EU funded Project
Innovation and Networks Executive Agency
(INEA)
Grant Agreement Number: 727734

CO_2 selective membranes for carbon capture: the NANOMEMC^2 experience

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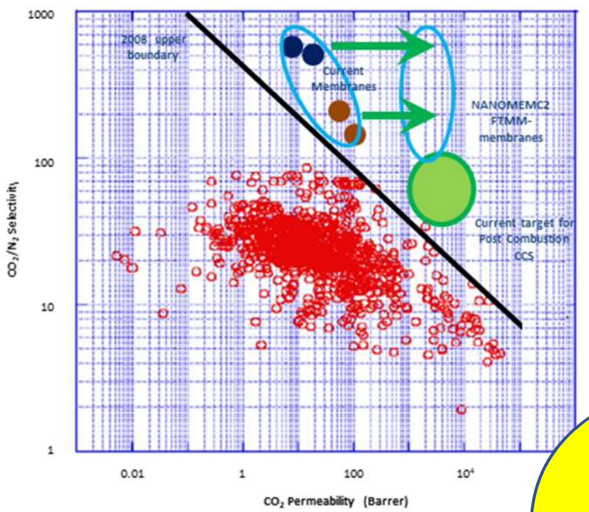
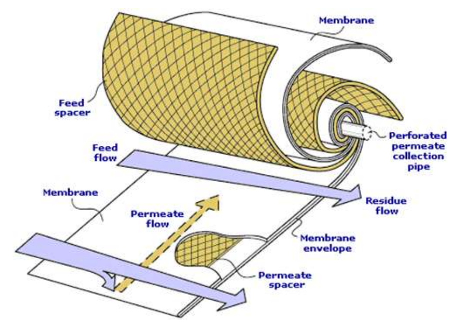
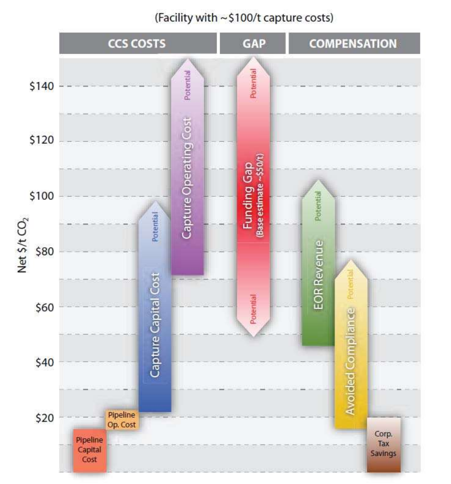
Paris July 3rd 2019

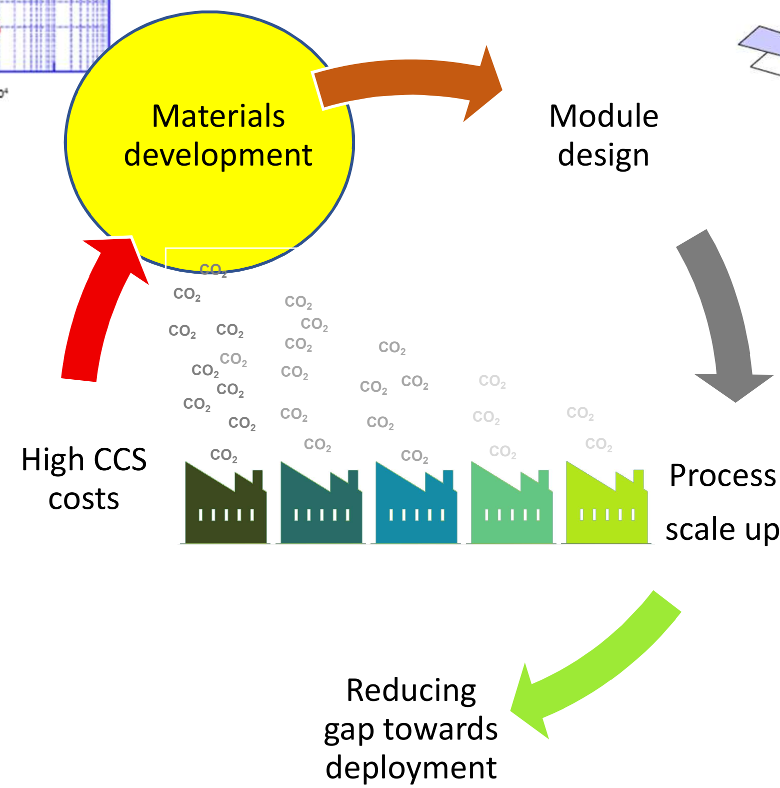
Strategy and objectives

NanoMEMC² – NanoMaterial Enhanced Membranes for Carbon Capture

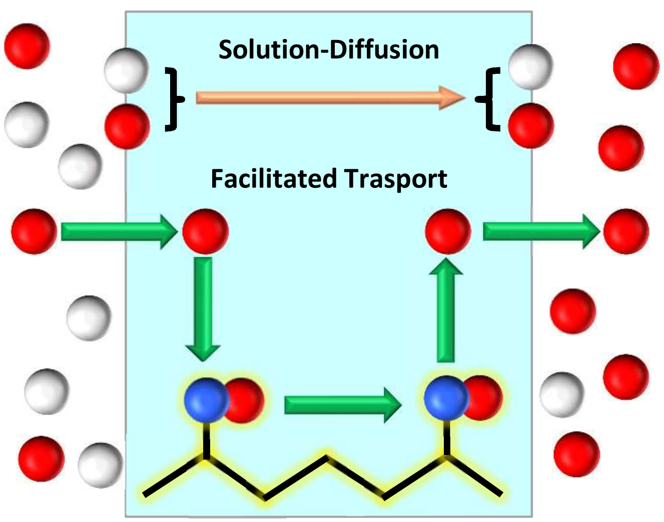


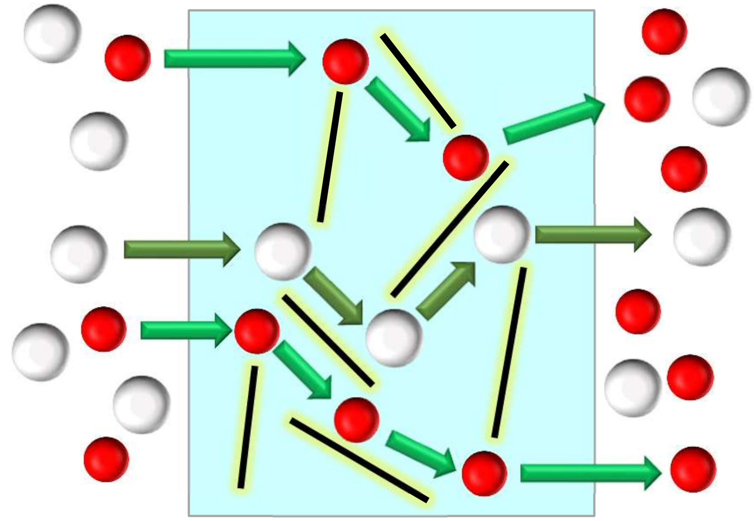




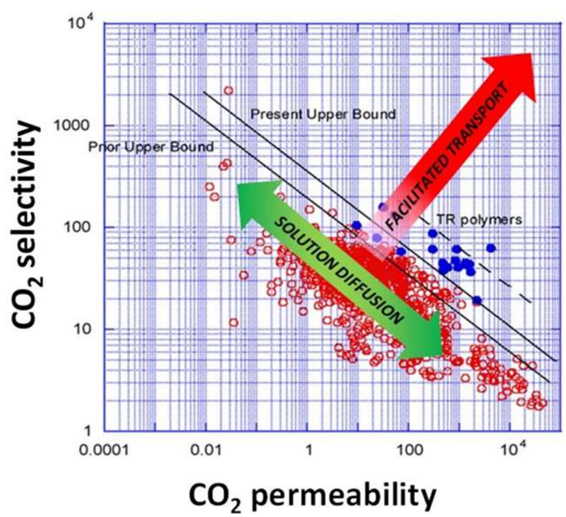


FTHM vs. CPHM

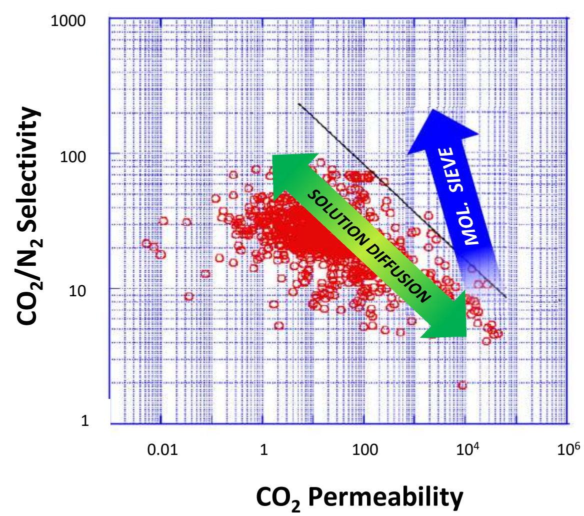




$$\alpha_{ij} \equiv \frac{y_i^d / y_j^d}{y_i^u / y_j^u} \underset{p_d \to 0}{\cong} \frac{P_i}{P_j}$$



$$J_i = \frac{P_i}{\delta}\left(p_{i-up} - p_{i-down}\right)$$

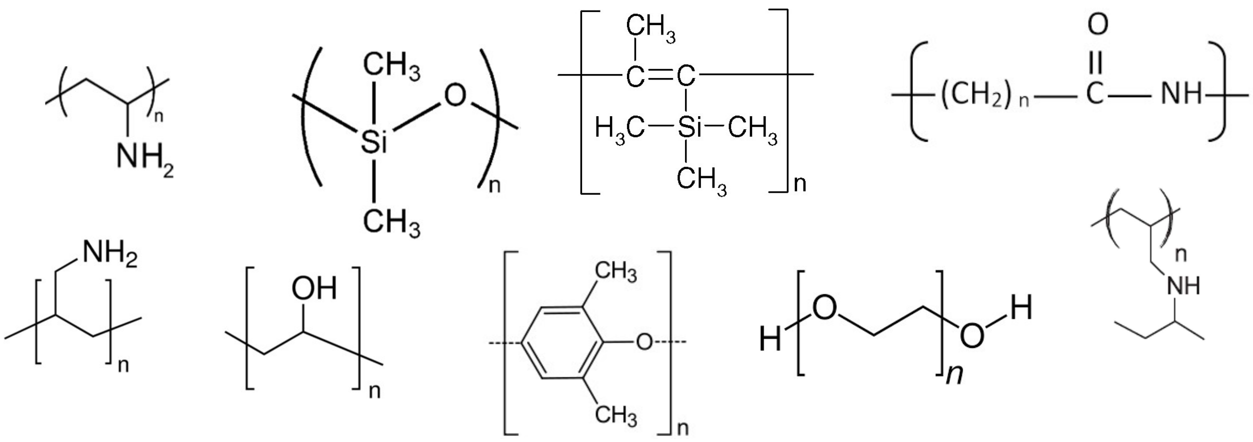


NANOMEMC² Materials

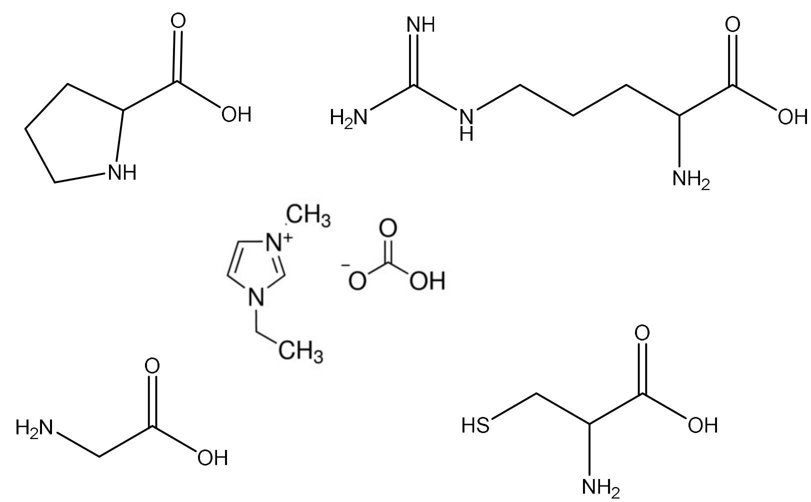
Horizon 2020

NanoMEMC² – NanoMaterial Enhanced Membranes for Carbon Capture

Polymers

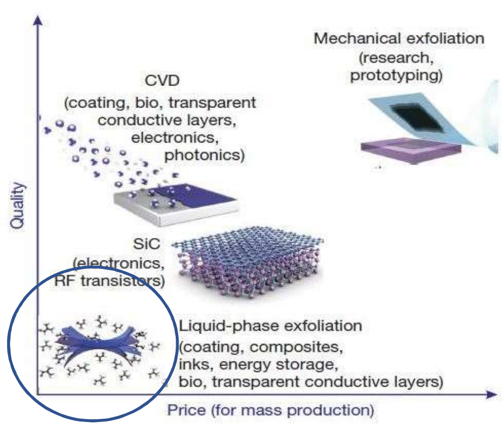


Additives

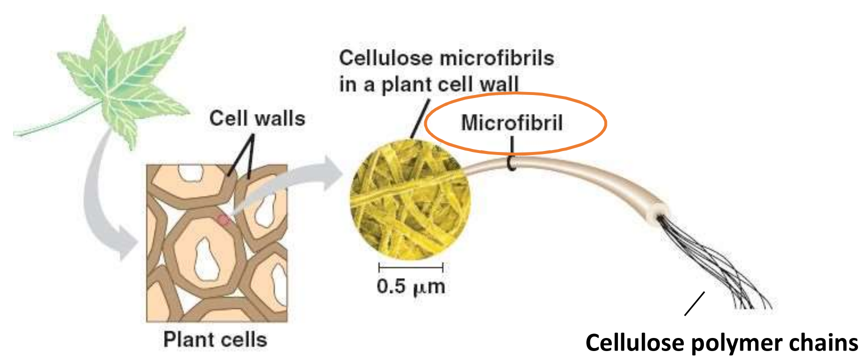


Fillers

Graphene



Nanocellulose



Journey through the membrane development

Horizon 2020

nano memc²

Polymer Matrix

PVAm, PAA, PVA, SHPAA, PTMSP, PDMS, PPO, PEG, ILs

+

Nanofiller

Nanocellulose or Graphene-based

Additives

Self standing films, >50 µm thick

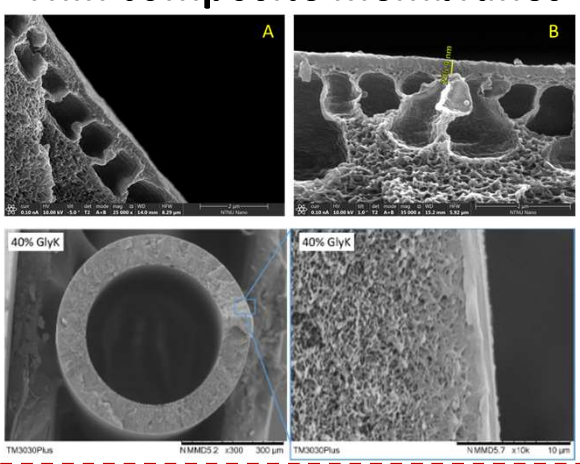
Basic Material Characterization

Physical & chemical properties

Transport properties

Water sorption
Single gas permeation

Thin composite membranes

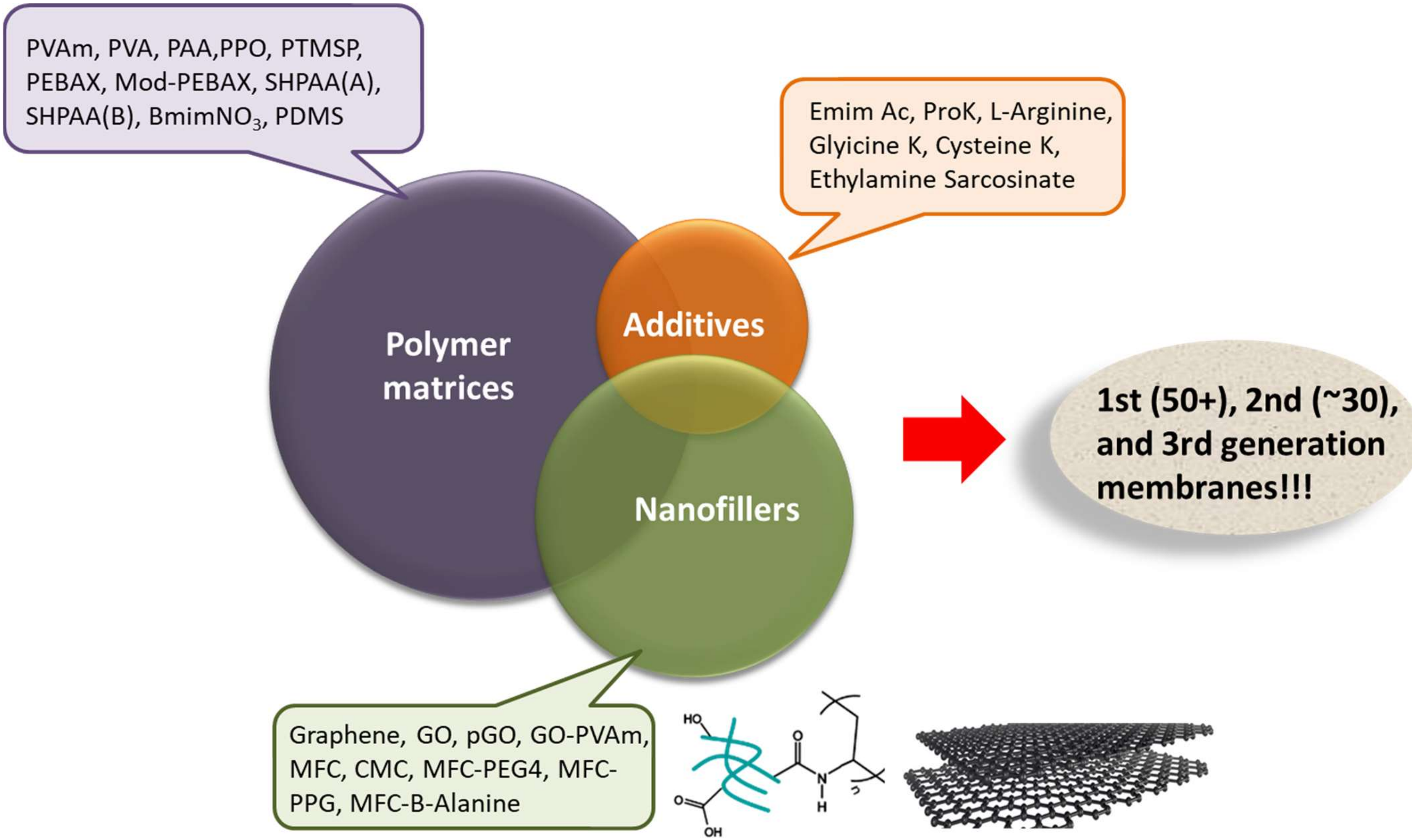


Advanced gas permeation tests

- *Mixed gas separation*
- *Durability*
- *Stability tests*

To scale up & pilot

NANOMEMC^2 Materials

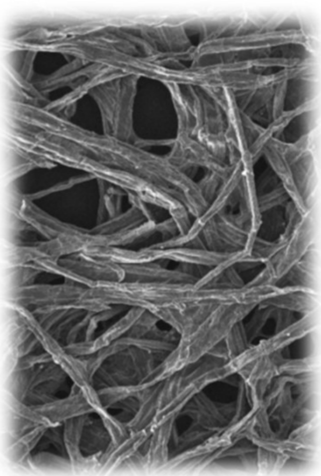


Nanocellulose production :

InoFib
From Nature to the Future

- Cellulose nanofibrils are obtained through mechanical disintegration of cellulosic fibres suspensions.
- INOFIB NFC are produced with a **Masuko grinder** after an enzymatic pretreatment (as well as a chemical pretreatment to obtain carboxymethylated NFC)

Fibers suspension + Enzymes or Chemicals + Mechanical shearing = Cellulose Nanofibrils



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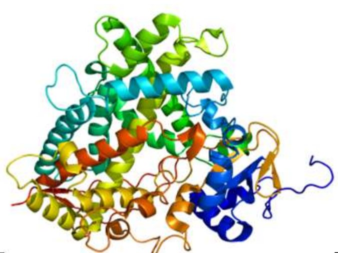

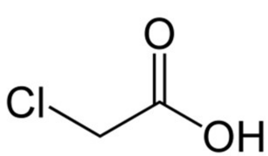

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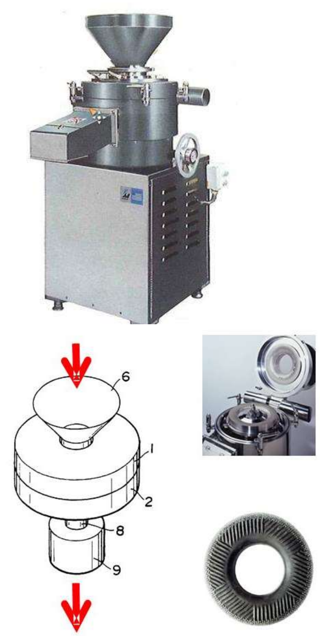

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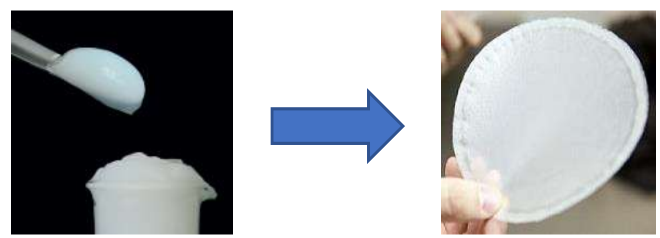
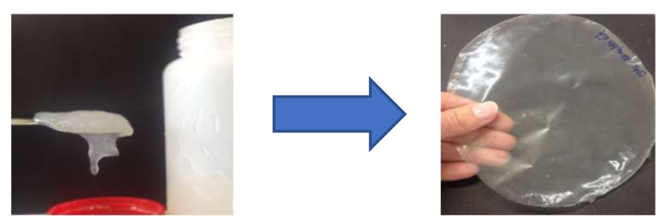
Native-NFC



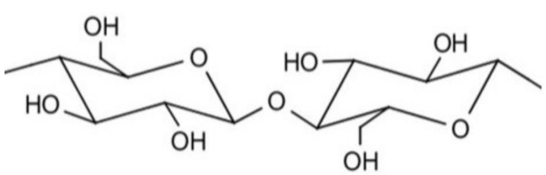
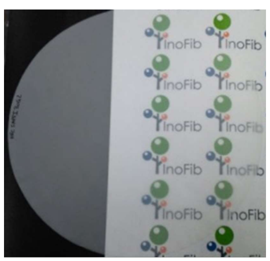
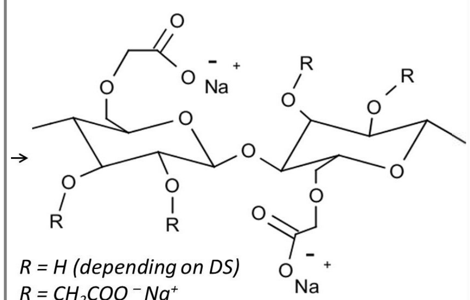
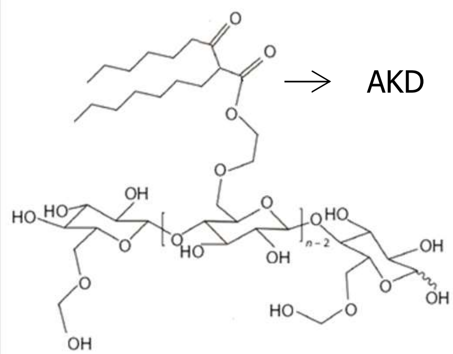
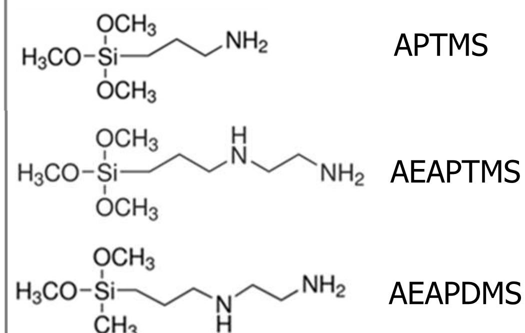
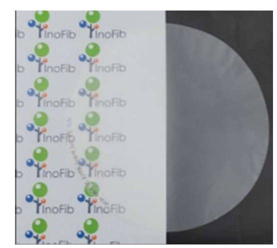
Carboxymethyl-NFC (cmNFC)



POST MODIFICATION

Nanocellulose modification : InoFib Production

- Thanks to the high amount of –OH group at the surface, NFC can be easily modified to obtain NFC with differents functionalities **keeping film forming capacity**

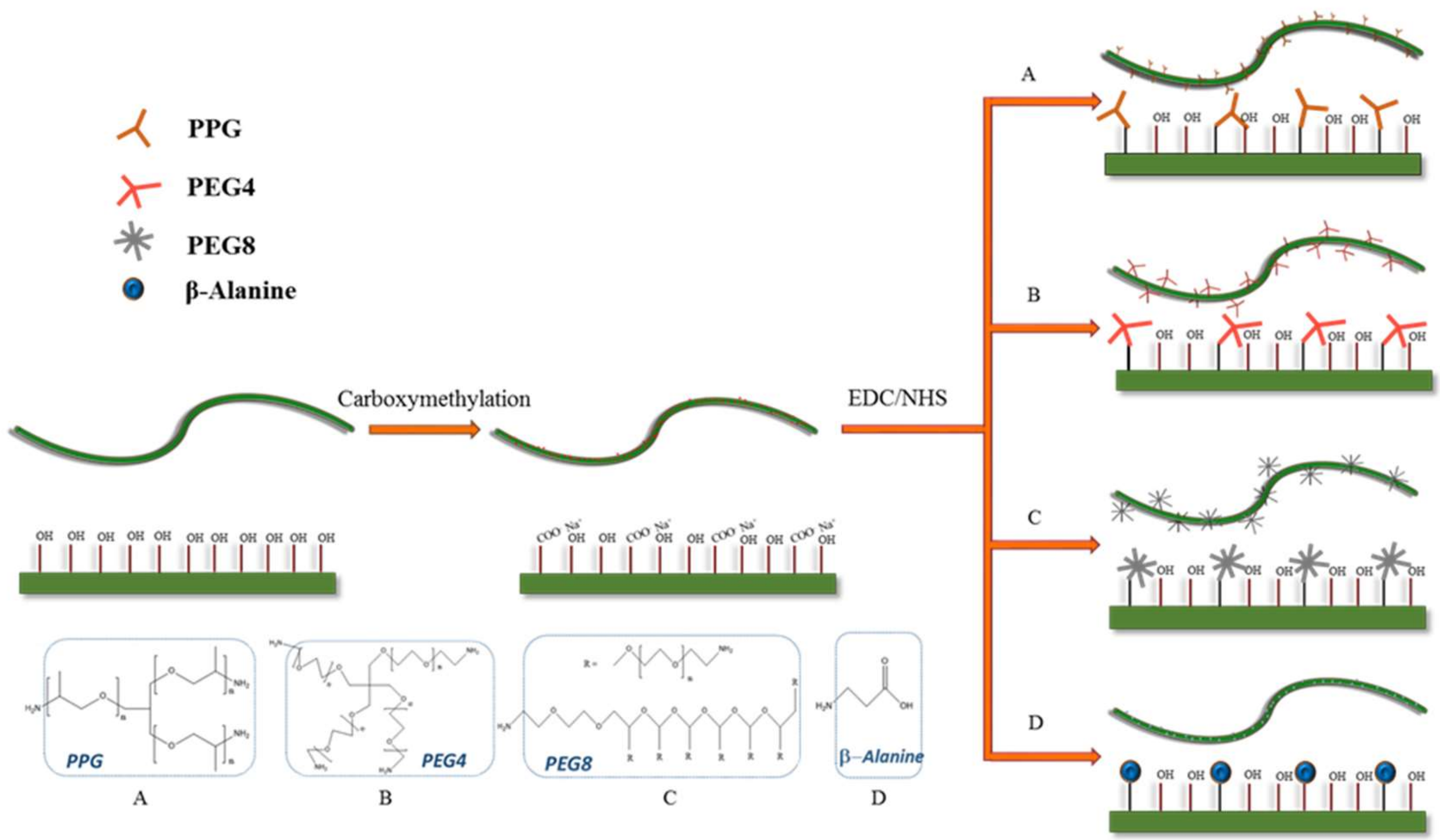
Native-NFC	Carboxymethyl-NFC	Hydrophobic-NFC	Aminosilane-NFC
 	 	 	 
Used as reference material	Suspension with high surface charge and stability -COOH functions	Increased barrier properties and water resistance	Grafting of amine group on the surface to increase CO2 affinity

Nanocellulose modification: NTNU actvity

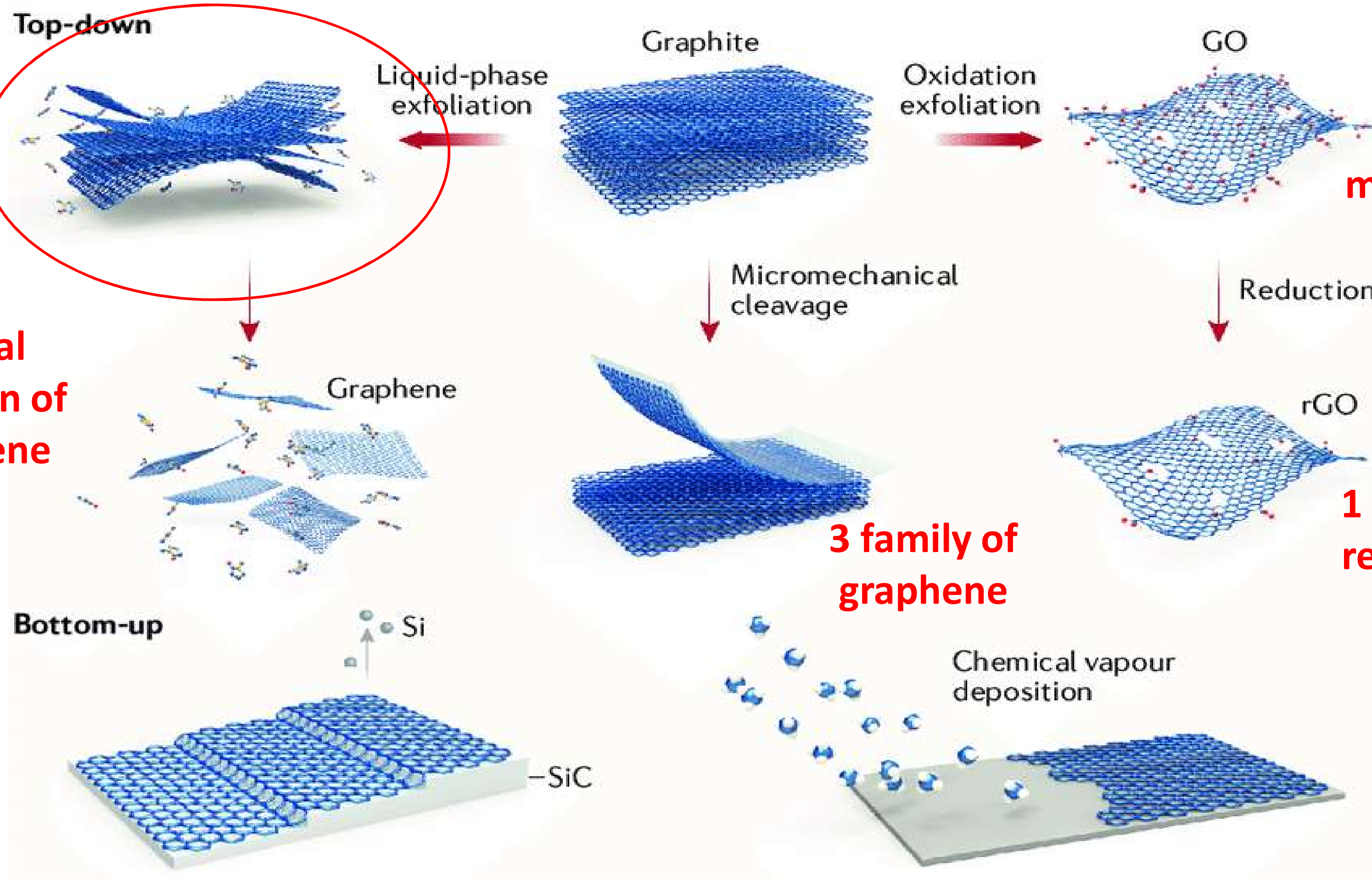
NTNU

- Thanks to the high amount of –OH group at the surface, NFC can be easily modified to obtain NFC with differents functionalities

NTNU modified cellulose nanofibrils by adding on the 4 different types of CO_2-philic molecules namely PPG, 2 different type of PEG and one aminoacids



Graphene & graphene oxide production



5 chemical modification of based GO

5 chemical modification of LPE graphene

3 family of graphene

1 family or reduce GO

Wang, X.-Y. *et al.* (2017) *Nat. Rev. Chem*

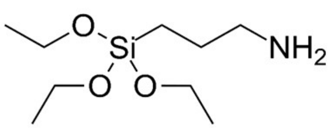
Selected material: LPE graphene and graphene oxide are supply on a continuous base to partners.

NANOMEMC^2 Nanofillers

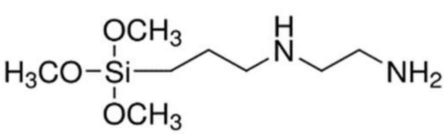
Graphene and GO modification

Modifying Graphene or GO is more critical than NFC, due to the lower amount of active site in the carbon nanosheets.

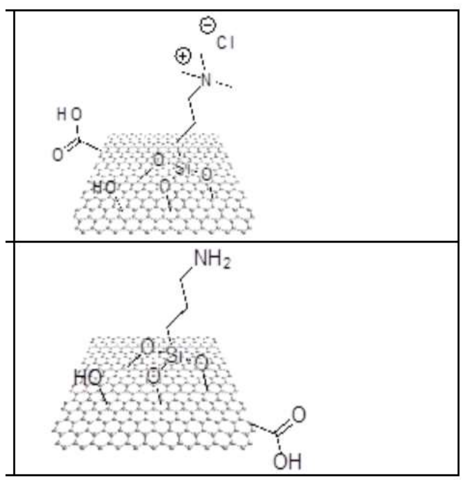
GNext, produced different types of modified graphene nanofillers, by using Ball Mill method: in N_2, CO_2, atmosphere and NH_3 in water. Chemically modified GO was prepared by the addition of amine functionalities.

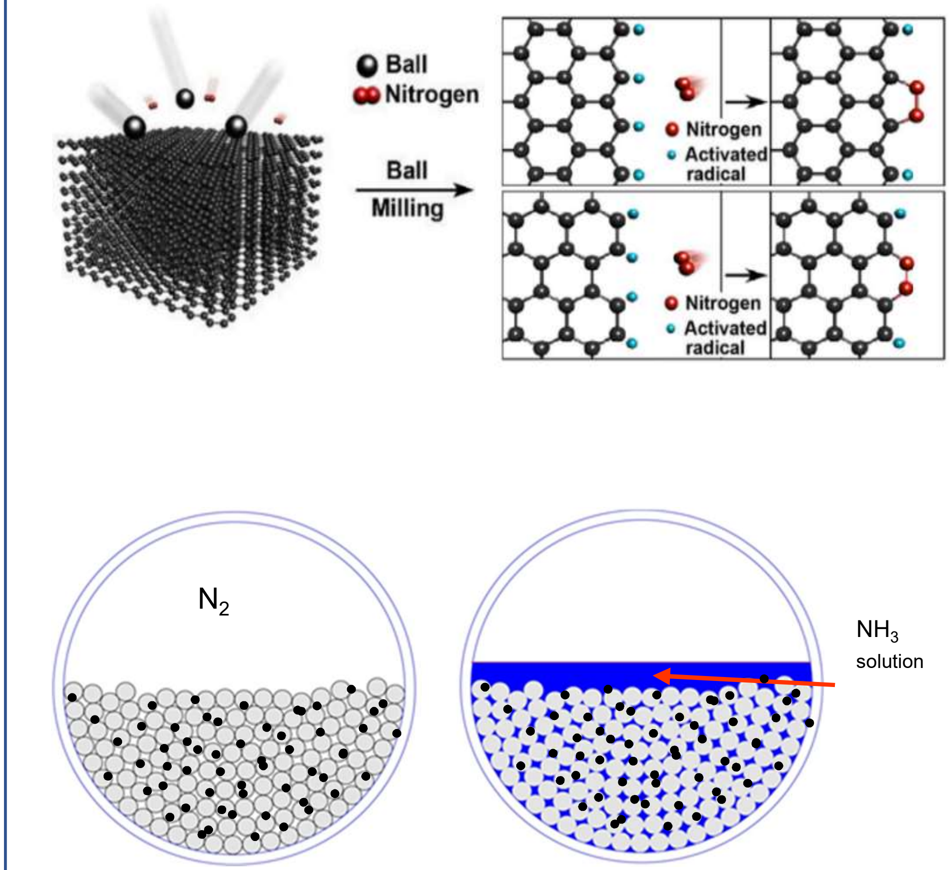


APTES



AEPTMS

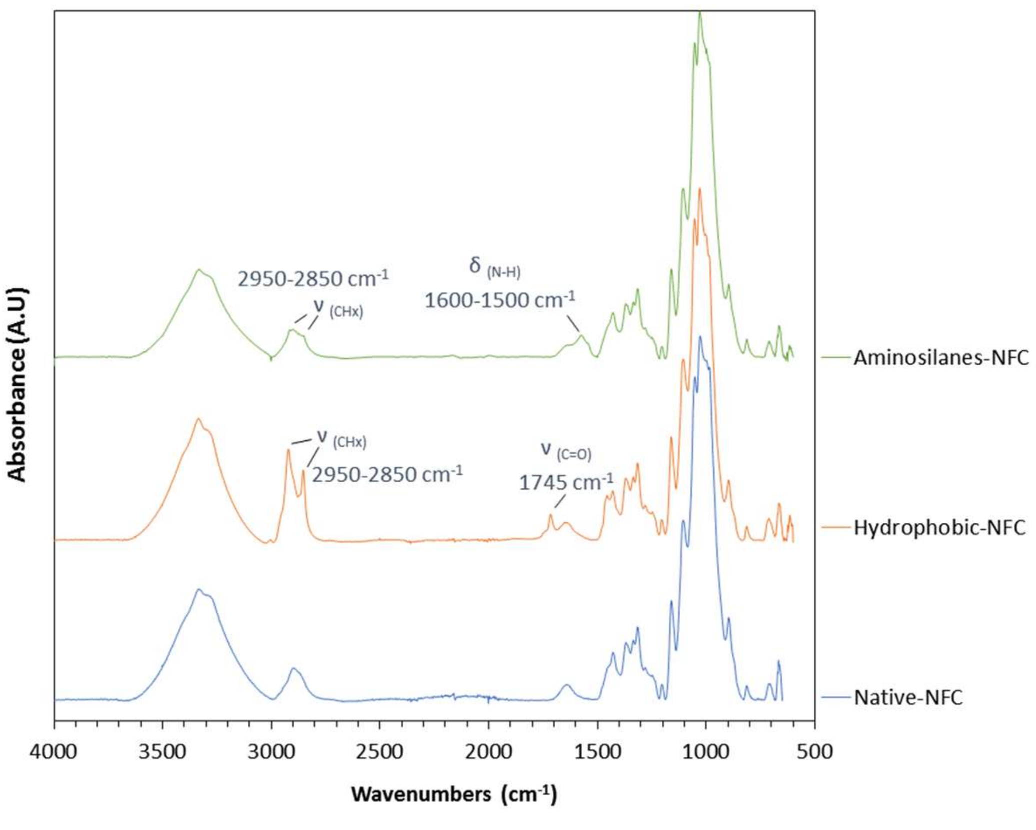


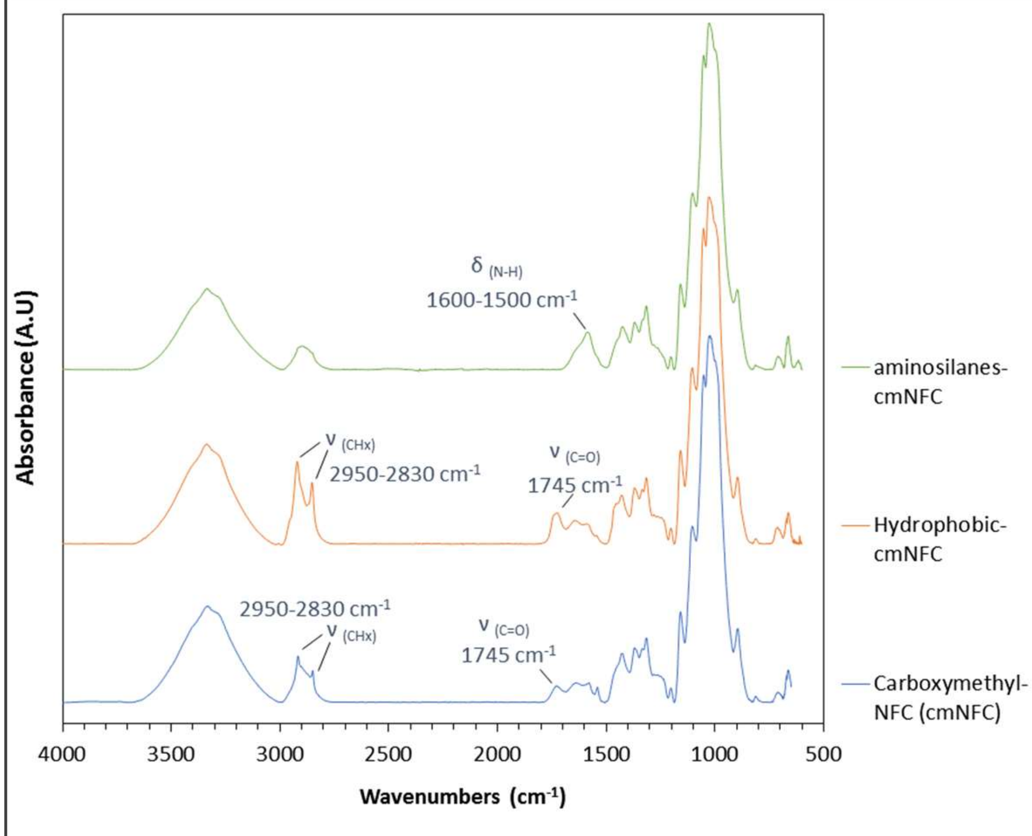


Nanocellulose characterization : InoFib Production

InoFib
From Nature to the Future

Native-NFC substrat :	Carboxymethyl-NFC substrat :





- Each spectrum displays specific characteristic bands which are attributed to the vibration or deformation of the corresponding molecules used for the chemical surface modification.

Nanocellulose characterization : InoFib Production

InoFib
From Nature to the Future

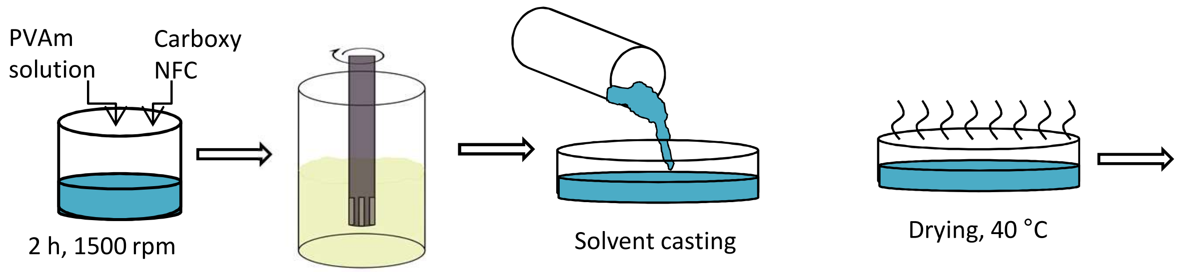
Membrane produced for a grammage of 20g/m²

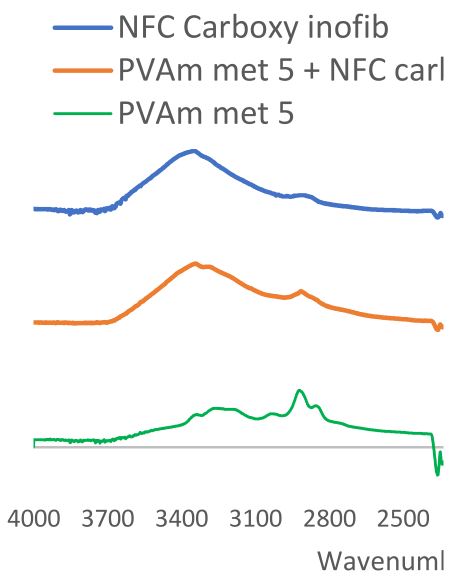
Main characteristics	Native NFC	Carboxymethyl-NFC*	Hydrophobic-NFC	Aminosilane-NFC
Young Modulus (GPa)	14.7 ± 3.2	7.5 ± 0.5	6.3 ± 0.2	13.6 ± 2.4
Intrinsic Air permeability ($x10^{-17}$ m²)	1.2 ± 0.2	1.1 ± 0.3	2.6 ± 0.6	1.6 ± 0.3
Water absorption 60 seconds $Cobb_{60}$ (g/m²)	27 ± 4	50 ± 6	14 ± 2	19 ± 2
Contact angle (°)	Not measurable	80 ± 2	120 ± 5	79 ± 6
Amount of negative charges (µmol/g)	< 50	500-3000	-	-

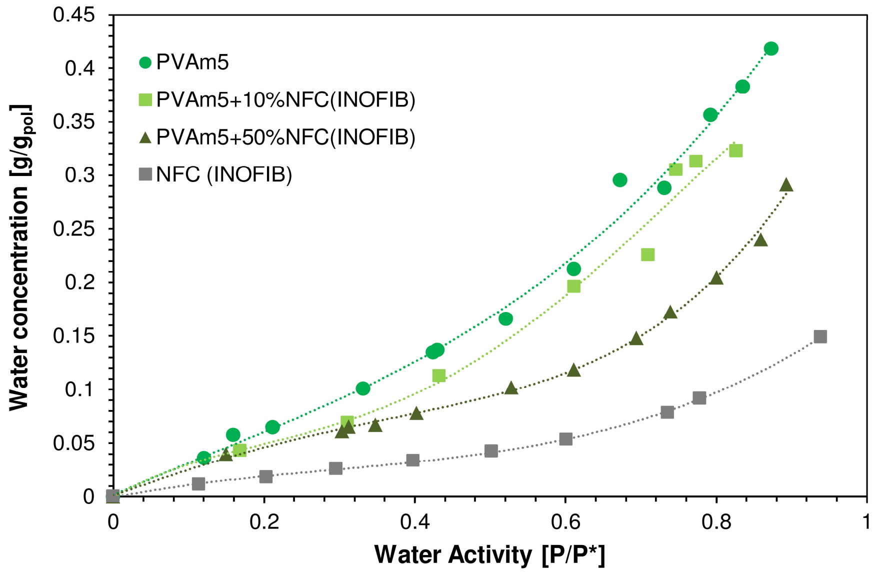
- Data corresponding to hydrophobic-NFC and Aminosilane-NFC have been made on native-NFC as substrates of modification.

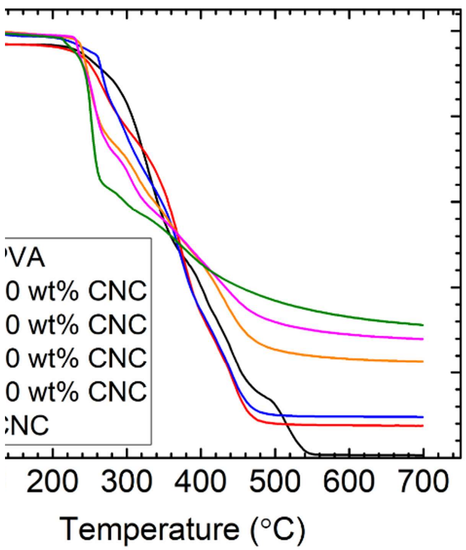
**Surface Charges : 780-860µmol/g*

Self standing Membranes Production and characterization.

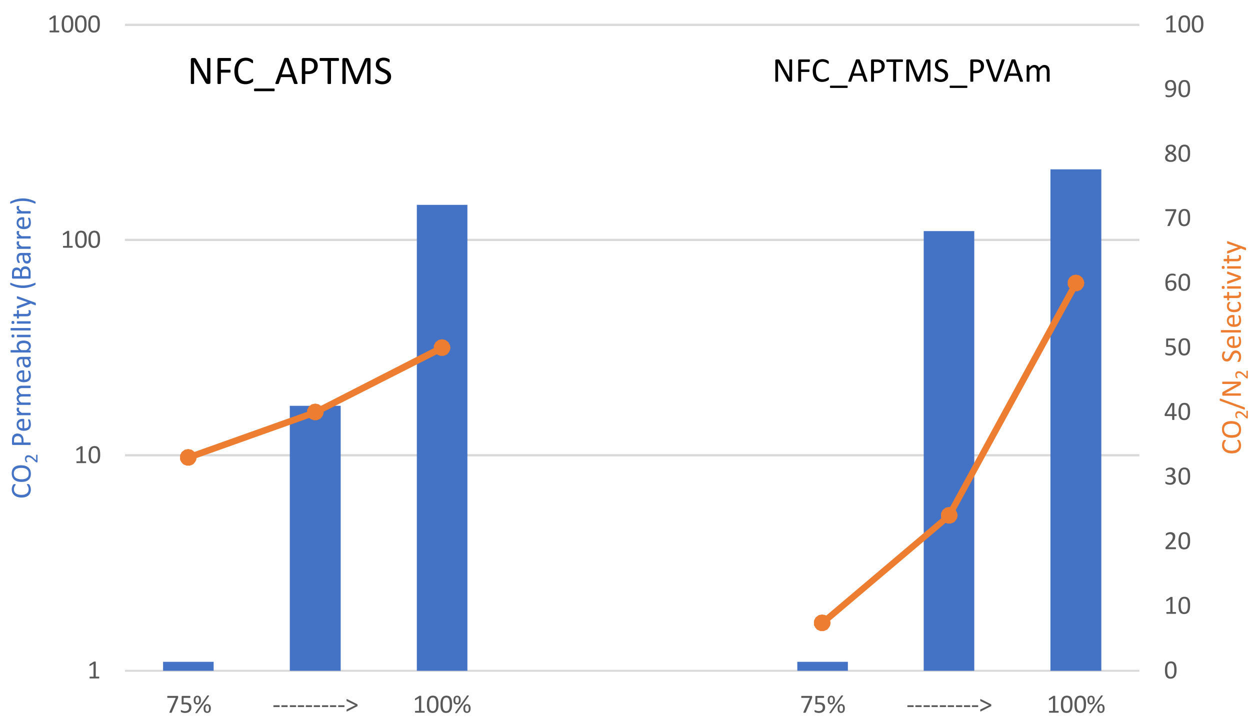








Membranes characterization – effect of RH

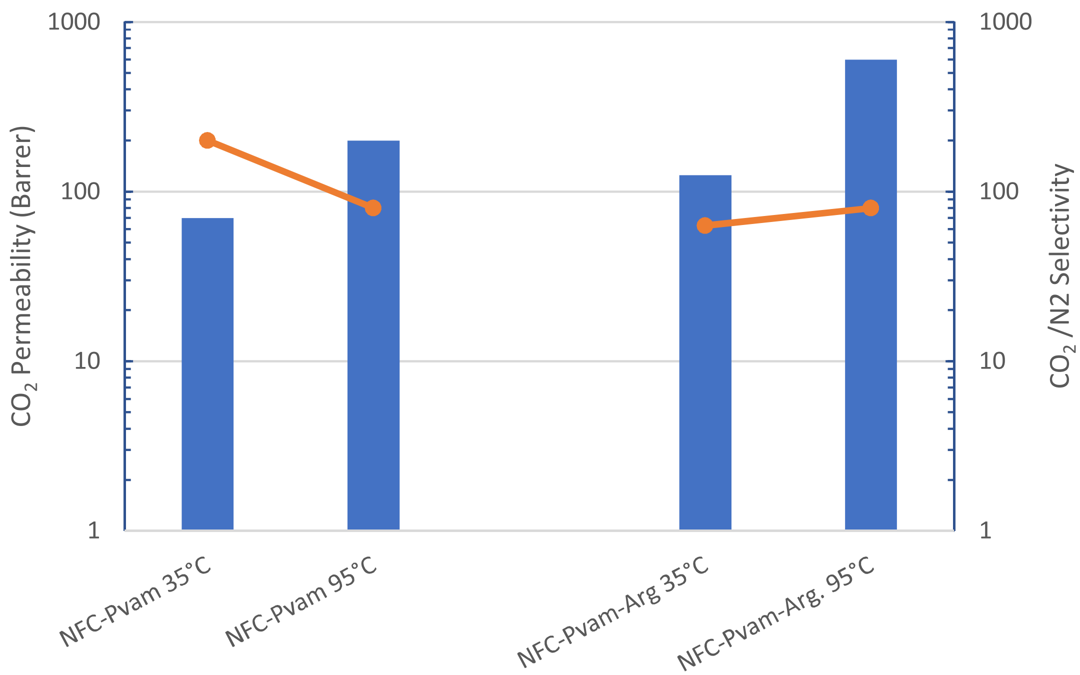


PVAm-aminosilane NFC – 35°C

Modified nanocellulose membranes show improved performances especially when added with PVAm.

No losses in water are evidenced suggesting good membrane stability due to strong ionic interactions.

Membranes characterization – effect of temperature and mobile carrier

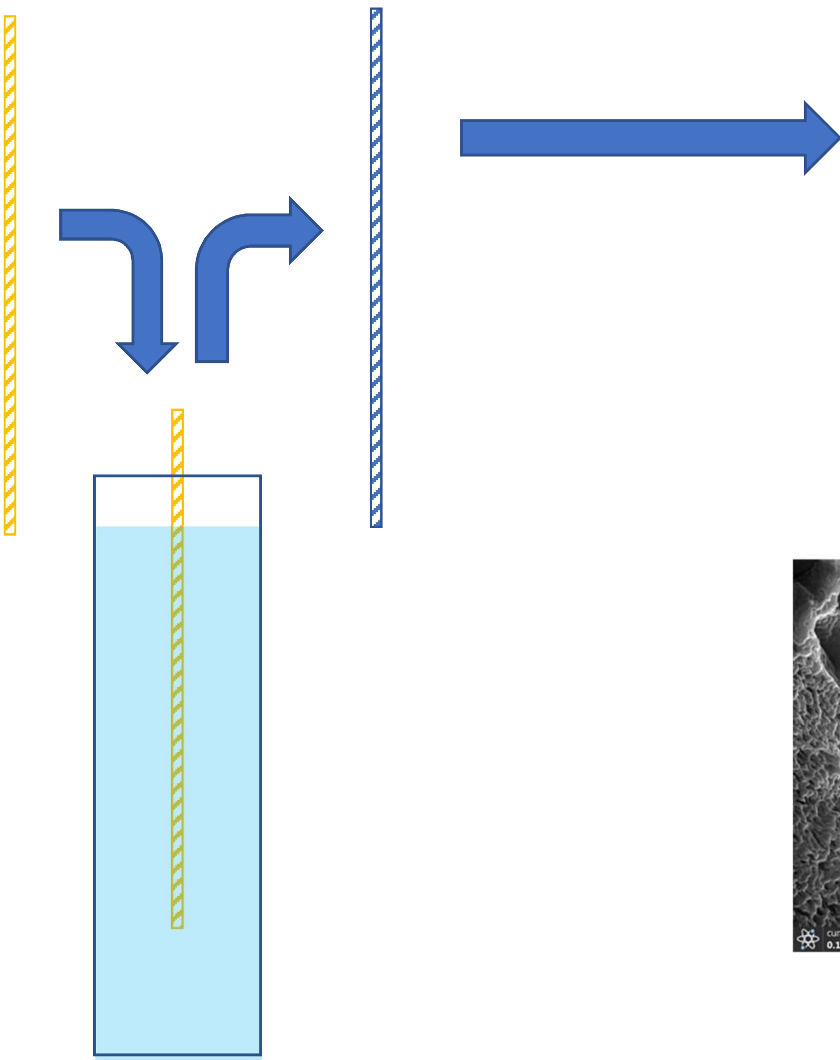


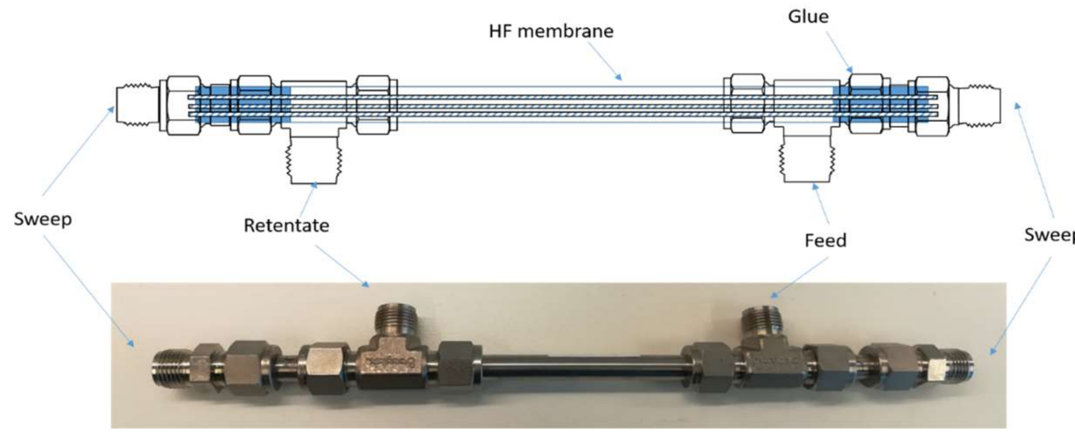
Arginine substantially increases membrane performance especially at high T.

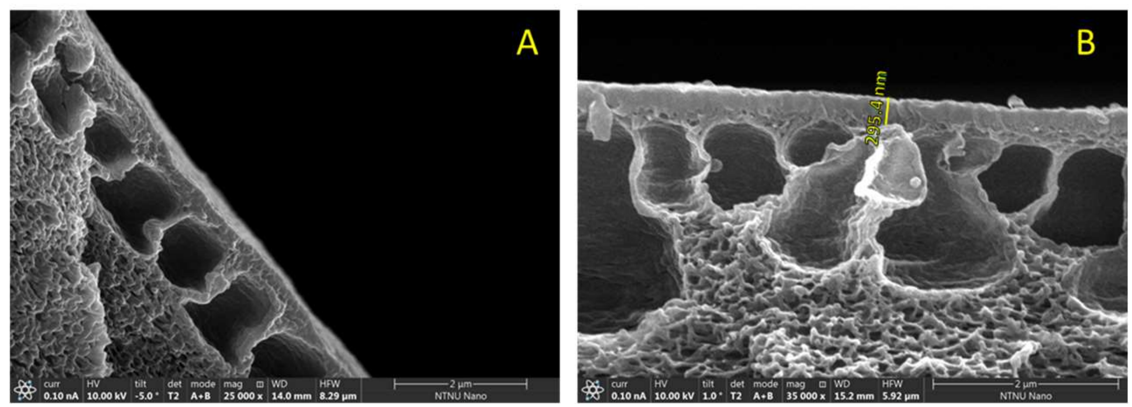
However there are some stability issues due to loss of mobile carrier in presence of liquid water

PVAm + carboxymethylated NFC + arginine 99% RH

Membranes Production: thin films NFC based membranes

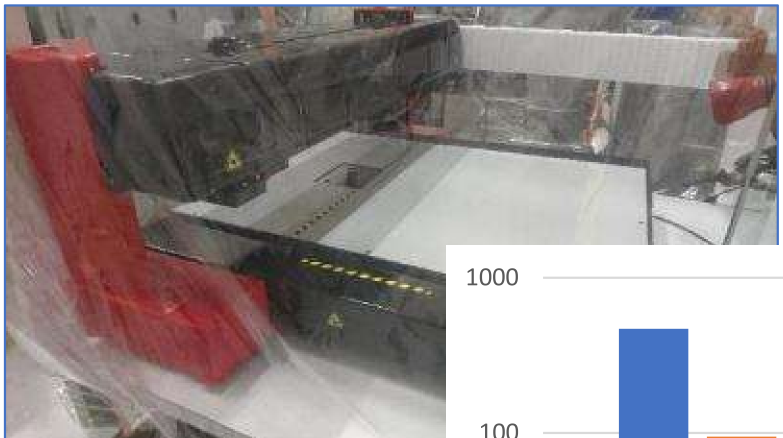




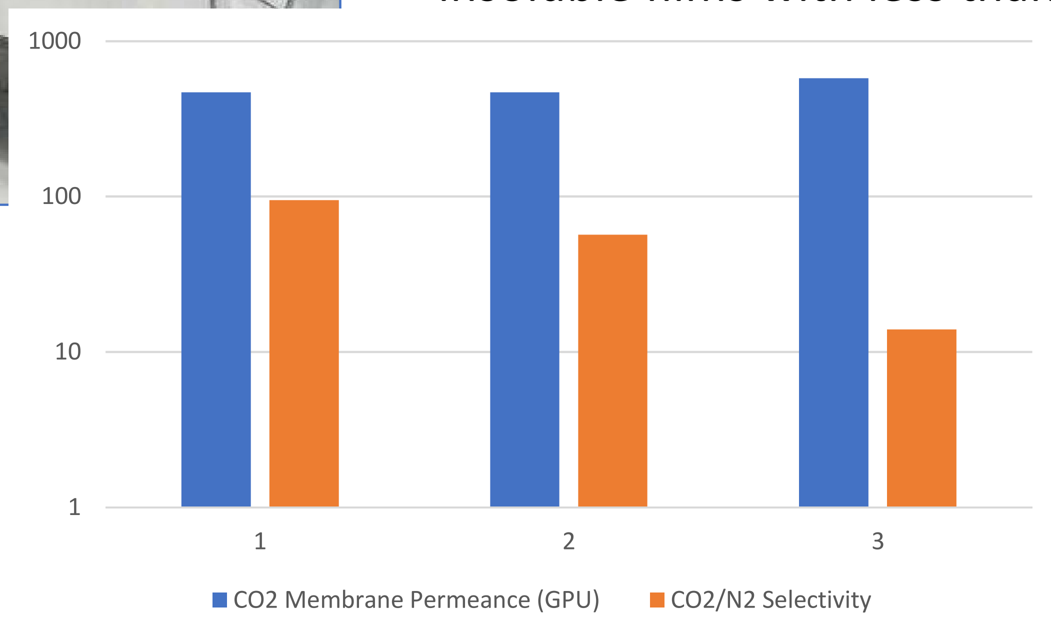


PVA + different types of aminoacid salt

Membranes Production: thin films Graphene based membranes



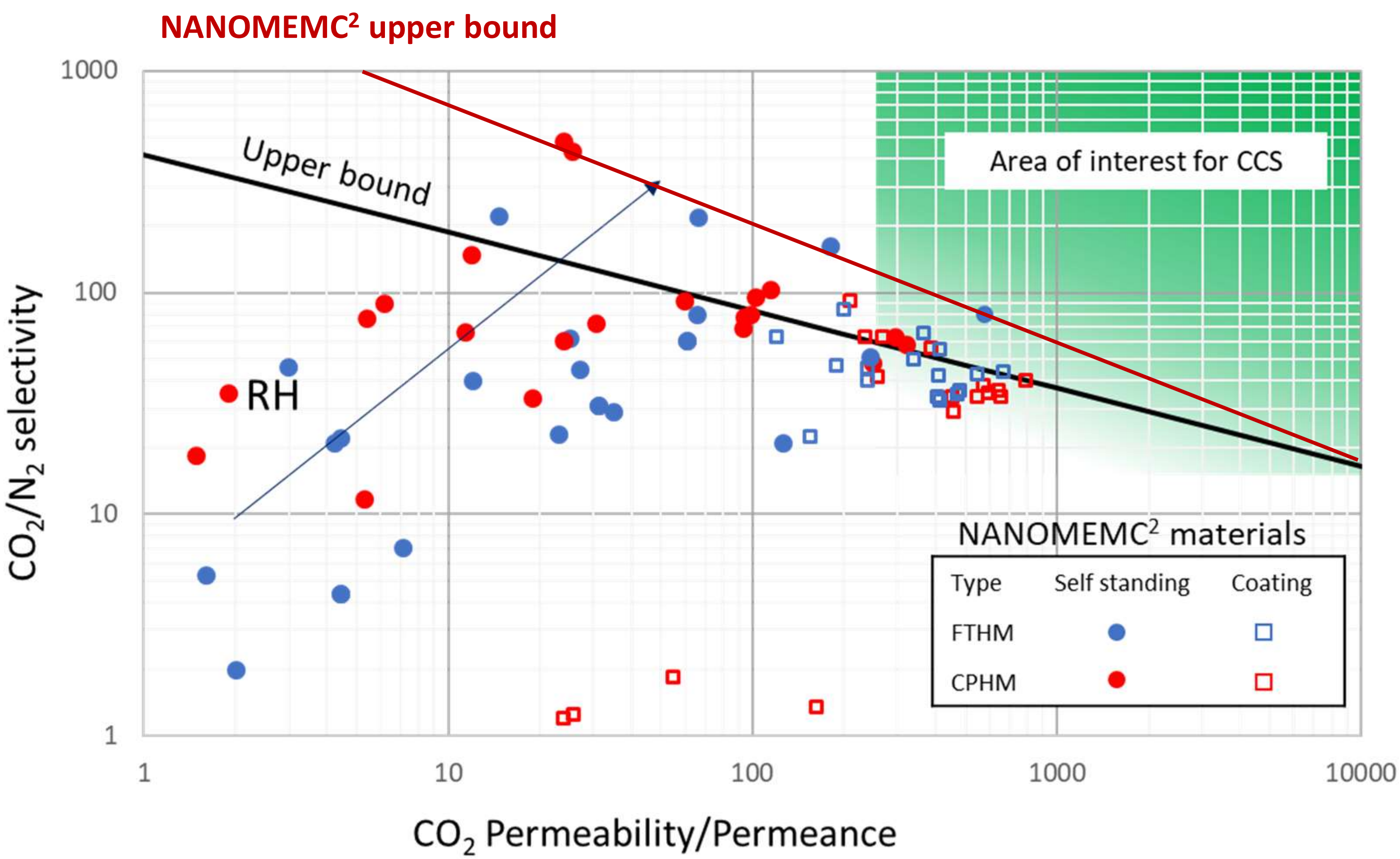
Stable films are obtained by subsequent printing of modified Graphene and PVAm layers. Thermal treatment allow to obtain water insoluble films with less than 1% graphene




PVAm-XT8 membrane after 1 month in water

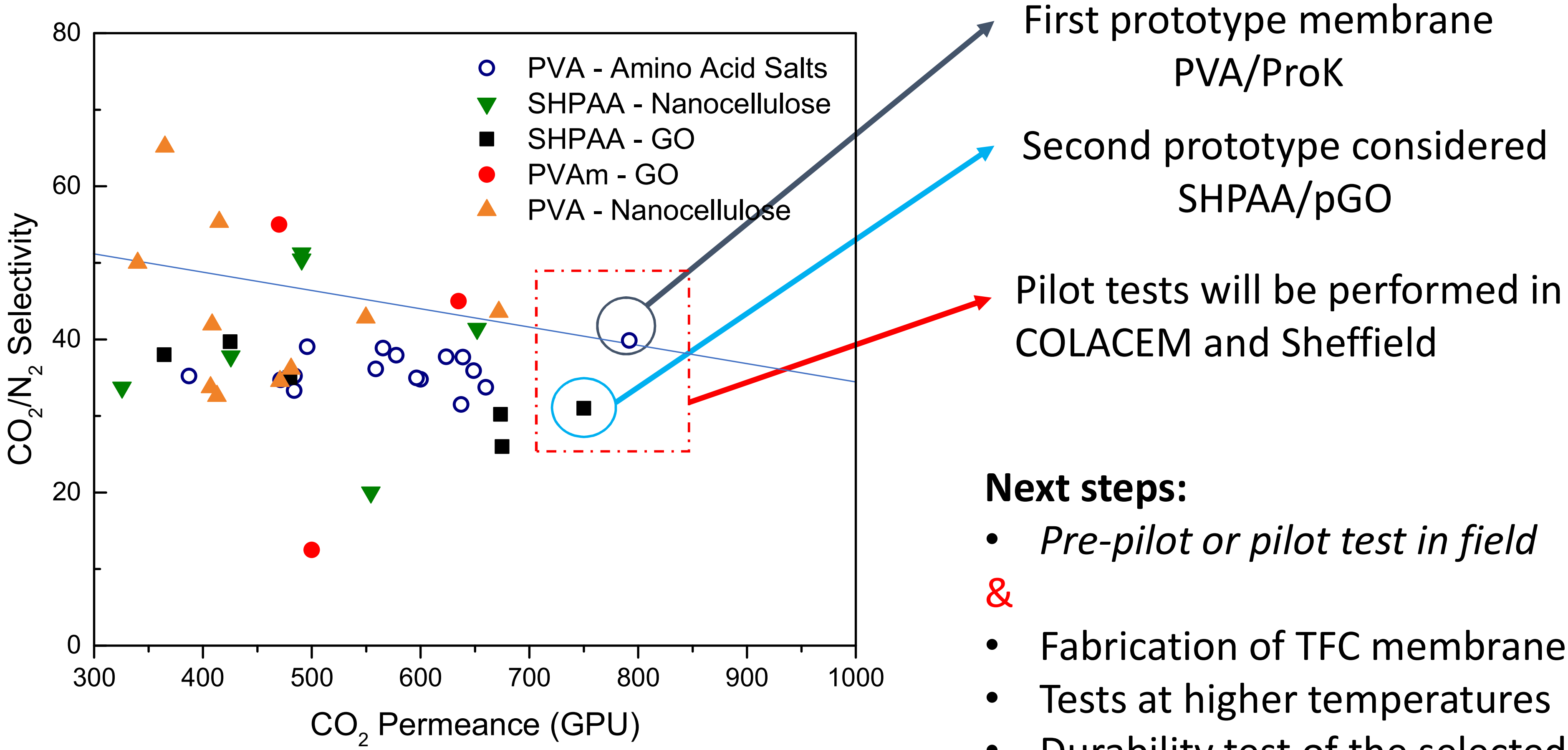
Patent has been submitted in June 2018
PCT extension ongoing.

Membrane characterization summary and conclusion



Please refer to NANOMEMC² website (https://www.nanomemc2.eu/public-documents/) to find the scientific publication on project's materials

Membrane characterization next steps



Next steps:

- *Pre-pilot or pilot test in field*

&

- Fabrication of TFC membranes
- Tests at higher temperatures
- Durability test of the selected membranes
- Tests on CO_2/CH_4 & CO_2/H_2 separation

Thank you!

www. nanomemc2.eu

This project has received funding from the European Union's Horizon 2020 research and innovation programme under Grant Agreement No 727734