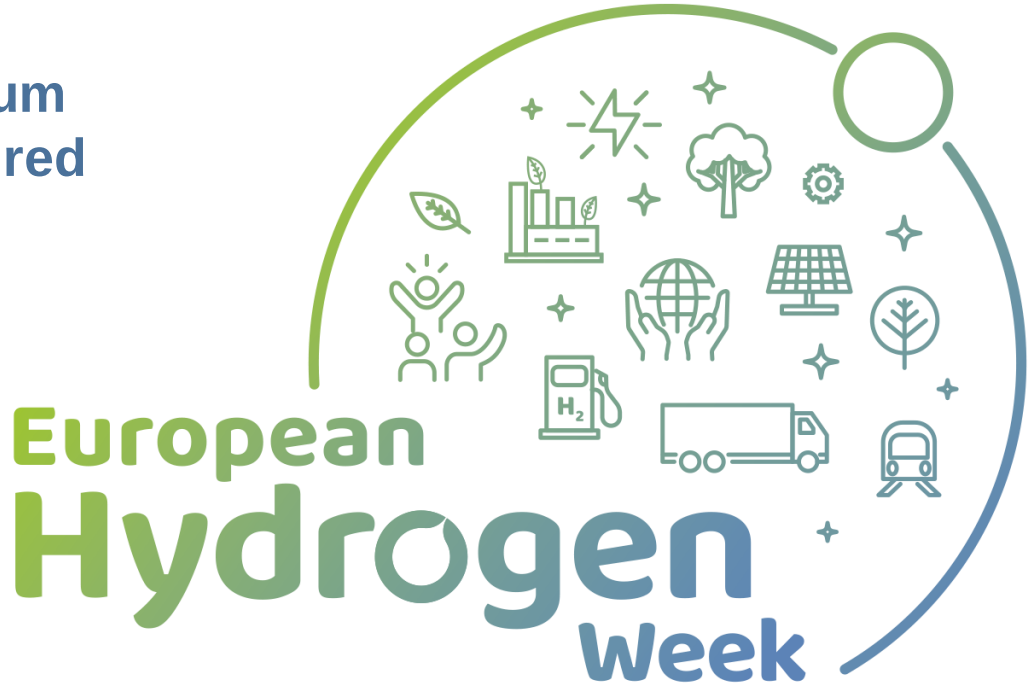
PEGASUS
PGM Free Catalyst

PEMFC Based on Platinum Group Metal Free Structured Cathodes



Pierre-André JACQUES

Commissariat à l'énergie atomique
et aux énergies alternatives

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FCH

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www-liten.cea.fr

PEGASUS : Executive summary

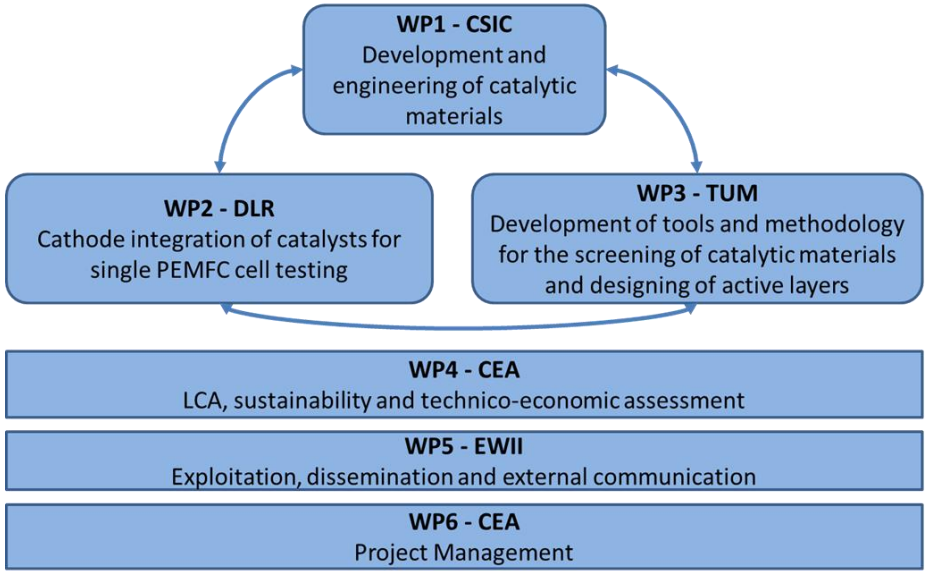
- Project ID :
  - Start date: February 2018
  - Duration: 36 months (extended to 41 months)
  - Budget: 2.8 M€
  - EU ref: 779550
  - Web site : https://www.pegasus-pemfc.eu/

- Consortium

#	Participant organisation legal name	Short name	Country
1	Commissariat à l'Energie Atomique et aux Energies Alternatives	CEA	FR
2	Deutsches Zentrum für Luft – Und Raumfahrt EV	DLR	DE
3	Technische Universität München	TUM	DE
4	Agencia Estatal Consejo Superior de Investigaciones Cientificas	CSIC	ES
5	Association pour la recherche et le développement des méthodes et processus industriels	ARMINES	FR
6	Heraeus Fuel Cells GmbH	HERAEUS	DE
7	EWII Fuel Cells A/S	EWII	DK
8	Toyota Motor Europe	TOYOTA	BE

PEGASUS : Objectives

- Develop Platinum Metal Group (PGM) free catalysts for the cathode side of PEMFC
  - Only PEMFC is addressed (acidic conditions)
  - Only cathode side is addressed (Pt loading is ~4 times higher at cathode than anode)
  - 3 mains levers :
    - active site – intrinsic activity / active site density.
    - Catalyst structure – active site accessibility
    - Active layer structure – active site accessibility
- Manufacturability / processability
  - Process cost / LCA and upscability
  - PMF (Precious Metal Free) and CRM (Critical Raw Material) free
  - Environment friendly raw material.



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PGM Free Catalyst

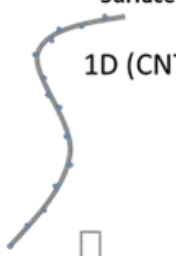
PEGASUS : Catalyst Synthesis

GEN1 - SINGLE STRUCTURATION

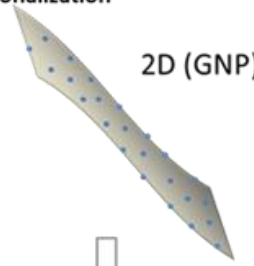
Catalysts - Nitrogen + Metal {Fe, Mn, Cu}

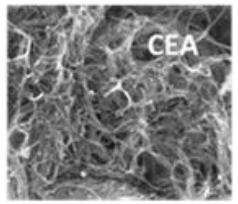
- Surface functionalization
- Bulk synthesis + Surface functionalization

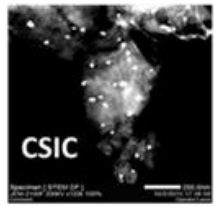
1D (CNT)



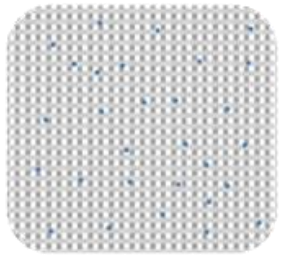
2D (GNP)

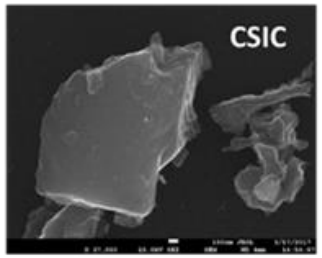






3D (polymer)

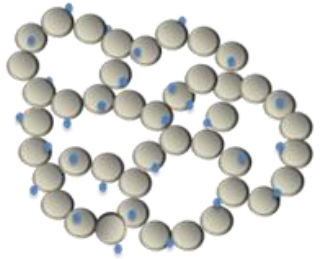


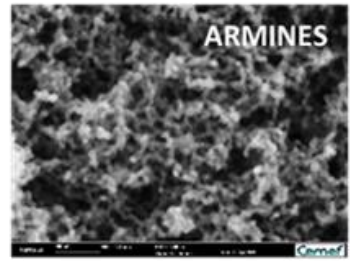


Catalysts -Nitrogen + Metal {Fe}

- Bulk synthesis
- Bulk synthesis + Surface functionalization

3D (aerogel)



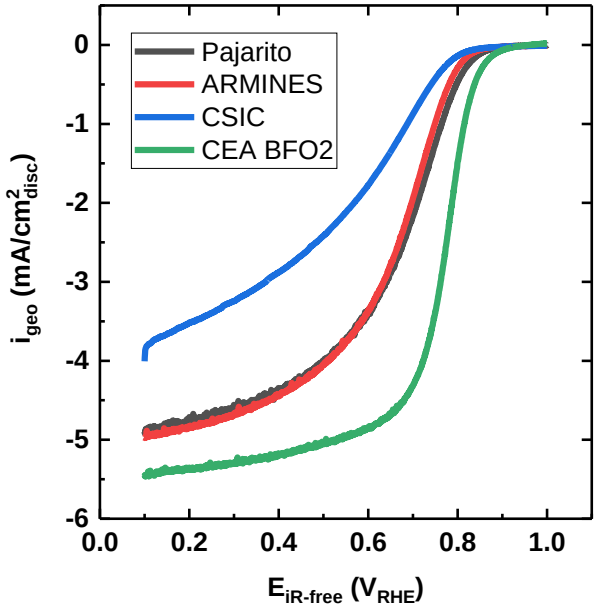


PEGASUS : Results

Best PEGASUS catalyst is 2 times more active than commercial SoA

- ORR activity measurement by partners not involved in catalyst synthesis
- Comparison with SoA commercial PGM free catalyst (thanks to Pajarito Powders company

CEA (BRF02) > Pajarito / Armines (CA52b) > CSIC (GEN#1-2D)



samples	I mass @ 0.85 V/RHE RDE – A/g	I mass @ 0.80 V/RHE RDE – A/g	I mass @ 0.80 V/RHE RDE – A/g
CEA – (BRF02)	1.17	4.7 +/- 0.5	3.54 +/- 0.13
Pajarito (PMF 011904)	0.4	1.5 +/- 0.3	2.37 +/- 0.35
Armines – (CA52b).	0.38	1.2 +/- 0.15	2.17 +/- 0.18
CSIC – (GEN#1-2D)	0.2	0.85 +/- 0.1	0.91 +/-0.07
Partner/ conditions	$HClO_4$, 25°C, O_2 std, 1600 RPM, 290 $\mu g_{cat}/cm^2$		H_2SO_4, 25°C, O_2 std, 1600 RPM, 400$\mu g_{cat}/cm^2$

PEGASUS : Results

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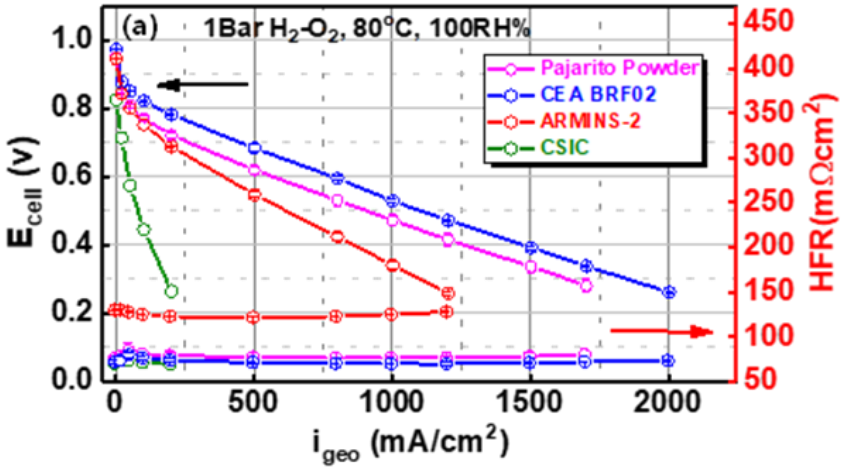
Same ORR activity ranking in RDE and single cell

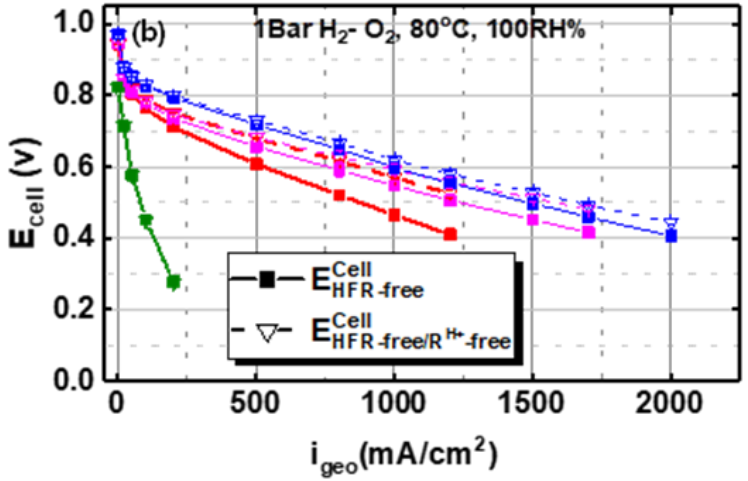
CEA (BRF02) > Pajarito / Armines (CA52b) > CSIC (GEN#1-2D)

Samples	I mass @ 0.80 V/RHE RDE (290 µg/cm²) – A/g	I mass @ 0.80 V/RHE MEA/ single cell (2 mg/cm²) – A/g
CEA – (BRF02)	4.7 +/- 0.5	106 +/- 5
Pajarito (PMF 011904)	1.5 +/- 0.3	35 +/- 2.5
Armines – (CA52b).	1.2 +/- 0.15	35 +/- 4
CSIC – (GEN#1-2D)	0.85 +/- 0.1	15 +/- 1
SoA[1]	N/A	Estimated : 60 (6,8 mg/cm²)



activity Vs SoA

	samples	i_{geo} @ 0.6 V H2/Air 5 cm² cell / 100%HR / 1 bar /80°C
PEGASUS (FCH-JU)	CEA – (BRF02) (2 mg_{cat}/cm^2)	420
	Pajarito (PMF 011904) (2 mg_{cat}/cm^2)	120
SoA[2] ELECTROCAT (DoE)	Pajarito (4mg_{cat}/cm^2)	180
	LANL (4mg_{cat}/cm^2) .	380



[1]: P. Zelenay et al., DOE 2018 Annual Merit Review.

[2]: https://www.hydrogen.energy.gov/pdfs/review20/fc160_myers_zelenay_2020_o.pdf

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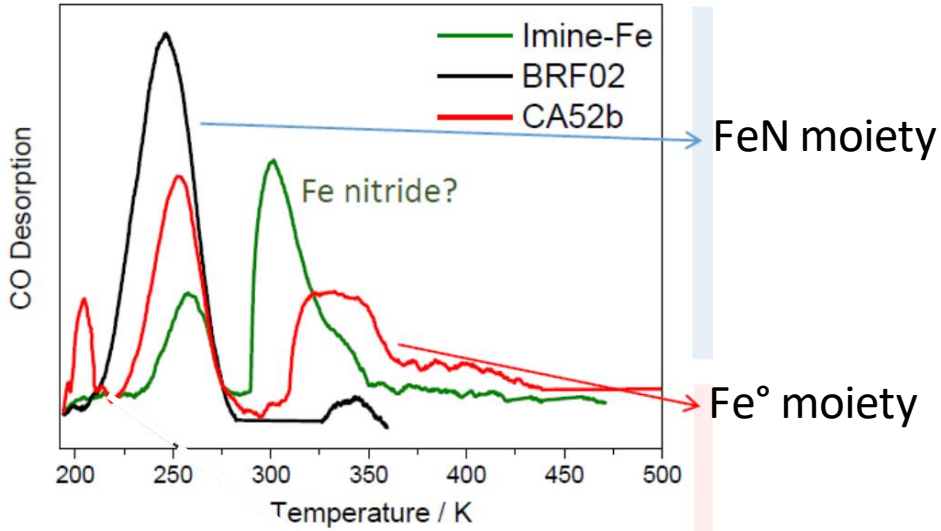
PEGASUS : Results

Active site structure and Active site quantification

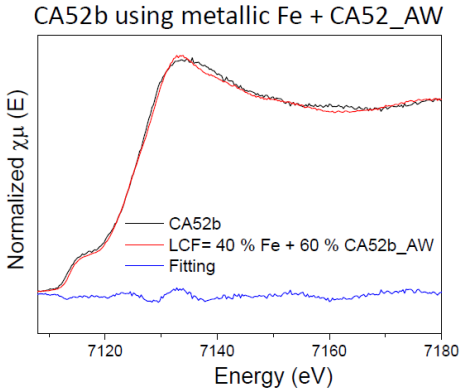
- FT-EXAFS shows that CEA-BRF02 contains almost no Fe° particles
→ There is no Acid Washing step in BRF02 synthesis protocol

- After acid washing : CA52b-AW (carbon aerogel) does not contain Fe°
→ Only metallic Fe is eliminated by Acid Washing step

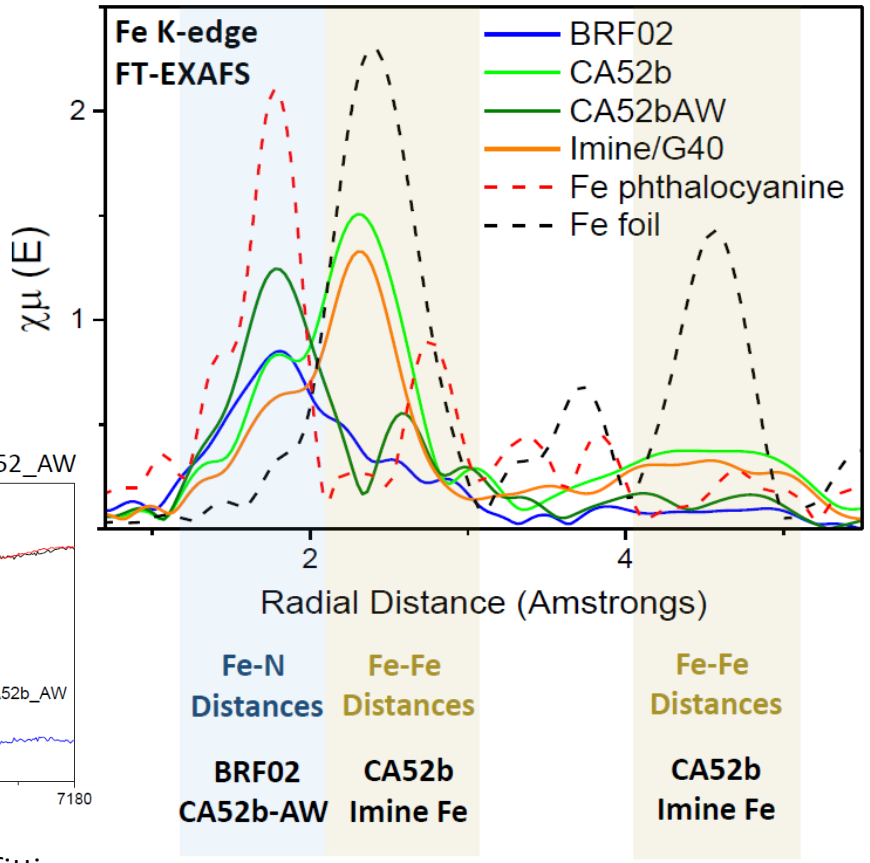
➢ Higher the FeN moiety concentration , higher the ORR activity



Temperature Programmed Desorption of CO



XAS linear combination fitting



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PEGASUS : Results

Active site structure and Active site quantification

- Cryogenic pulse chemisorption of CO followed by Temperature Programmed Desorption of CO

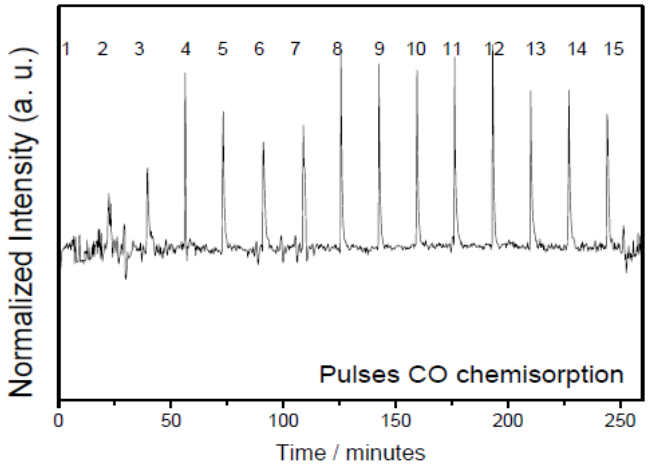
→ Pretreatment in He @ 600°C, CO chemisorption @ -80°C under HE, 13 pulses of CO,
→ CO desorption from -80 to 600°C under He

- The material showing highest Fe-N moiety quantity shows higher surface active quantity.

→ Higher the surface active site quantity, higher the ORR activity

samples	CO chemisorbed ($mmol_{CO}/g_{cat}$)	Active sites number Surface sites $/g_{cat}$
CEA – (BRF02)	0.4	2.4×10^{20}
Armines – (CA52b).	0.29	1.7×10^{20}
CSIC – (imine-Fe)	0.05	3.0×10^{19}

SoA[1] : ~ $0,8 \times 10^{20}$



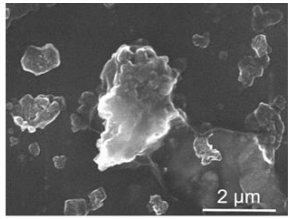
[1]: ACS Catalysis 8, 1640, **2018**.

PEGASUS : Results

Catalyst activity at agglomerate level

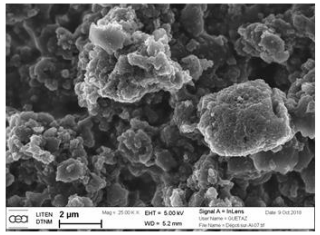
- Ranking ORR activity of PGM free catalyst at the agglomerate scale

→ benchmark of material
→ Measurement of intrinsic activity
→ Injection into an Active Layer model to better understand the limitation of PGM free based cathode

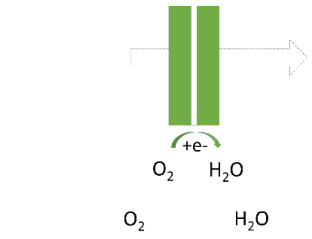


Pajarito catalyst dispersed on a substrate for SECM measurement

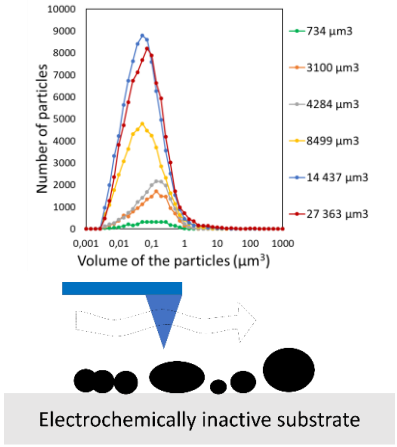
Similar agglomerates



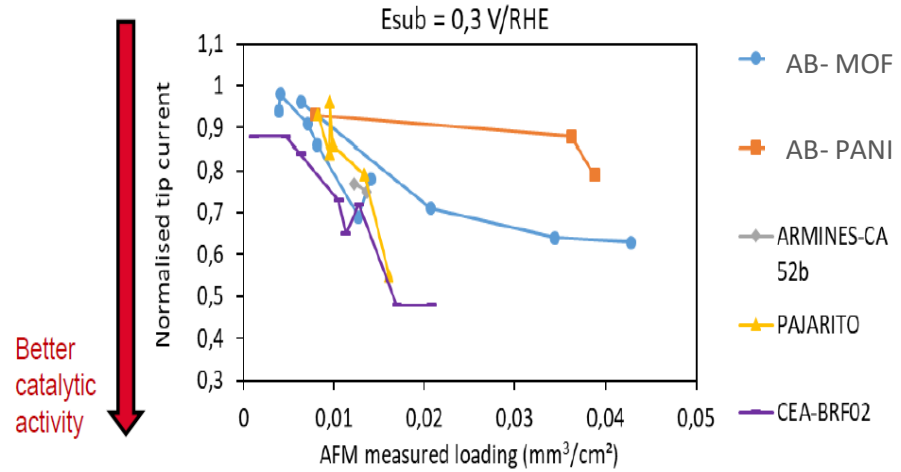
Pajarito catalyst within a thick active layer



Local electrochemical performance (SECM)



Agglomeration state (AFM)



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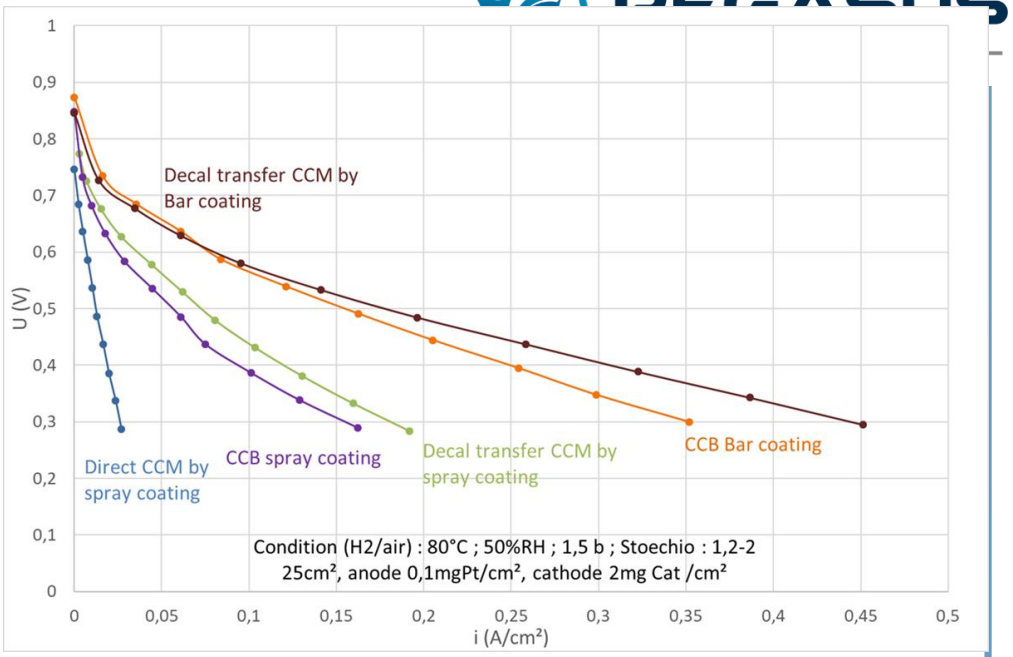
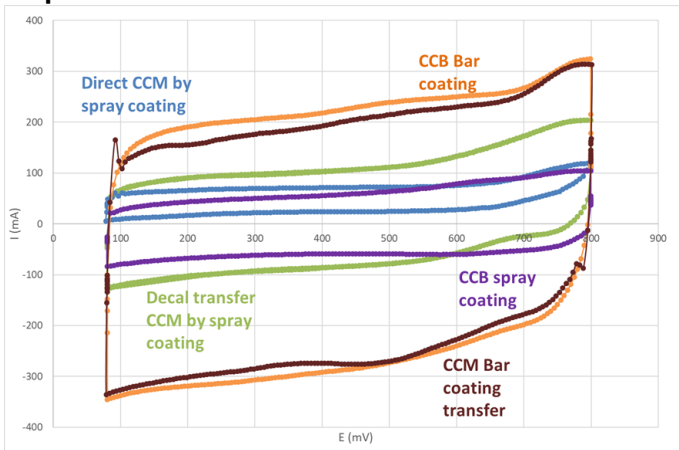
PEGASUS : Results

Impact of fabrication process

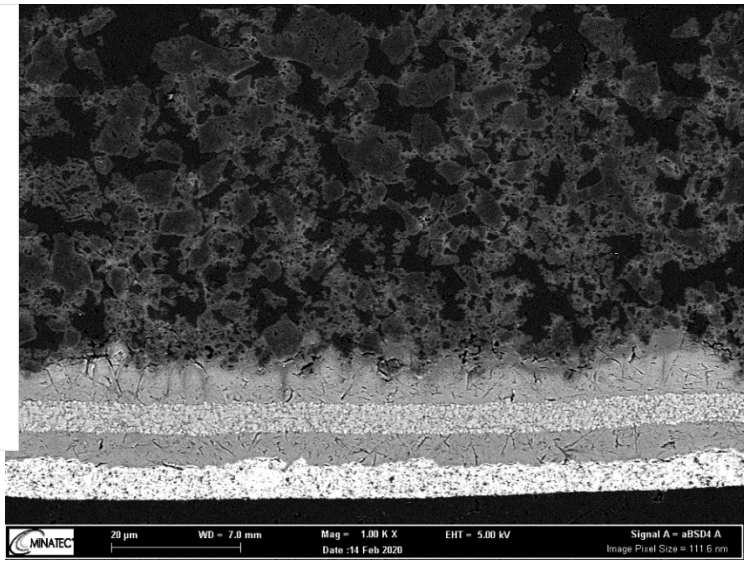
- Fabrication of CCM (catalyst coated membrane)
- integrating PGM free catalyst @ cathode side
- Thin membrane (18 µm)
- Easily scalable manufacturing process
- Cathode thickness ~ 50µm-100 µm.
- Relation : process / Active layer structure / MEA performance



coating technique	Average EAS (m2/g)	Uf (%)
direct CCM spray	63 +/- 16	12 +/- 3
CCB spray	116 +/- 14	22 +/- 3
decal CCM spray	237 +/- 48	46 +/- 9
CCB bar	489 +/- 21	94 +/- 4
CCM bar transfer	411 +/- 11	79 +/- 4



Cyclic voltametry



SEM / cross section

EAS (Electrochemical avctive surface): calculated thanks to CV, assuming 0,2 F/m^2

Uf (Utilisation factor) : $Uf = \frac{EAS}{S_{BET}}$

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PEGASUS : Conclusions / Next Steps

- Catalyst synthesis and characterization :
  - ✓ synthesis of PGM free material sowing high mass activity regarding PGM free SoA
  - ✓ Limited number of steps in the synthesis process, only largely available raw material
  - ✓ Synthesis made up to 5 gr per batch.
  - ✓ Active site quantification and correlation between Fe-N moiety quantity and ORR activity.
  - ✓ Implementation of SECM technique to quantify the catalyst activity @ agglomerate level.

- CCM fabrication using easily scalable printing process / relation between structure property and performances.

❖ Next Step :

- ➢ Integration of GEN2 catalyst and MEA performance evaluations
- ➢ Durability study
- ➢ LCA and tech-eco analysis

PEGASUS : Thanks !

- FCH-JU and European Commission for financial contribution to PEGASUS under the grant agreement number : 779550
- All the consortium members and implicated people into the project.
- The Advisory board members and more specifically our friends from US-DoE projects.

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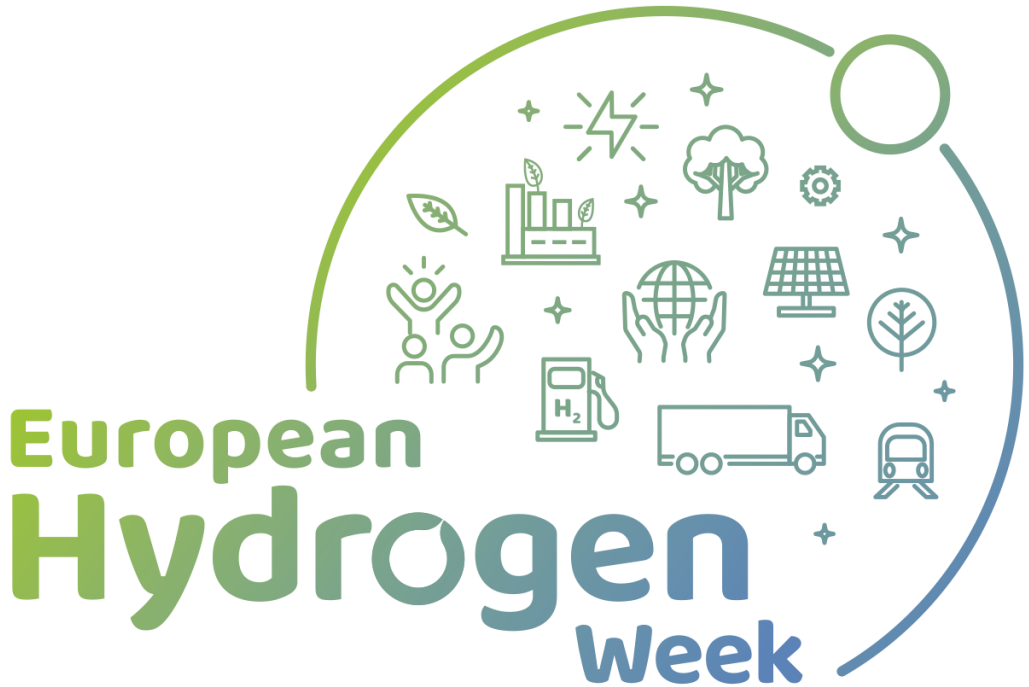

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