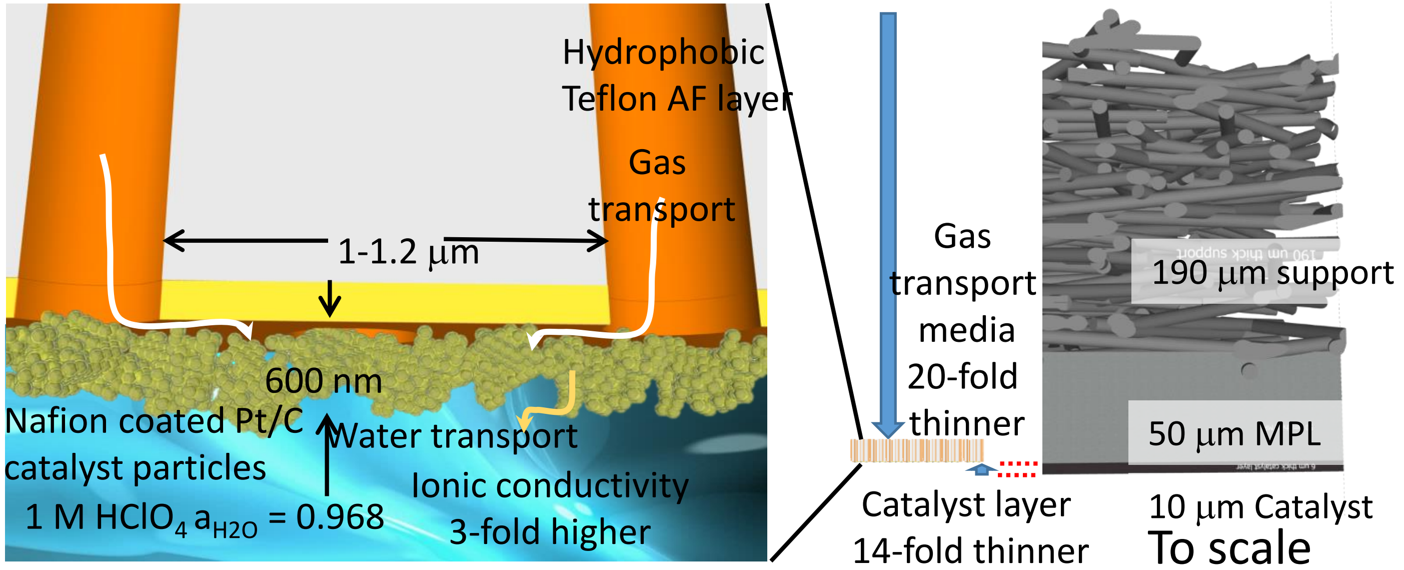
Proton conductivity in catalyst layer is liable to be a limiting factor in performance

Electrocatalysis

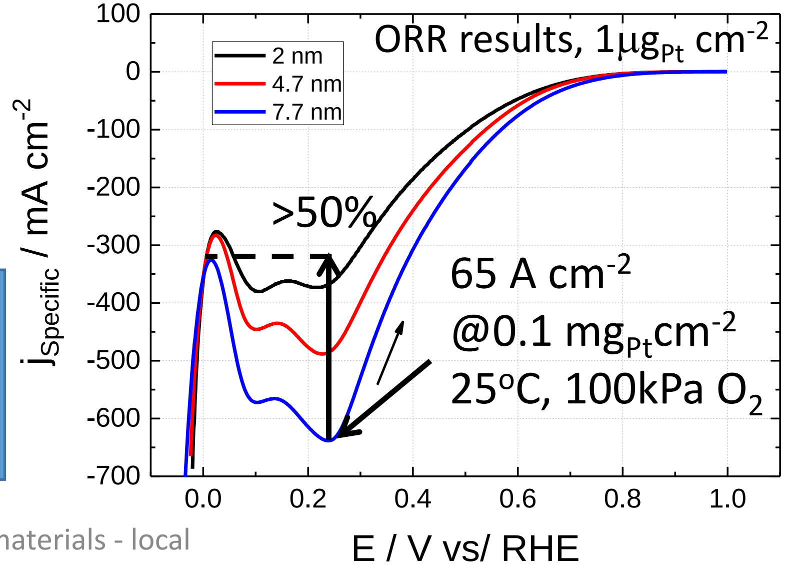
Ultra-low loading electrodes – Ex situ







3-electrode ORR on “mass transport free” electrodes



C. M. Zalitis, D. Kramer and A. R. Kucernak, “Electrocatalytic performance of fuel cell reactions at low catalyst loading and high mass transport. ”*Phys. Chem. Chem. Phys.*, 15, 4329, (2013).

Electrocatalysis

Ultra-low loading electrodes – Ex situ

- Performance as function of E,T
- Model for ORR which highlights availability of surface adsorption sites

$$\theta_{HOO,H}(E) = \frac{1}{1 + e^{(E-E_{0,H})q_H F / RT}}$$

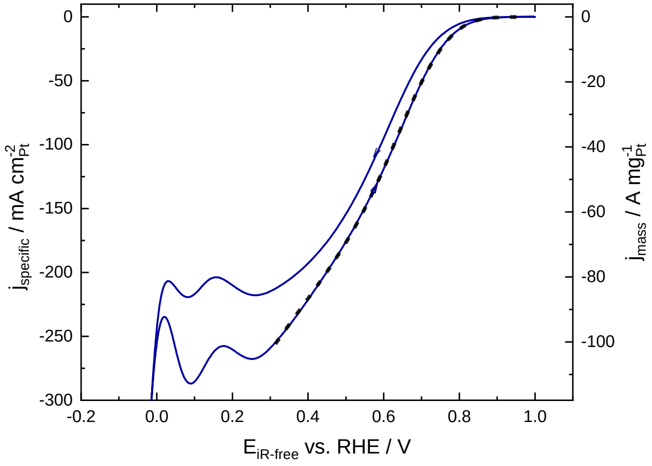
$$\theta_{OH,O}(E) = \frac{1}{1 + e^{-(E-E_{0,O})q_O F / RT}}$$

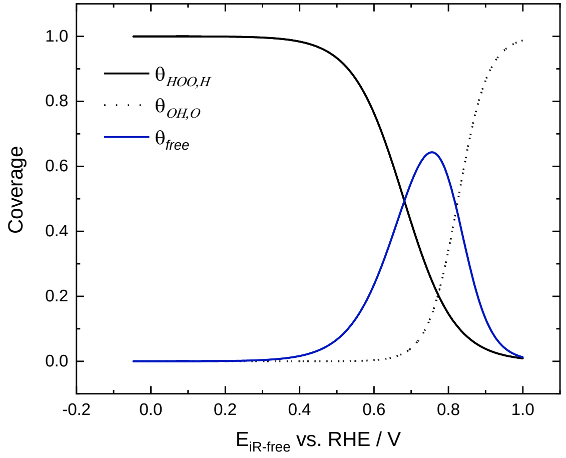
$$\theta_{free}(E) = (1-\theta_{HOO,H})(1-\theta_{OH,O})$$

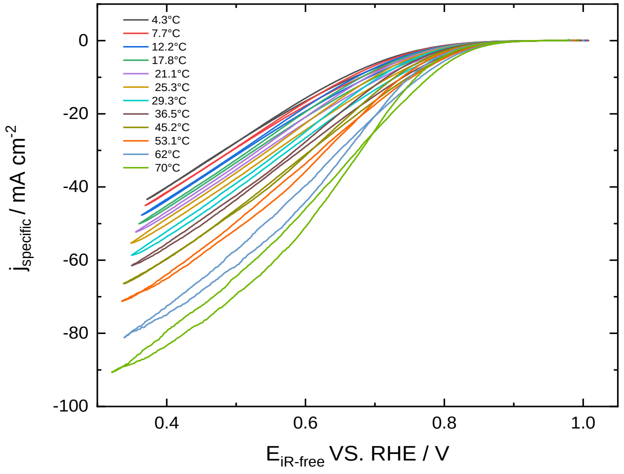
- $j = j_0 \left(\frac{c}{c_0}\right) \theta_{free} e^{\left(\frac{\alpha n F (E-E^0)}{RT}\right)}$

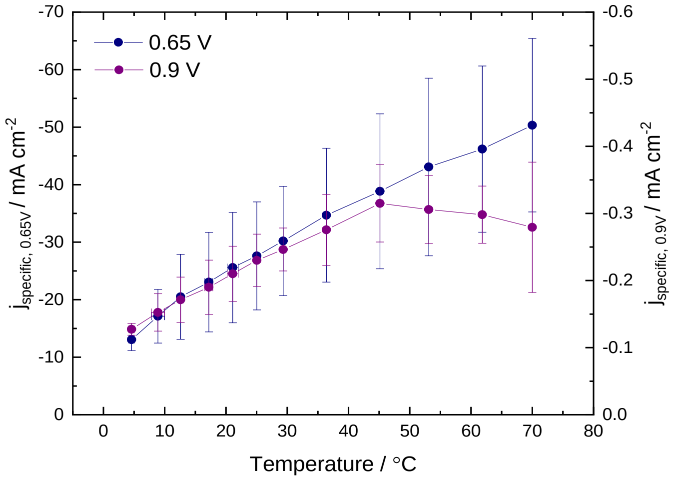
- Model fits of data 0.3..1.0 V
  - j_0, $E_{HOO,H}$, $E_{OH,O}$, αn, q_H and q_O

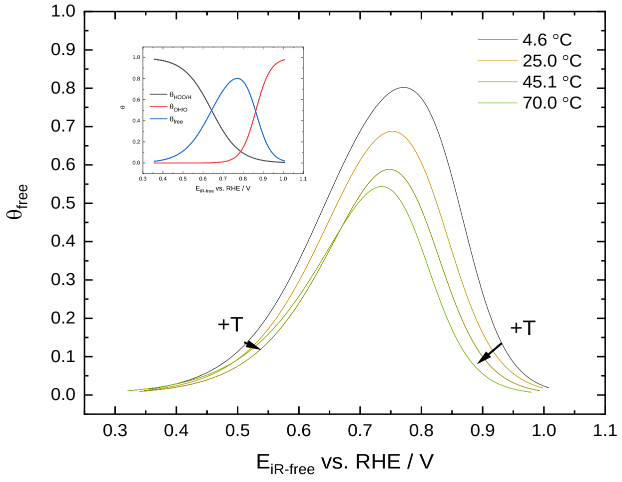
1 M HClO$_4$. 100 kPa O$_2$, 298K











j$_o$ $\theta_{OH,O}$, $\theta_{HOO,H}$ as function of temperature

The TEAM

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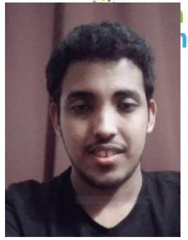
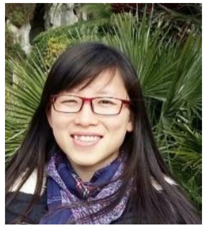
PhD Konrad Guelicher


Dr. Isotta Cerri


PhD Ahmed Maloum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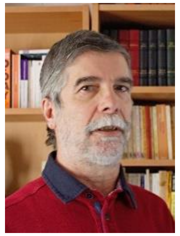
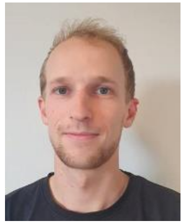

Dr. Michel Quintard


Dr. Marc Prat


PhD Florian Chabot

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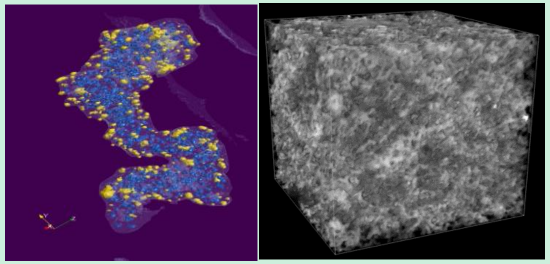
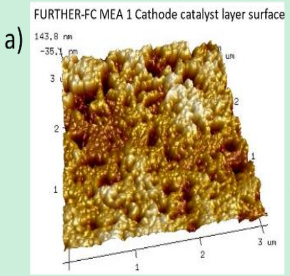
Thank you for your attention.
Your questions are welcome

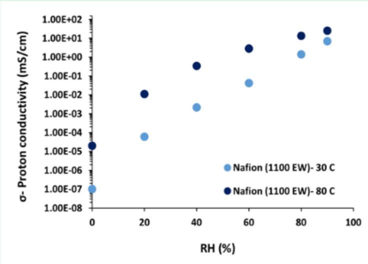
Multiscale characterization



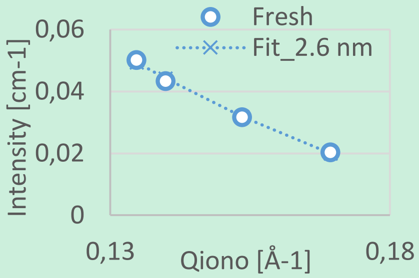
3D TEM and FIB/SEM



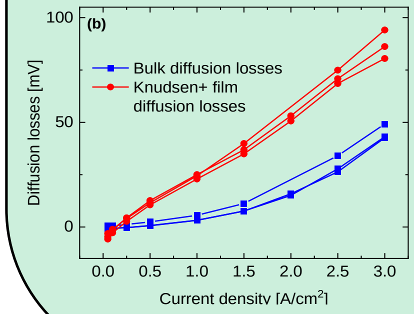
AFM



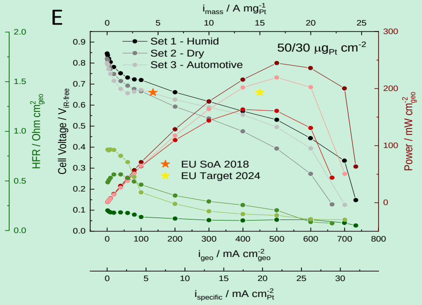
Ionomer transport properties



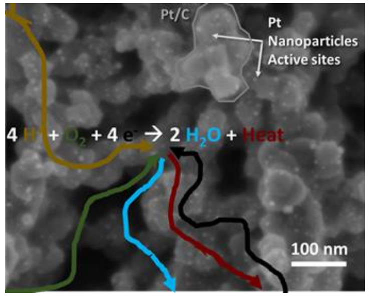
Ionomer swelling

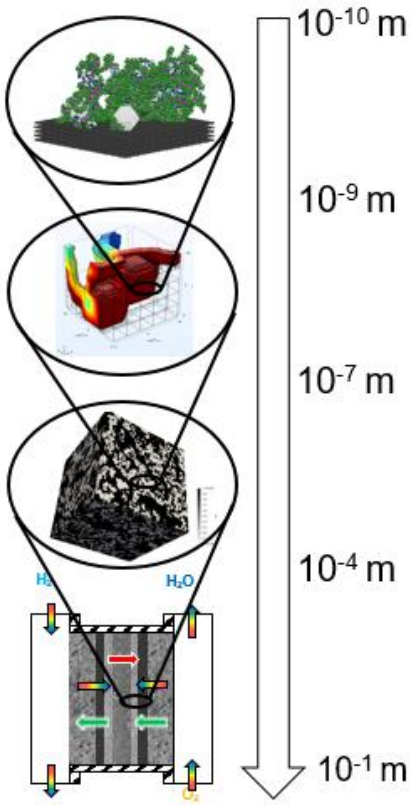


Mass transport losses



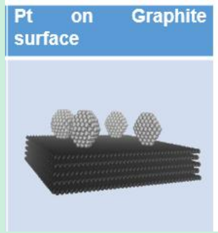
Ultra-thin electrode

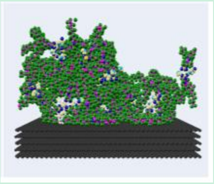


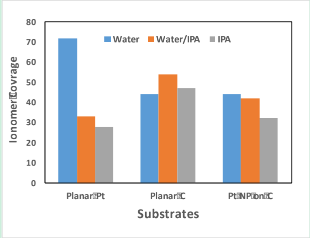


Multiscale modeling

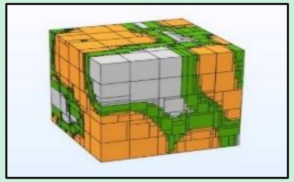
Ionomer film scale



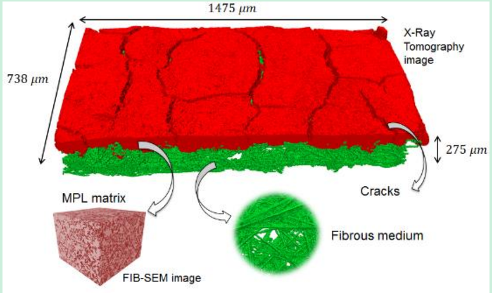




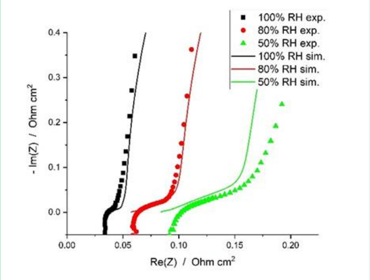
Sub µm scale

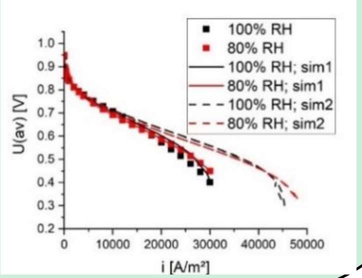


CCL scale



Cell scale





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Imperial College London

Imperial College London

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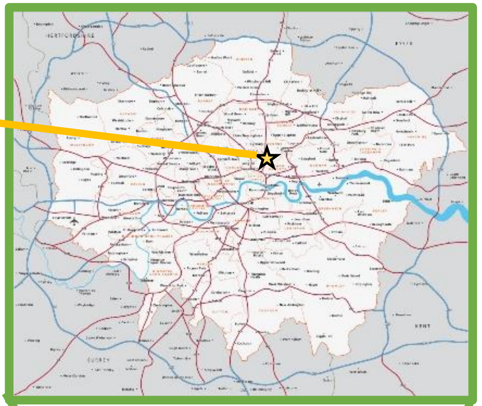
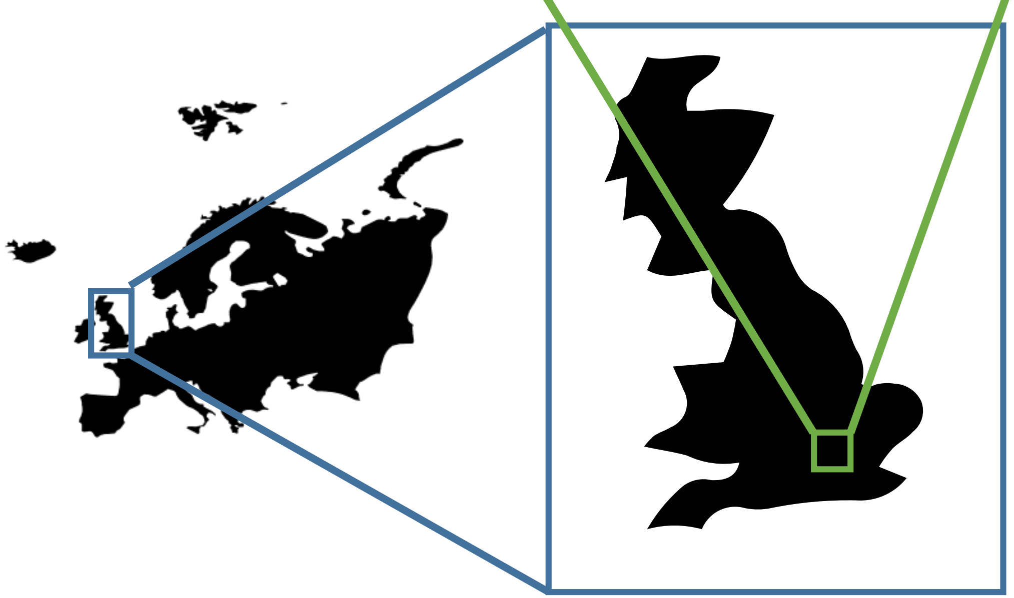
Molecular Sciences Research hub





4 Faculties
Business
Engineering
Medicine
Natural Sciences

£969M Turnover
Student Fees £223M
Research income £427M
Fundraising £31M

6 Global Challenge institutes

3,782
Academic & Research Staff
15,290
Full time Students

110 years old
14 Nobel prizes

World-class scholarship, education & research in science, technology, engineering, medicine & business

35 full time academics
Aeronautics
Business School
Center for Environmental Policy
Chemical Engineering
Chemistry
Dyson School of Design
Engineering
Earth Sciences and Engineering
Materials
Mechanical Engineering

Light driven systems
Photocatalytic And Photo-electrocatalytic systems

Room temperature systems
PEM/AEME Electroctrolysers
Redox Flow systems

Electrocatalysis
Hydrogen/Oxygen evolution
CO_2, N_2 reduction, H_2O_2, O_3 production

CCU, CCS properties of fluids

High temperature Systems
SOEC/SOFC, syngas production, Other fuels, ammonia

Technoeconomics Optimised systems /processes /networks, LCA

Imperial College London

- Electrocatalysis including non precious metal catalysts (e.g. Crescendo)
- Hydrogen purification/hydrogen pumps (Memphys)
- Hydrogen fuel cells and electrolysers including alkaline membrane systems
- Redox flow batteries, especially H_2-X (X=Mn, Organic, V, Br_2…)

of. Anthony Kucernak

Dr Colleen Jackson

- Spinout companies:

BRAMBLE ENERGY

High volume fuel cell and electrolyser manufacture

RFC POWER

Grid scale electricity storage

SWEETGEN LTD.

Electrochemical wastewater treatment

Imperial College London

- Contribution to project
  - WP1:SPECIFICATION, VALIDATION AND RECOMMENDATION
    - Ultra low loading CCMs
  - WP2: CHARACTERIZATION OF CCL STRUCTURE AND COMPONENT PROPERTIES
    - Effective transport properties in the CCL
  - WP3: ADVANCED OPERANDO DIAGNOSTICS AND PERFORMANCE LIMITATIONS
    - Toward operando fundamental electrochemistry