Institut Charles Gerhardt Montpellier

CHEMISTRY: MOLECULES TO MATERIALS

Société Chimique de France

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Fondation de la Maison de la Chimie

FRANCE CHIMIE

Matériaux de coeur de pile à combustible et d'électrolyseur basse temperature : performance, durabilité et soutenabilité

Materials for low temperature fuel cells and electrolysers: performance, durability and sustainability

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3èmes rencontres académie-industrie du CNC

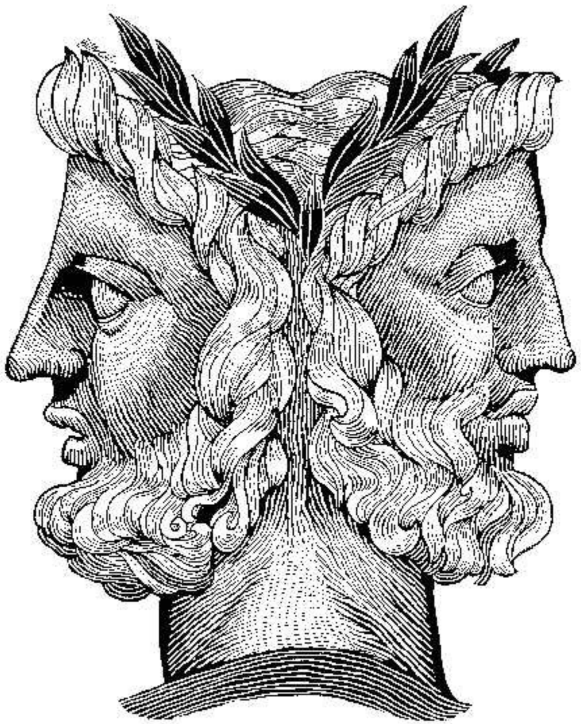
cnrs UNIVERSITÉ DE MONTPELLIER ENS CM Chimie Montpellier INSTITUT CARNOT Chimie Balard Cirimat

Challenge

Performance – Durability through PGM and PFSA

Hydrogen technologies are an essential component of routes to net zero greenhouse gas emissions by 2050

Clean hydrogen is a key enabler as an energy vector and a sustainable chemical feedstock



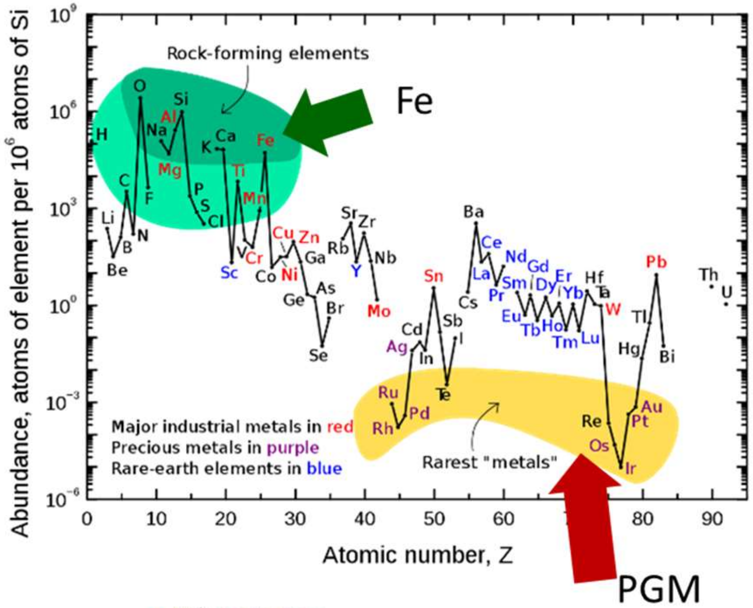
Current fuel cells and electrolysers are heavily dependent on platinum group metals and other critical raw materials

Proton exchange membrane fuel cells and electrolysers use perfluorosulfonic acid (PFSA) membranes. PFSA is included in the PFAs debate

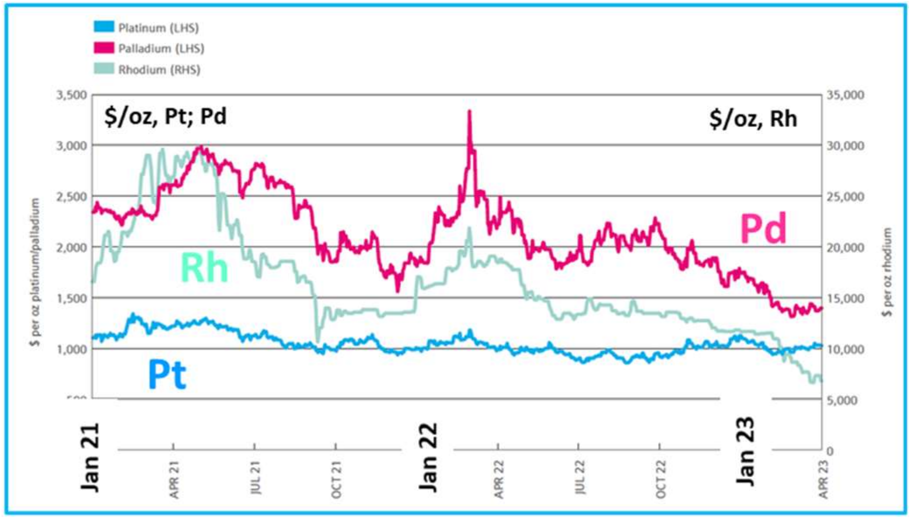
Addressing the sustainability and criticality of electrolyser and fuel cell materials to safeguard the future development of the hydrogen sector

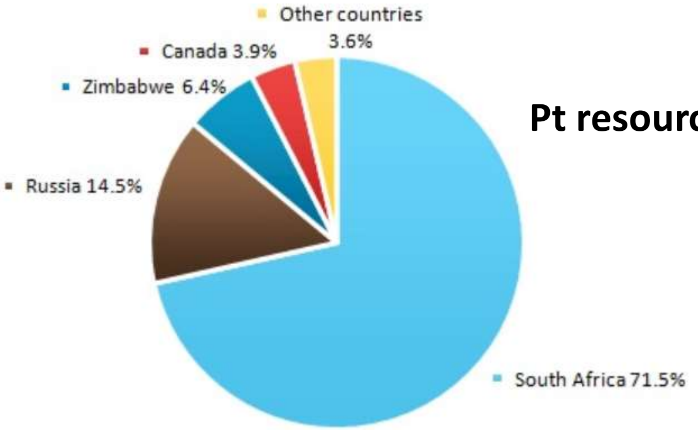
PGMs – rarity, geographical location, price

Pt relative abundance



Pt price



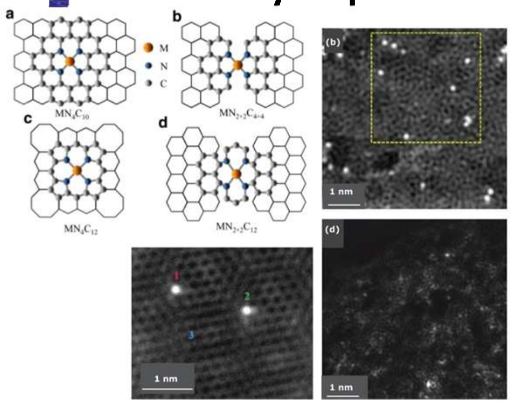


Pt resource

- Reduce Pt loading ; increase kW power obtained with a fuel cell per gram Pt
- Replace Pt by more abundant elements
- Recycle

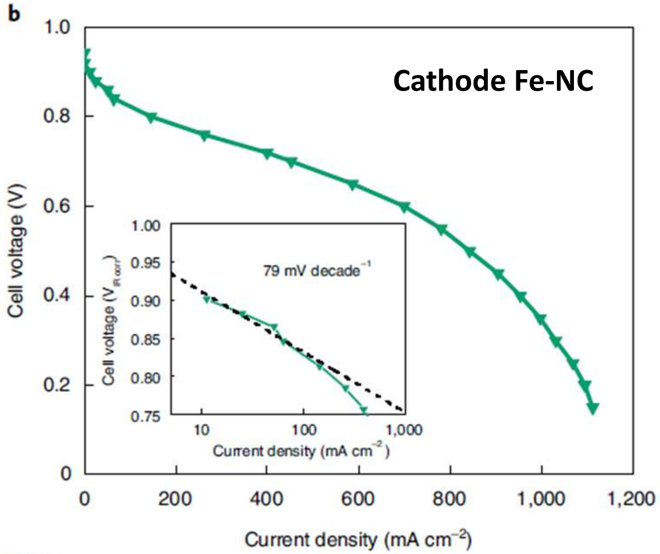
Replacing Pt at the PEMFC cathode

Atomically dispersed Fe-NC



Jaouen, Jones, Artero, Kucernak, Strasser, *Johnson Matthey Technol. Review,* 2018, **62**, 231-255.

Performance



Mehmood, Jaouen, Roy, Martinez Bonastre, Strasser, Kucernak, *Nature Catal.* 2022, **5**, 311-323

Durability

- N-carbon coating of Fe-NC using CVD significantly reduces the rate of voltage loss

Liu, … Myers, Litster, Cullen, Wu, *Nature Energy,* 2022, **7**, 652–663.

Critical Raw material Electro-catalystS replacement ENabling Designed pOst-2020 PEMFC (CRESCENDO)
Clean Hydrogen JU 2018-2021
Coordination ICGM
www.crescendo-fuelcell.eu

- The current performance of MEAs with PGM-free cathodes with air feed to the cathode is low and, despite the low catalyst cost, FC stacks using PGM-free cathodes are not cost-effective for high power applications
- Fe-NC catalysts reduce dependence on CRM, and more research is needed to improve their activity and durability.

Iridium – oxygen evolution reaction of PEMEL

- 200 mV lower overpotential for OER than Pt
- Amongst the most corrosion resistant PGMs
- Amount of Ir needed for future PEMEL growth depends on the forecast electrolysis capacity
- <1 GW PEMWE capacity today, France targets 6,5 GW, EU targets 100 GW by 2030

Ir requirement mg/W

- Currently, a 1 MW PEM electrolyser uses 0.4 kg Ir, Ir loading 1.5 mg/cm^2

Matching Ir requirement to expansion in PEMEL capacity

- Reduce Ir loading
- Improve performance to increase current density
- Recycle: Recycling reduces the amount of new Ir needed for new PEMEL, helping to balance supply and demand, and to stabilise the Ir market price

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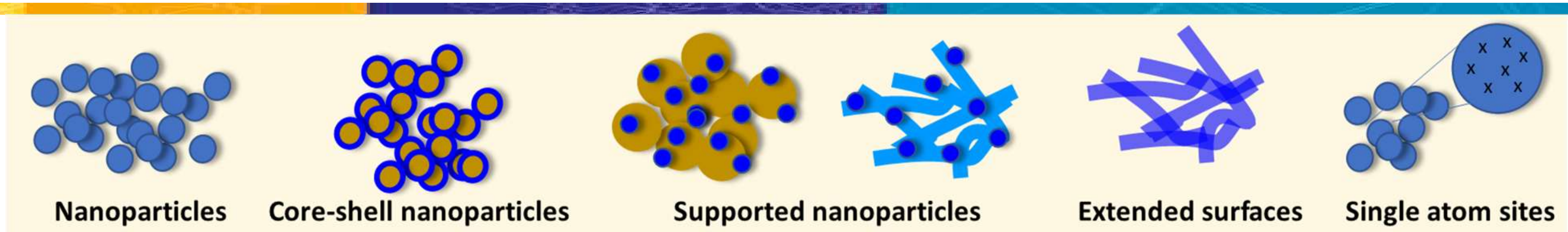
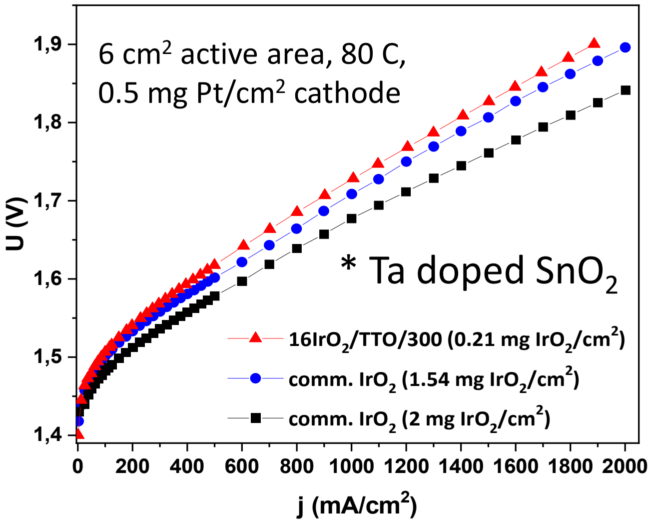
Clapp, Zalitsis, Ryan, *Catal. Today,* 2023, **420** 114140
Mittelsteadt et al. *Energy Fuels*, 2023, **37** 12558-12569

Materials strategies to reduce Ir loading



Conducting nanofibre supported IrOx nanoparticles
- ICGM



0.21 mg/cm^2 Ta-SnO_2 supported IrOx

Jimenez Morales, Cavaliere, Al Bacha, Millet, Rozière, Jones, *in preparation*

Core-shell nanoparticles
- Giner/Plugpower

0.25 mg/cm^2 W-TiO_2 supported IrOx

Mittelsteadt et al. *Energy Fuels*, 2023, **37** 12558-12569

Extended Ir surface
- 3M

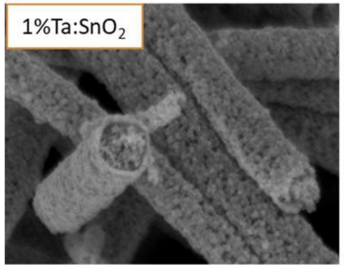
0.25 mg/cm^2 perylene supported Ir

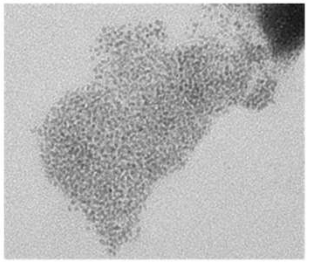
Mittelsteadt et al. *Energy Fuels*, 2023, **37** 12558-12569

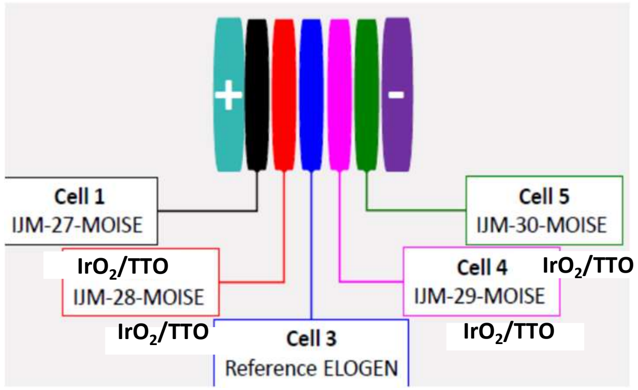
Status: 0.25 mg/cm^2 loading without impacting performance with dispersed/supported IrOx → 1 MW requires ~~400 g~~ ca. 60 g Ir

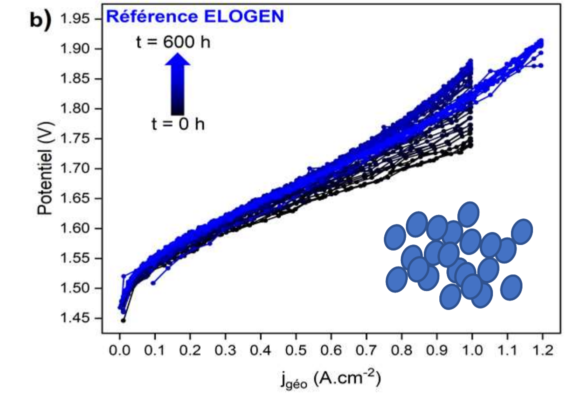
Durability even with Ir thrifting

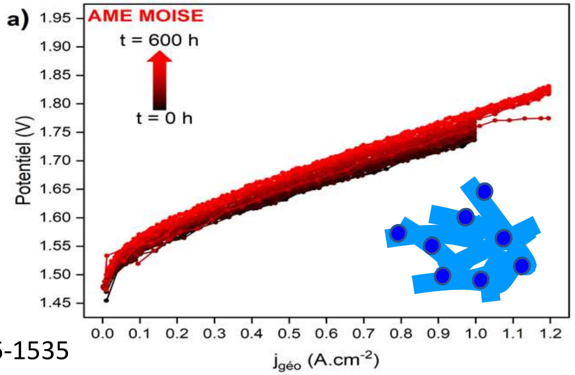
- Continuous preparation methods to upscale IrOx nanoparticles and TTO nanofibres
- 250 cm^2 electrodes and MEAs for rainbow short stack characterisation

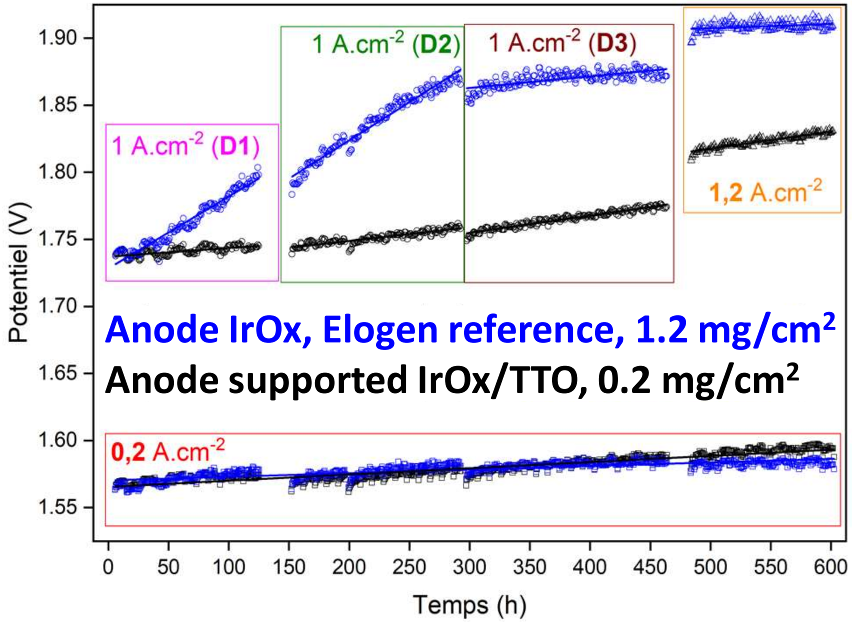












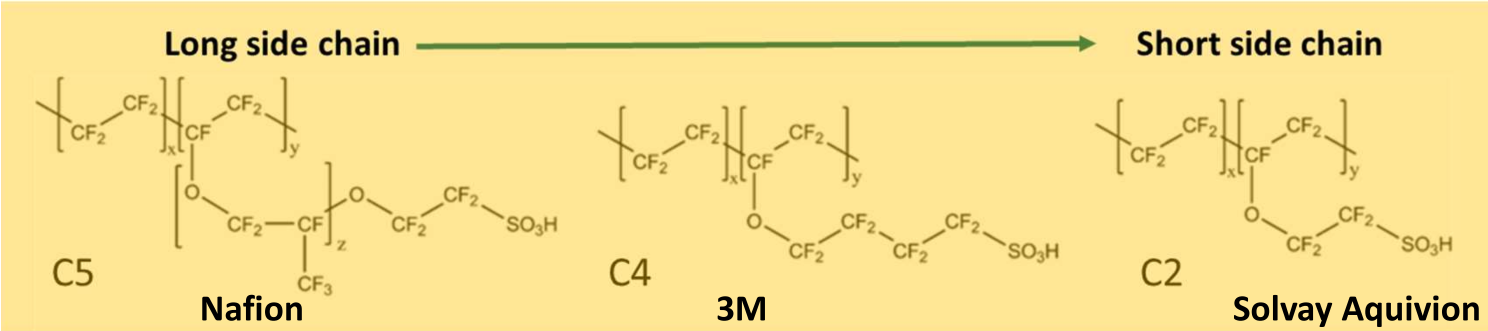
Cavaliere *et al. J. Phys. Chem.*, 2013, **117**,18298-18307
Jiménez-Morales *et al. Sustainable Energy & Fuels.*, 2019, **3** 1526-1535
Jiménez-Morales *et al. ACS Catal.* 2020, **10**, 10399-10411
Jimenez Morales, Cavaliere, Al Bacha, Millet, Rozière, Jones*, in preparation*

Collaboration elogen ANR MOISE anr

Perspective - PEMFC performance state of the art with PFSA

Current technology readiness is due (amongst others) to the exceptional properties of PFSA

More amorphous
Lower IEC before becoming water soluble
Lower Tg
Temperature of operation to 80-90 °C
Higher gas crossover



Higher crystallinity
Higher IEC before becoming water soluble
Higher Tg
Temperature of operation to 110 °C
Lower gas crossover on operation

Jones, *Materials Matters*, 10 (3) (2015) 88-94

Paradigm shift: From conductivity to conductance

Most substantial improvements in fuel cell membrane performance obtained by simply *reducing* the membrane *thickness* → *high conductance membranes*

Antagonistic requirements: Thin membranes for high conductance, but most other properties – chemical and mechanical stability, gas crossover – are improved with thicker membranes

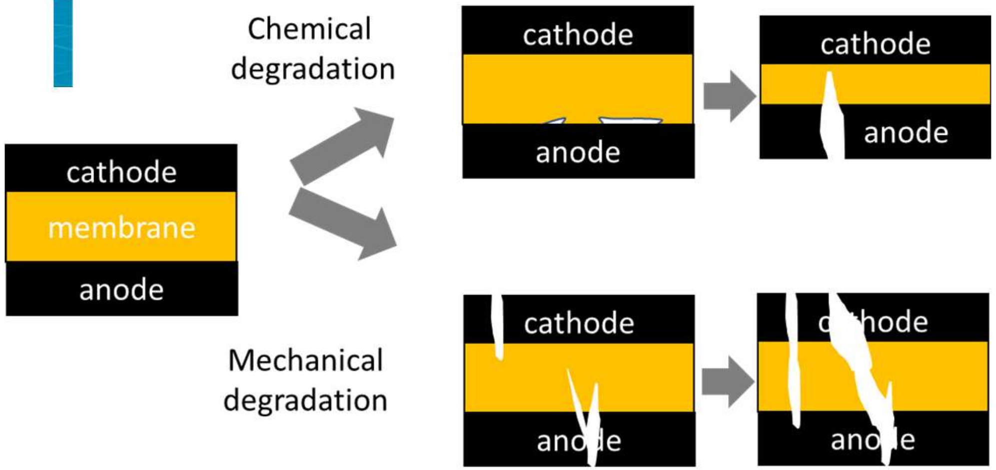
Membrane	EW	Thickness (μm)	Ionic Conductivity (S/cm)	Conductance (S/cm^2)
NAFION® 117	1100	200	0.14^a, 0.10^b	5-7
NAFION® 112	1100	60	0.10^b	17
Dev. Dow	800	100	0.15^b	15
GORE-SELECT®	1100	20	0.052^a,0.053^b	26
GORE-SELECT®	1100	5	0.028^a	56
GORE-SELECT®	900	12	0.096^b	80

[a] z-direction, sulfuric acid immersed sample measured with a four-point probe
[b] x-y direction, high-frequency measurement for membrane immersed in deionized water.

Kolde, Bahar, Wilson, Zawodzinski, Gottesfeld, Proceedings of the First International Symposium on Proton Conducting Membrane Fuel Cells I, Electrochemical Society Proceedings, Volume 95-23, P. 193-201 ©1995

Target membrane thickness
→ 8 - 12 µm for fuel cell transport
→ 80 – 100 µm for water electrolysis

Chemical and mechanical degradation on fuel cell operation



Zatoń, Roziere , Jones,
Sustainable Energy Fuels, 2017, **1**, 409-438

$\mathbf{R_f{-}CF_2COOH} + {}^{\bullet}OH \rightarrow R_f{-}CF_2^{\bullet} + {}^{\bullet}OH \rightarrow \ldots \rightarrow R_f{-}COF + HF$

$R_f{-}COF + H_2O \rightarrow \mathbf{R_f{-}COOH} + HF$

Alavijeh et al., *J. Electrochem. Soc.*, 2015, **162**, F1461-F1469

Mechanical

- Dimensional change between wet/dry conditions, especially for low EW/high IEC membranes → fatigue-induced fracture
- Thin membranes <20 µm for low electrical resistance and water back diffusion

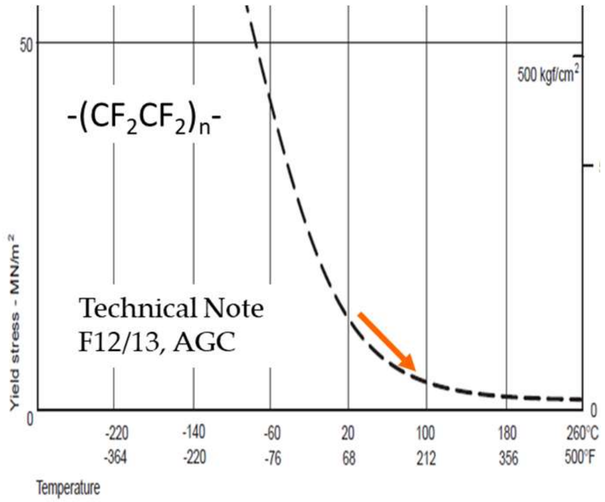
Chemical

- Reactive oxygen species generated during FC operation that attack membrane, causing thinning via main chain degradation - "unzipping", attack at ether link, or tertiary carbon and cleavage of SO_3H

« Active » membrane reinforcements

Disruptive reinforcement technology

- **Multifunctional reinforcements**: providing mechanical strength and radical quenching properties, and increased efficiency and safety as supports for radical scavengers and recombination catalysts



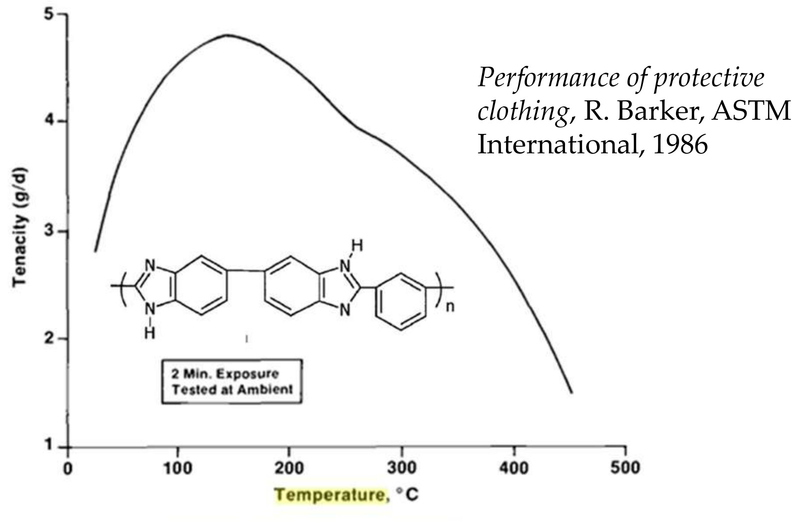


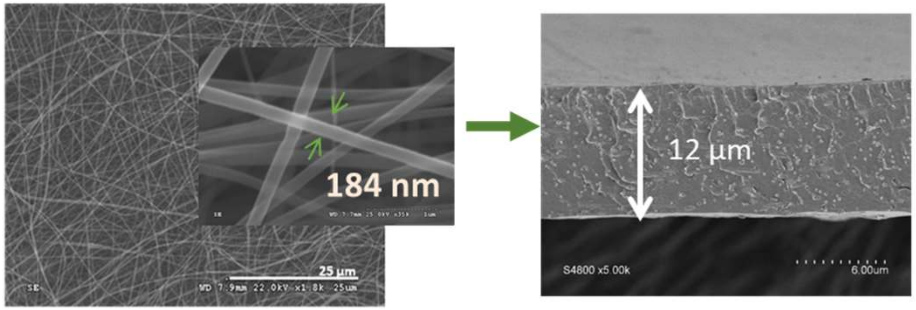
FIG. 4—*Strength of PBI fiber at an elevated temperature.*

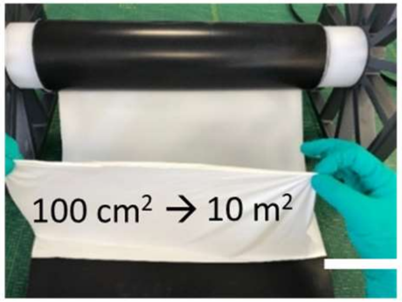
- Polybenzimidazole (PBI) has the highest tensile, shear, and compressive strength of any thermoplastic
- Mechanical strength of PBI increases with temperature up to ca. 150 °C
- Basic character allows ionic cross-linking or hydrogen bonding with PFSA or sulfonated hydrocarbons
- Electrospun polymer webs – range of polymer type with tuning of chemical and mechanical stability and interactions with PFSA matrix

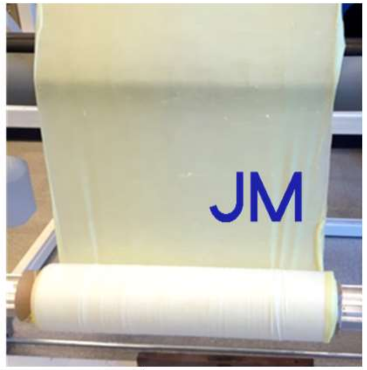
High performance membranes for LDV PEMFC

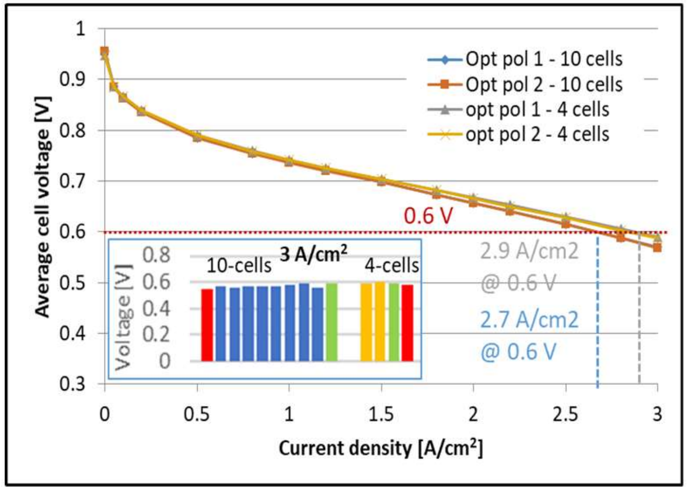
Clean Hydrogen JU 2019-2022
Coordination ICGM
www.gaia-fuelcell.eu

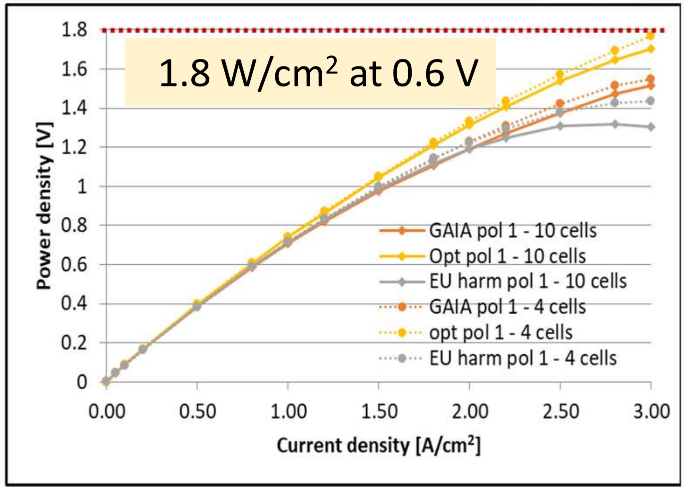
Success stories winner 2022











- PBI reinforced PFSA membranes (13 µm) in MEAs with 0.45 mg/cm² Pt total provided 1.8 W/cm² at 0.6 V, short stack testing in an automotive drive cycle, including 5% time at 105 °C.
- High power MEAs reduce MEA cost/kW

WO2016020668A1 to CNRS-UM-JM

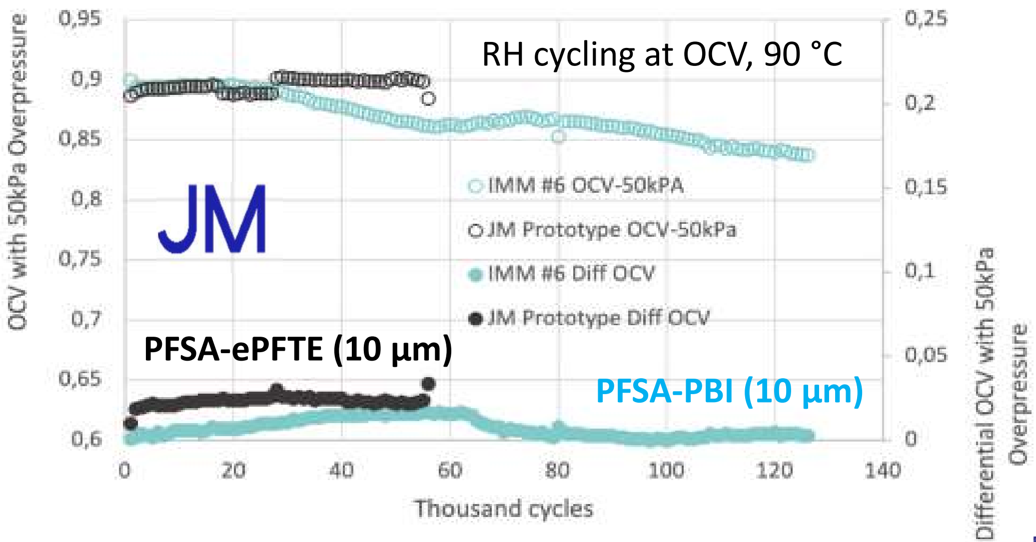
Zaton, Cavaliere, Buche, Rozière, Jones *in preparation*

Durable membranes for HDV PEMFC

IMproved lifetiMe stacks fOR heavy duty Trucks through ultrA-durabLe components

- Develop load profile tests (LPT) for heavy duty membrane electrode assemblies (MEAs) performance and durability assessment
- Develop high performance and high durability MEAs specifically designed for heavy-duty truck application
- Validate MEA performance and durability using AST and LPT protocols
- Develop robust algorithm for lifetime prediction to 30,000 hours of operation
- Satisfy the project target in terms of performance, stack cost, and efficiency

Clean Hydrogen JU 2021-2024
Coordination ICGM
www.immortal-fuelcell.eu



- Combined mechanical/chemical accelerated stress test at 90 °C on PBI nanofiber reinforced PFSA membrane, 10 µm thickness
- 120,000 AST cycles, i.e. around 2,100 hours AST, to end of test with no rupture failure
- Surpassed previous generations and reference membranes in MEAs of otherwise identical construction

Zaton, Cavaliere, Nesling, Buche, Rozière, Jones *in preparation*

Spotlight on PFAs

- Increasing international scrutiny of poly and perfluoroalkyl substances (PFAs) for their persistence in the environment, mobility, bio-accumulation
- May 2020: 5 EU countries initiated a call for universal PFAs restriction; the European Chemicals Agency published a restriction proposal in February 2023.
- Hydrogen Europe – Hydrogen Europe Research, European industries have contributed information, data …
- Fluoropolymers are essential in current membrane electrode assemblies in PEM fuel cells and electrolysers as hydrophobic agents, binders, membrane reinforcements, seals, ionomer and membrane: PTFE, ETFE, perfluorosulfonic acid (PFSA)
- https://news.3m.com/2022-12-20-3M-to-Exit-PFAS-Manufacturing-by-the-End-of-2025

Current technology readiness is due (amongst others) to the exceptional properties of PFSA and advances in understanding of membrane degradation – and its mitigation - on operation

ECHA restriction proposal: **Overall, ALL PFAs to be banned with an 18-month transition period after entry into force (potentially in 2025/2026), with a ban on manufacture, placing on market and use of PFAs**

5 or 12 years' derogation granted for sectors that have no ready alternatives

Proposal acknowledges fluoropolymer use in PEMFC, PEMEL

But only derogates on PEMFC (6.5 years period) not on PEMEL

Massive potential impact on timely implementation of PEM technologies for H_2 generation and H_2 end uses

…Spotlight on PFAs

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Future sustainability considerations for PEMFC and PEM electrolysis must include possible replacements for PTFE and PFSA. What alternatives ?

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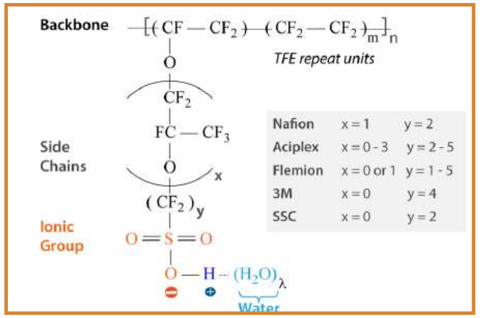
Hydrocarbon alternatives to PFSA ionomer and membrane



PFSA	Sulfonated hydrocarbon type
Strong phase separated structure that favours proton conduction	Less phase separation, strong dimensional swelling in water
Superacidic	Not superacidic
Exceptional chemical stability	Lower chemical stability
High oxygen permeability	Lower oxygen permeability
Ionomer colloids for catalyst layer processing	Ionomer solutions

2000- Direct sulfonation of high performance polymers (Jones, Rozière).

2010- Block copolymers (Mercier, McGrath, Jannasch).

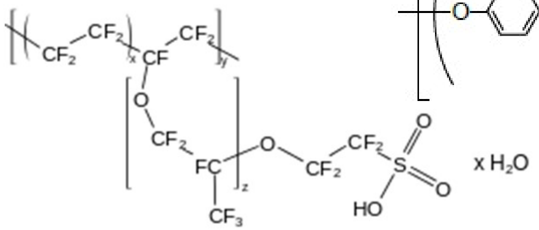
2015- No weak links – polyphenylenes (Holdcroft, Miyatake).

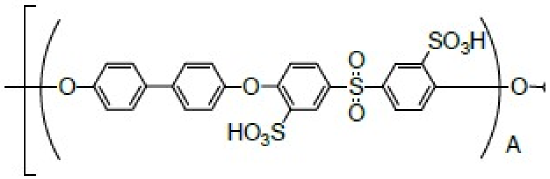
Recent advances in the functionalisation of polybenzimidazole and polyetherketone for fuel cell applications,
Jones, Rozière, *J. Membr. Sci*. 2001, **185** 41 – 58.
Non-fluorinated polymer materials for proton exchange membrane fuel cells
Rozière, Jones, *Annu. Rev. Mater. Res.,* 2003, **33**, 503 – 555.

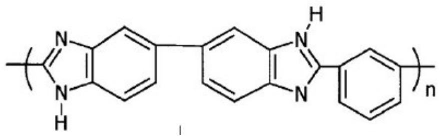
Brittle in dry state, high degree of sulfonation → high swelling with water, low phase separation.

- Regain of research on sulfonated hydrocarbon polymers and membranes is essential, that integrates the experience in mechanical and chemical reinforcement gained with PFSA membranes

Fuel cell and electrolysis membrane development - summary







1969

Nafion, LSC PFSA

1995-2010

Sulfonated polyaromatics

Random and multiblock copolymers of polyetherketones, polysulfones, polyphenylenes, polyimides…

1980 Dow
2000 Solvay
and 3M

SSC ionomers

1980: Dow SSC
2000: Solvay Aquivion and 3M ionomers

1995

HT PEMFC

H_3PO_4 doped polybenzimidazole

1994 – ePTFE
2008 – Mn^{2+}, Ce^{3+}, CeOx

Mechanical and chemical stabilisation of PFSA

PFAS restrictions

New generations of mechanical (hydrocarbon) and chemical stabilisation associated with new generations of sulfonated polyaromatics

Acknowledgements

Silvain Buche
Emily Nesling
Josef Bobolecki

Johnson Matthey – Inspiring science, enhancing life

Luca Merlo
Bertrand Pavageau

SOLVAY

Fabien Gaboriaud
Benoît Lafitte
Julien Thuilliez

MICHELIN

H_2 The French Research network on Hydrogen energy

anr

FRANCE 2030

PEPR H2 – PEMFC95

Clean Hydrogen Partnership

GAIA

next Generation AutomotIve membrane electrode Assemblies 2019-2022

Ivan Ponomarev – elmarco

IMMORTAL

IMproved lifetiMe stacks fOR heavy duty Trucks through ultrA-durabLe components 2021-2023

Mark Muggli – dyneon

FCH – Fuel Cells and Hydrogen Joint Undertaking

Co-funded by the European Union

Outlook

The past

- Main driver: highly performing and robust materials to satisfy end-user requirements to enable (PEM) fuel cell and electrolyser deployment
- Less attention to sustainability in the use of critical raw materials or the environmental impact of the chemistries

The future

- Thrifting - doing more with less ; Circularity by design ; Environmentally benign chemistries
- Research is essential to underpin the fuel cells and hydrogen industry and safeguard against future supply or legislative constraints

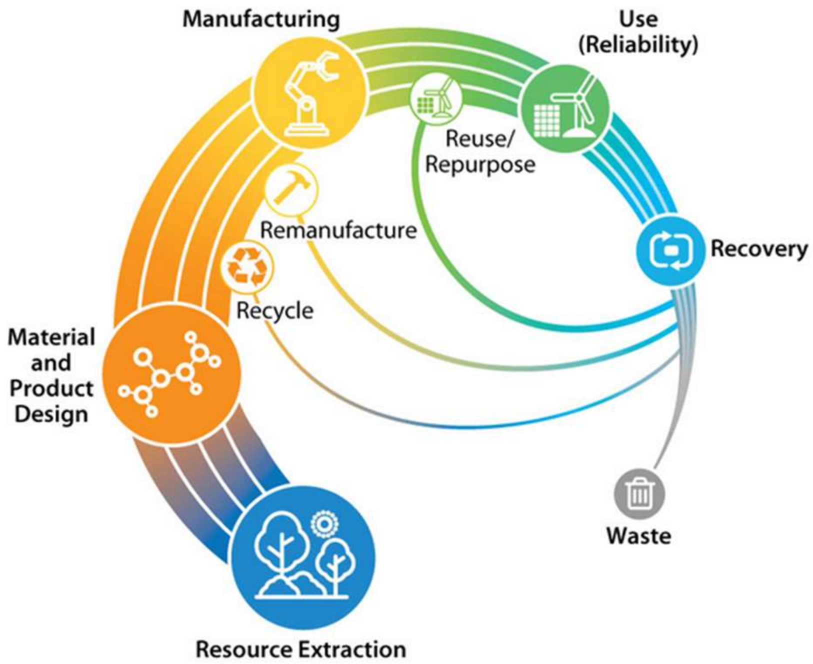


Figure from: https://www.nrel.gov/research/circular-economy.html