CARBON AEROGELS

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Aerogels

„A little almost nothing"– NASA



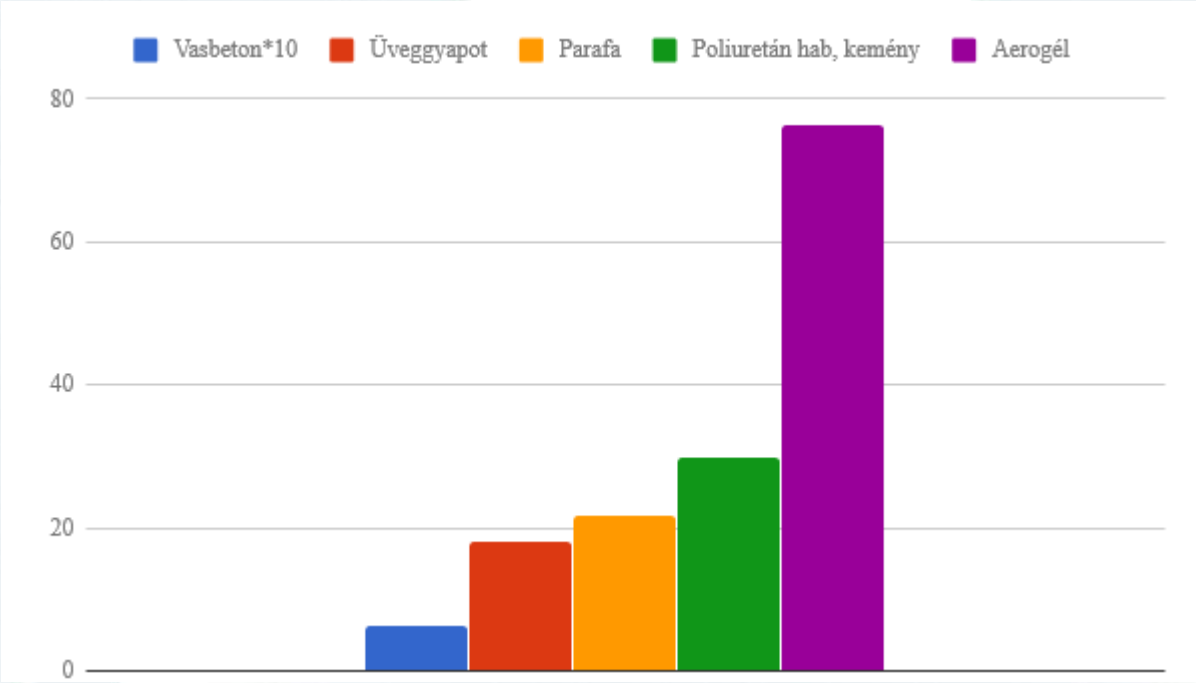






IUPAC definition of aerogel:
Gel comprised of a microporous solid in which the dispersed phase is a gas.

Thermal resistance (1/λ, mK/W)



Thermal insulation performance

A little hystory…



Kistler, 1931

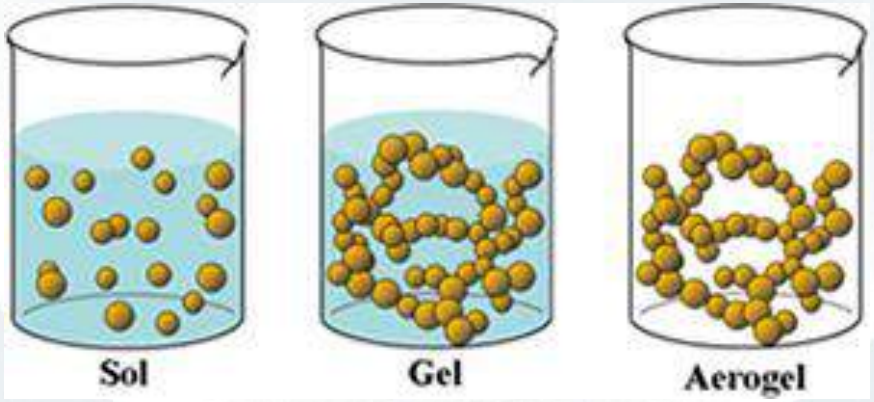
„ result of a bet with Charles Learned over who could replace the liquid in "jellies" with gas without causing shrinkage"

Carbon aerogels since the 1989 (**Pekala**)

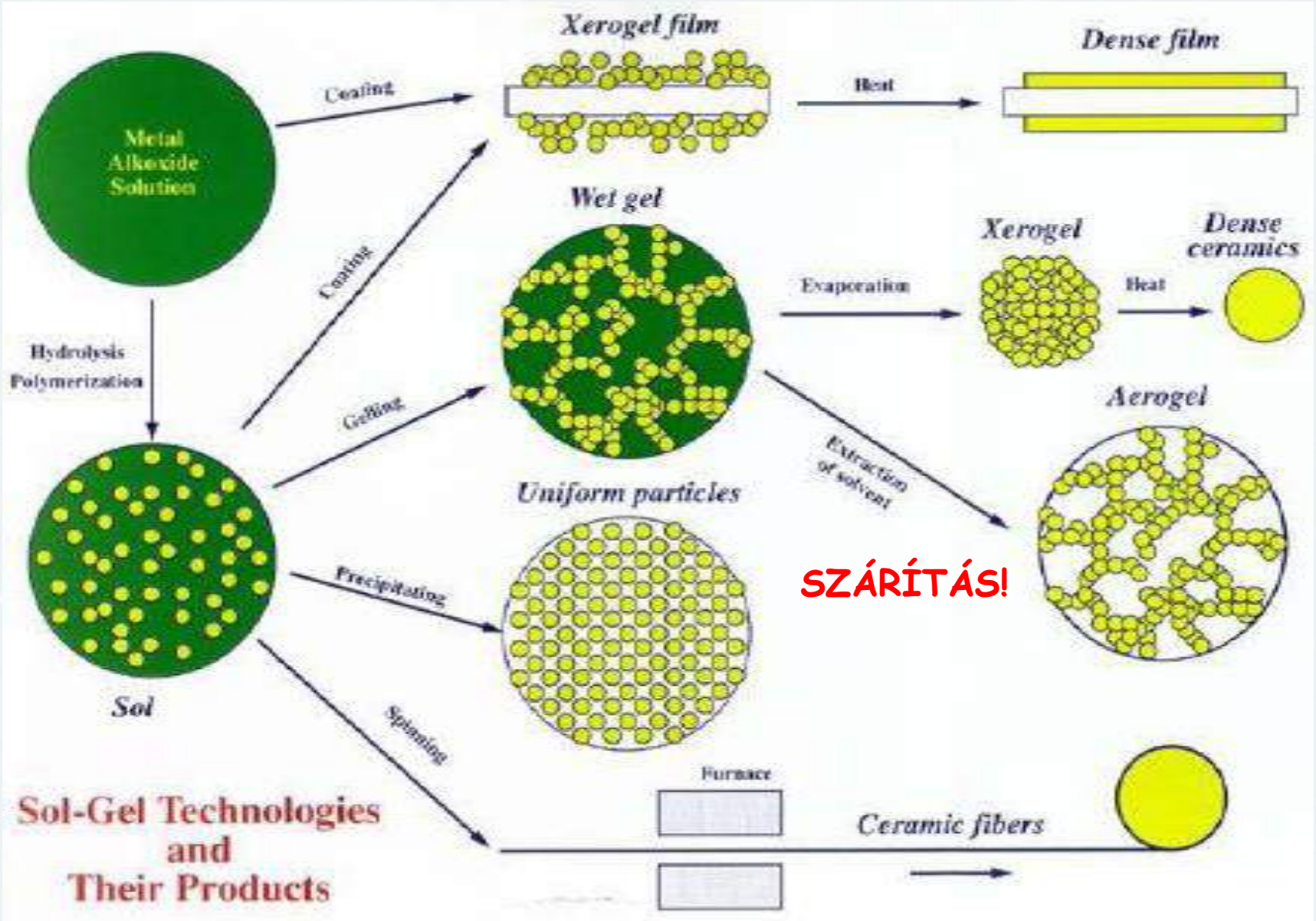
Gels

„Nonfluid colloidal network or polymer network that is expanded throughout its whole volume by a fluid"

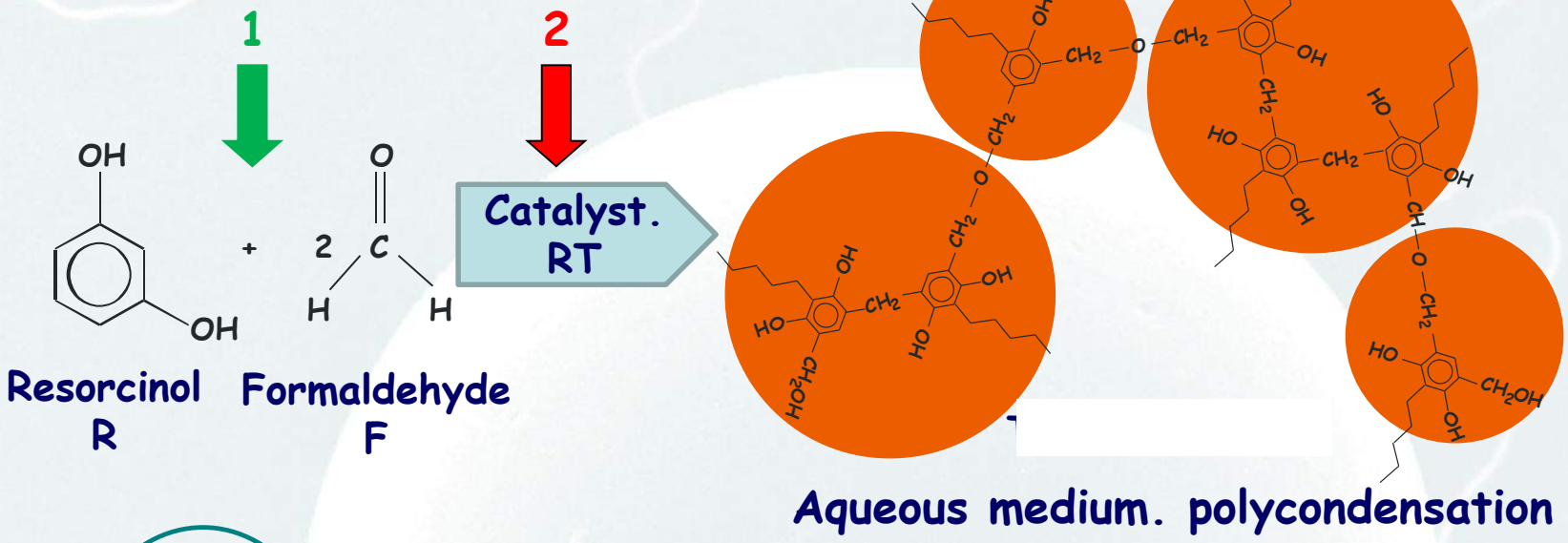
Polymer or colloidal
Physical or chemical bonding

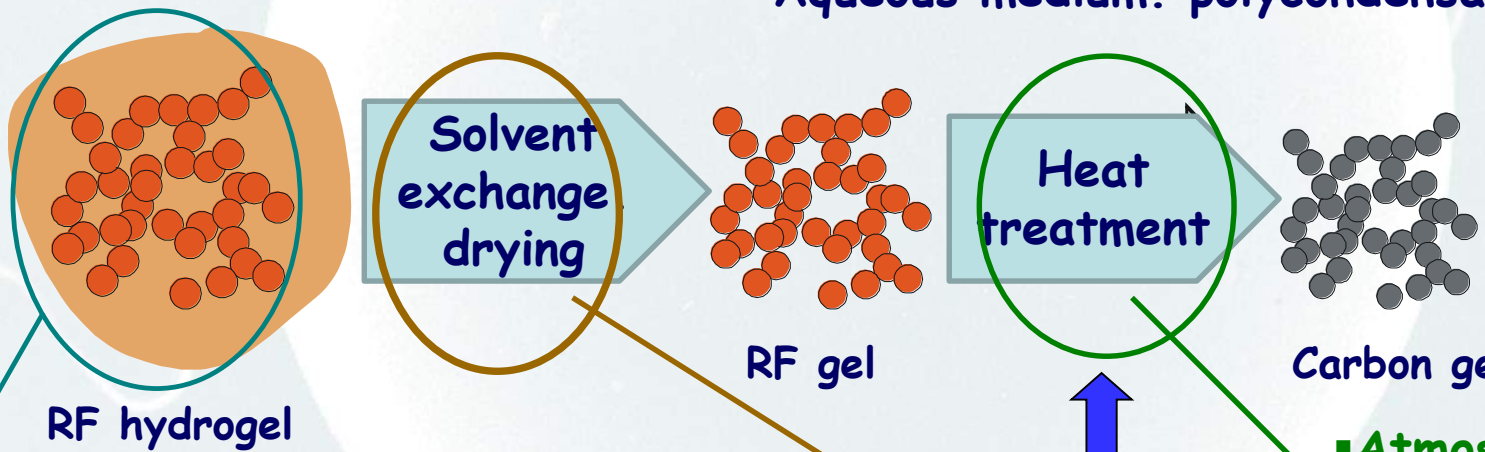


Versatility



CA, SYNTHESIS



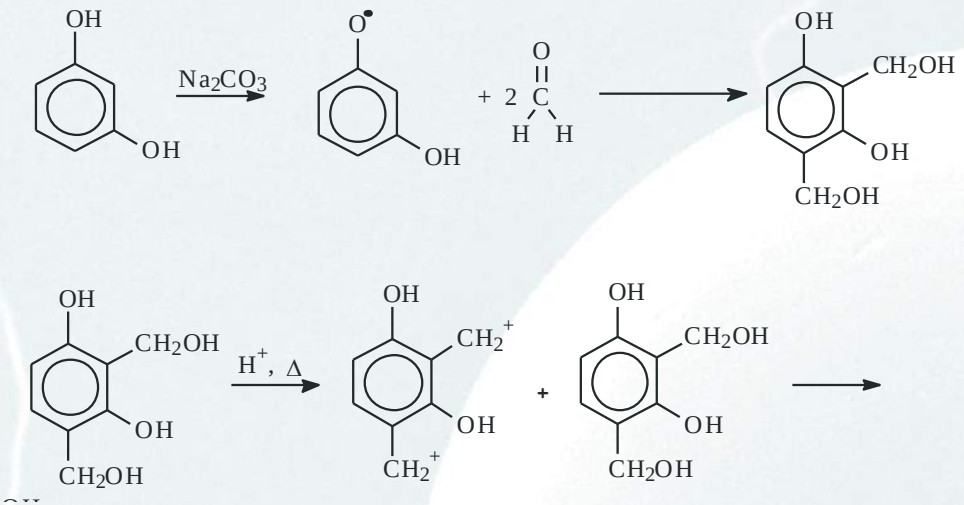


- pH (6.0)
- Catalyst C (Na_2CO_3)
- Stoichiometry (R/C=50;R/F=0.5;c=5 wt/v%)
- T (85°C)
- Time (1 week)

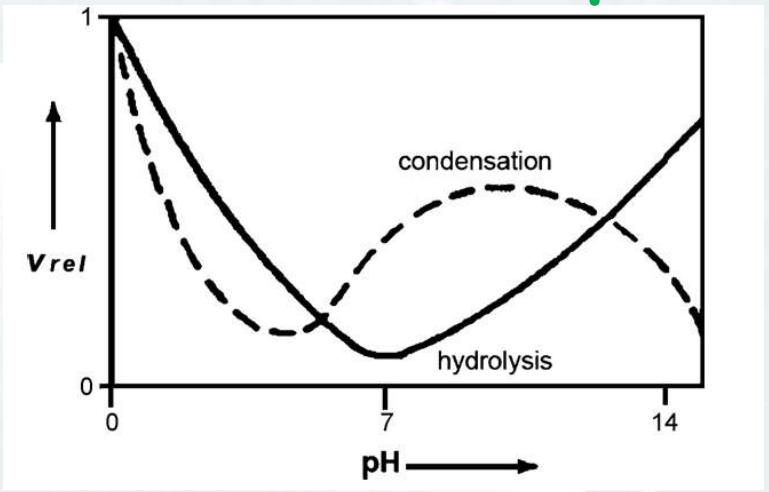
- Heat treatment
- Freeze drying
- Supercritical extraction

- Atmosphere (N_2)
- T (900 °C)
- Time (1h)

Mechanism



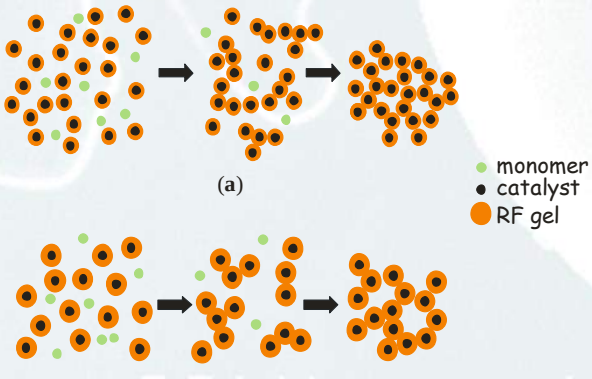
Effect of pH



Acidic: mainly hydrolysis
smaller particles
microporous system

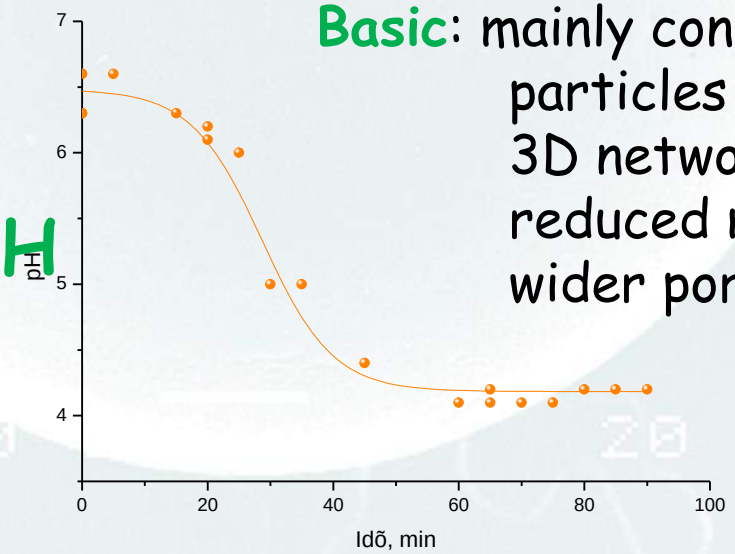
Basic: mainly condensation, larger particles
3D network
reduced microporosity
wider pores

Effect of catalyst concentration



(a) High concentration
(b) Low concentration

pH



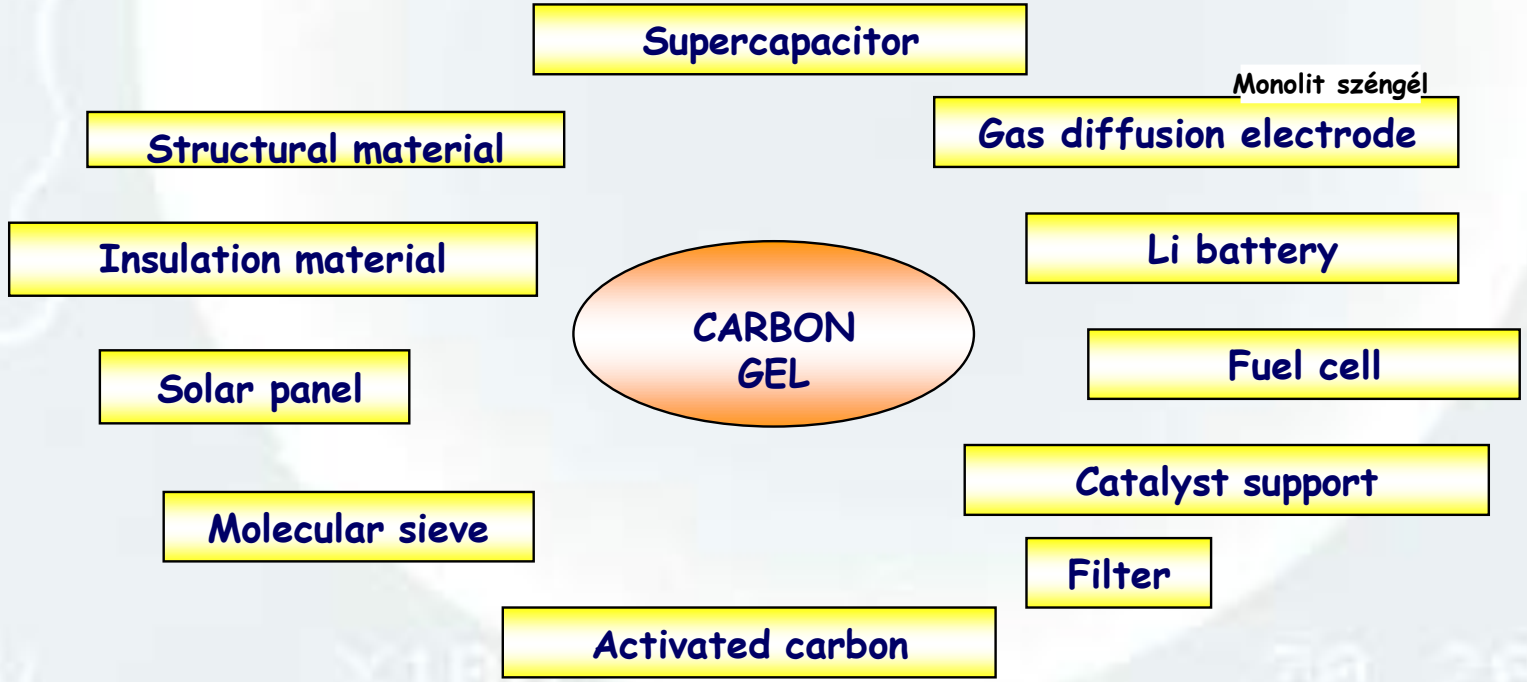
Application of carbon aerogels



- Insulation and electric conductivity
- Low density (0.4-1 g/cm^3)
- High surface area (~1000 m^2/g)
- Tunable porosity
- Poor IR reflectance (0.3 %)
- Design (microsphere – monolith)

Szénszál erősítésű vékony lap

Rugalmas lap



Drying and carbonization

aceton

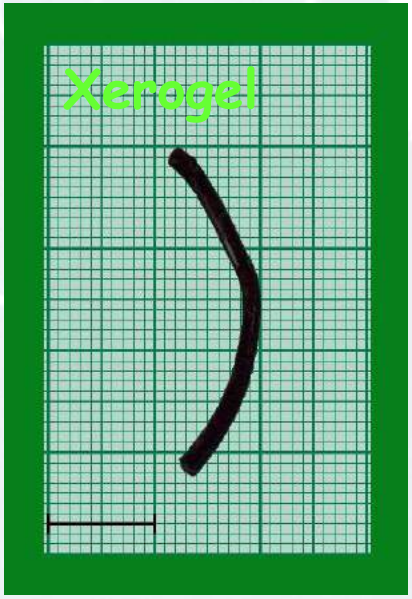
CO_2(l), RT

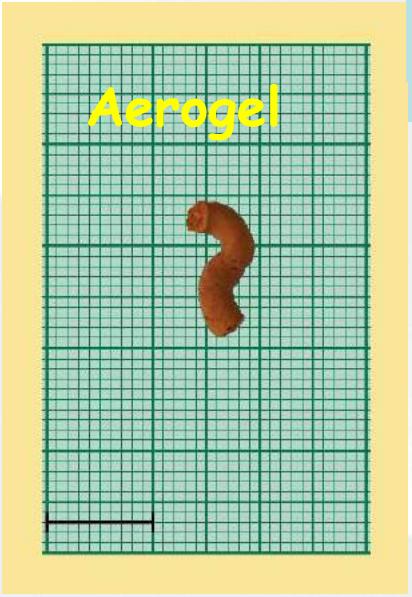
80 bar

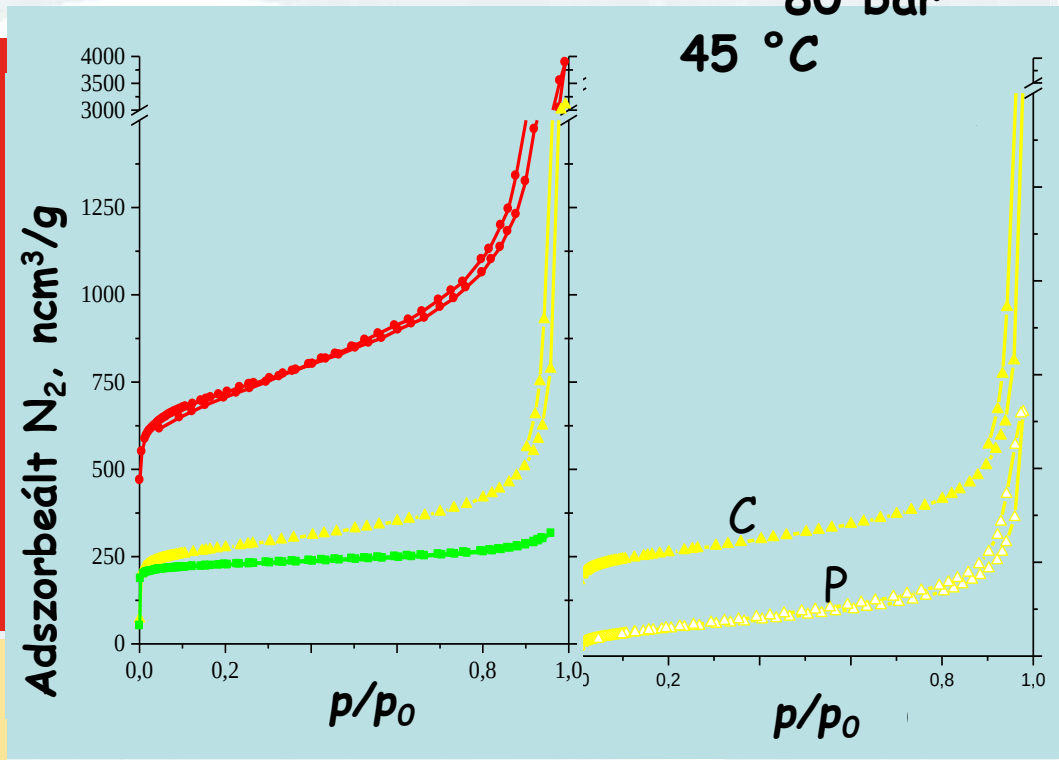
45 °C









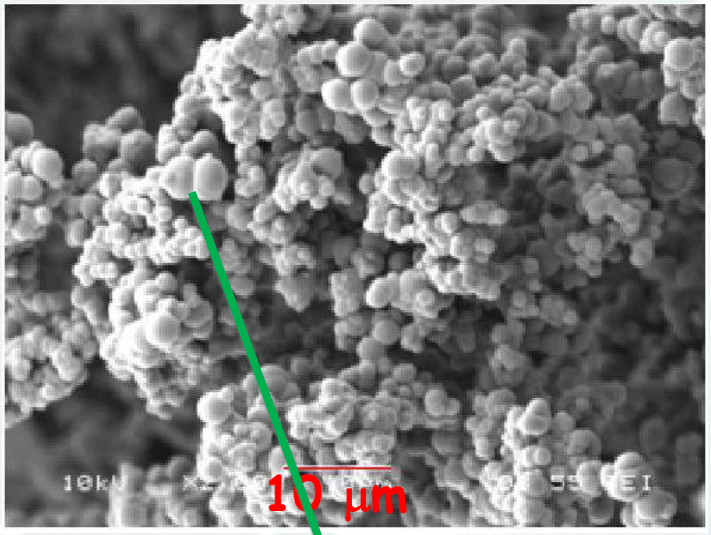


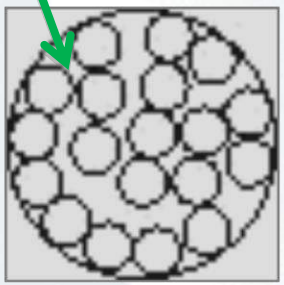
	Polymer		Carbon	
	S_{BET} m^2/g	V_{TOT} cm^3/g	S_{BET} m^2/g	V_{TOT} cm^3/g
X	111	0,13	730	0,44
C	572	0,76	2240	2,05
A	270	0,36	885	0,79

Czakkel et al: Micropor Mesopor Mater 86, 124-133 (2005)
Czakkel et al: Micropor Mesopor Mater 148, 34-42 (2012)
Czakkel et al: J. Supercritical Fluids 75, 112-119 (2013)

SEM

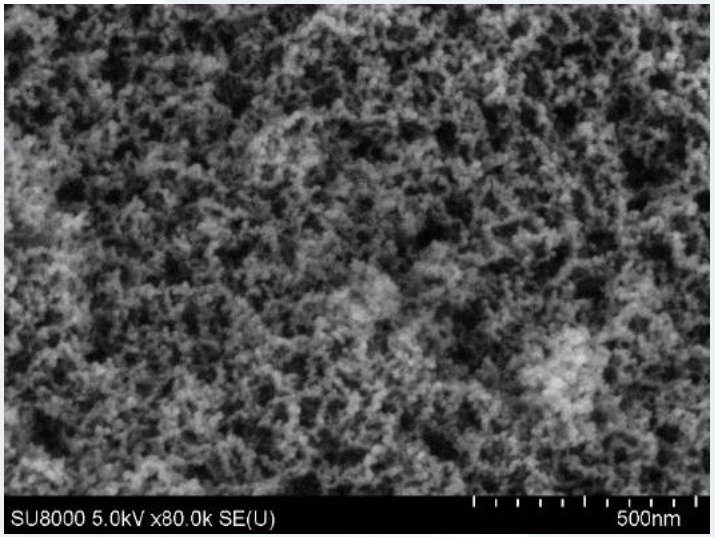
POLYMER

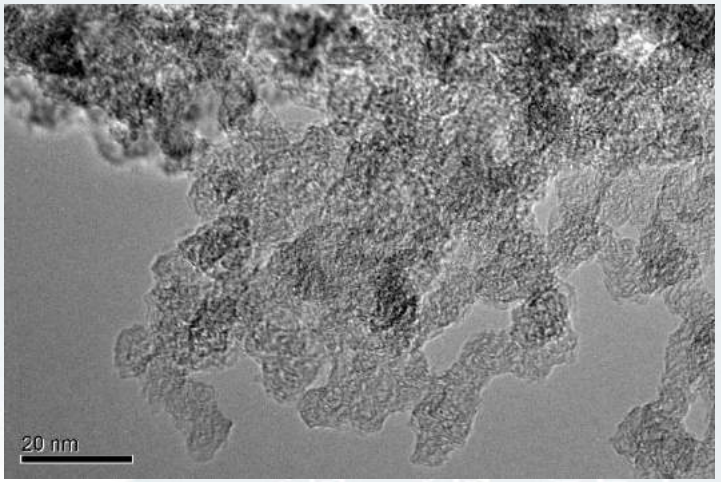




GEL	Size (SAXS)
POLYMER	72 Å
CARBON	60 Å

CARBON

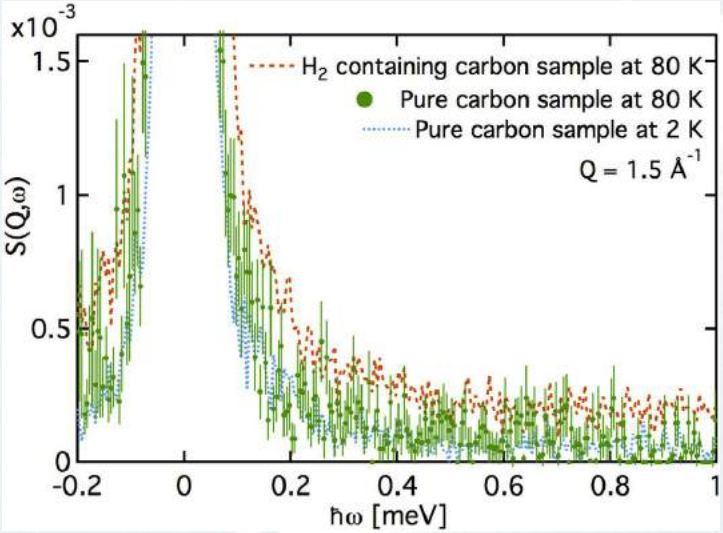


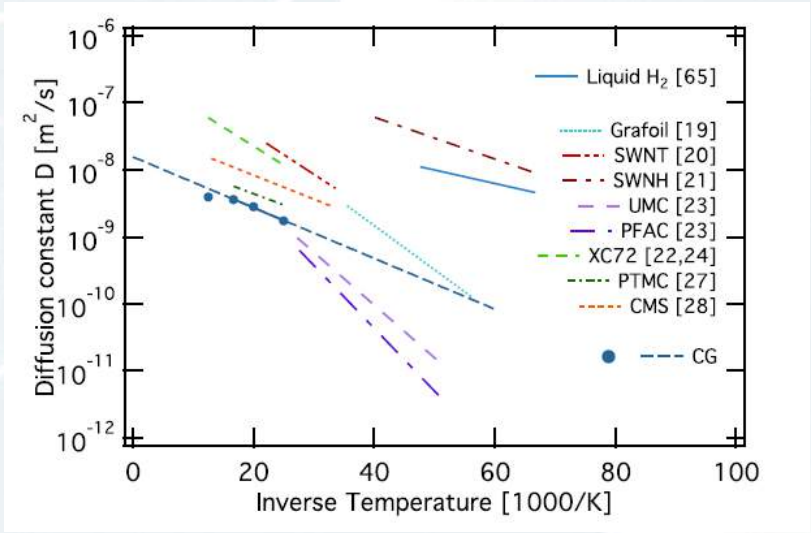


Model for interconnected mesoporous (carbon) systems

INTERACTION WITH PURE VAPOUR AND/OR LIQUID PHASES

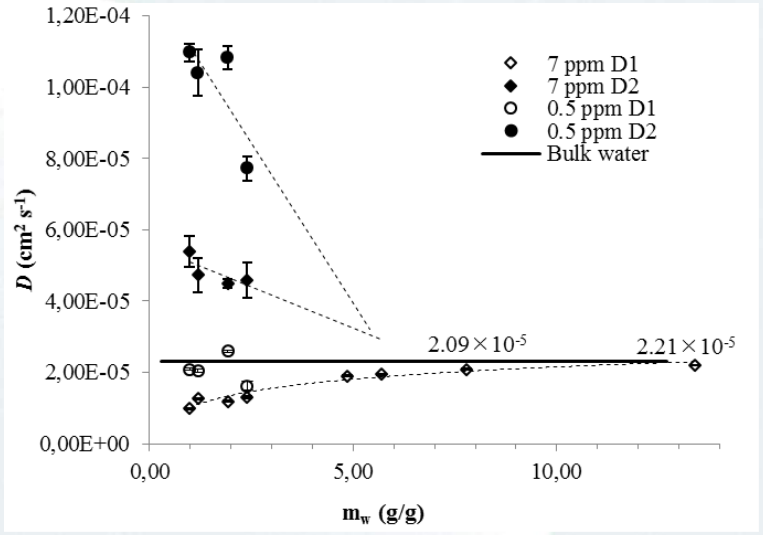
H_2

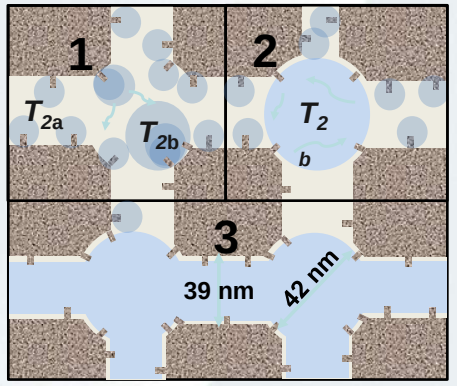




Bahn et al: Carbon, 98, 572-581, 2016

H_2O

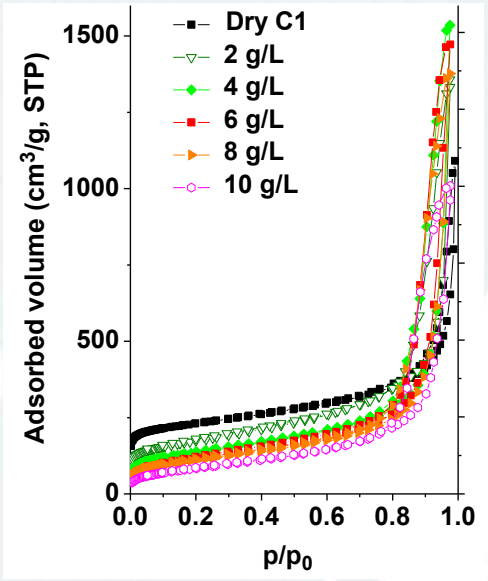


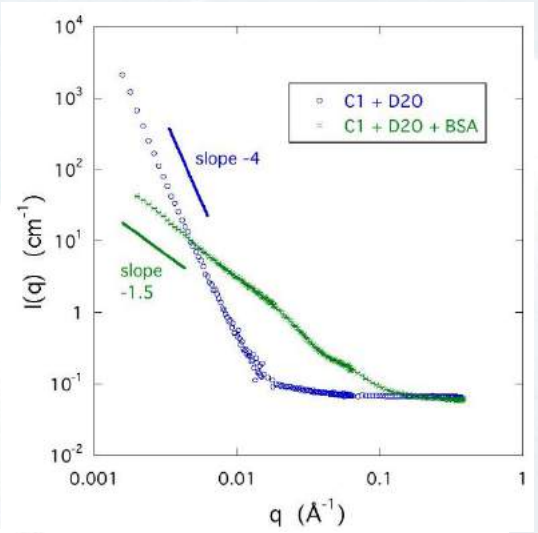


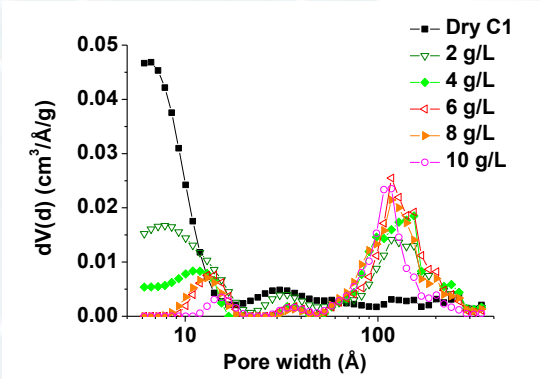
Kéri et al: in preparation

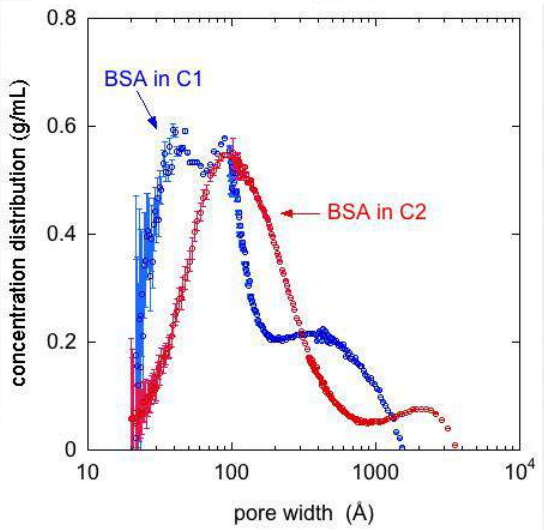
CA as support material

1) PROTEIN

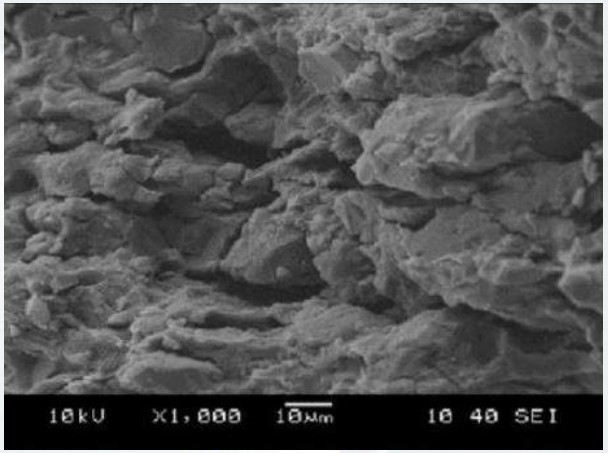


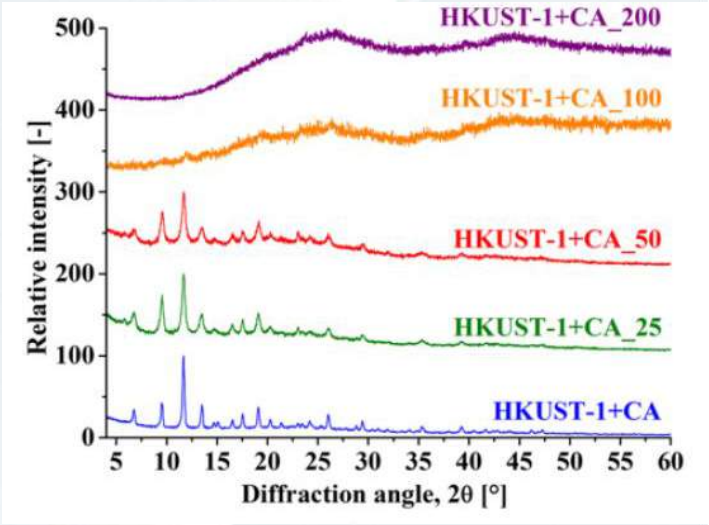






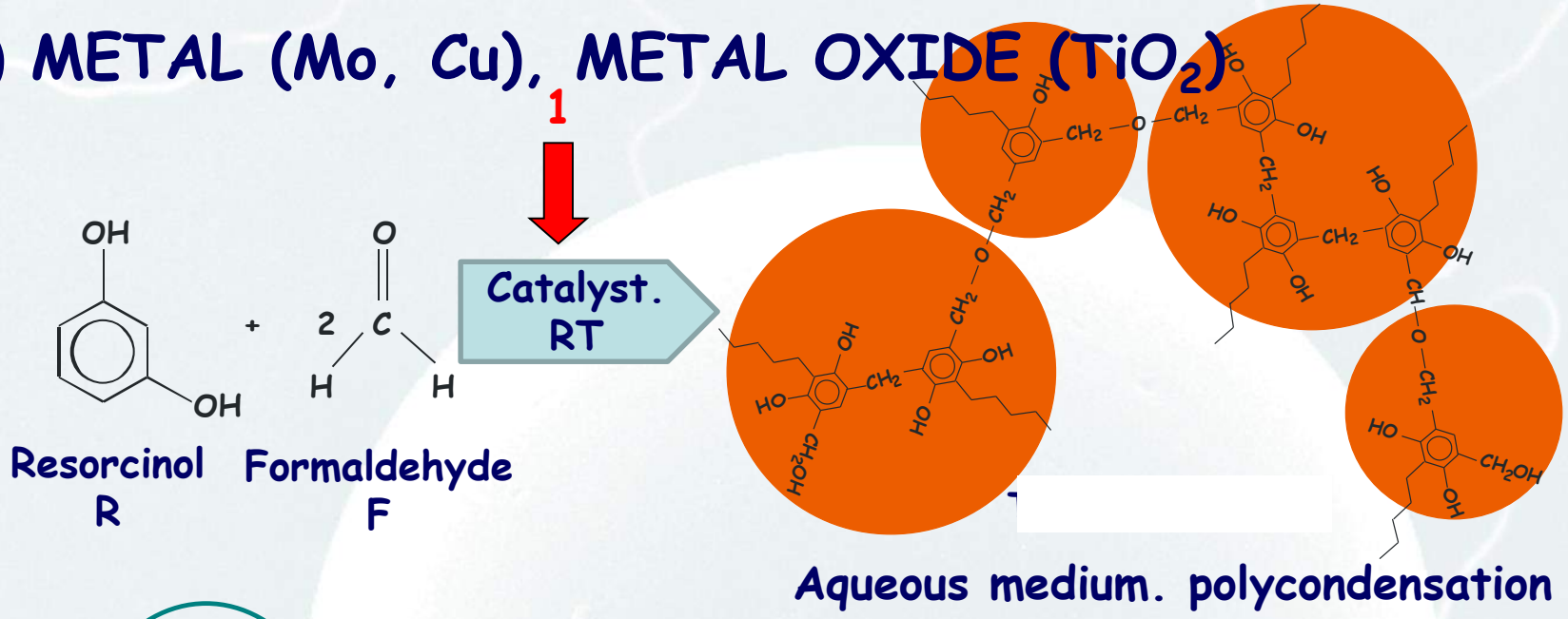
2) MOF

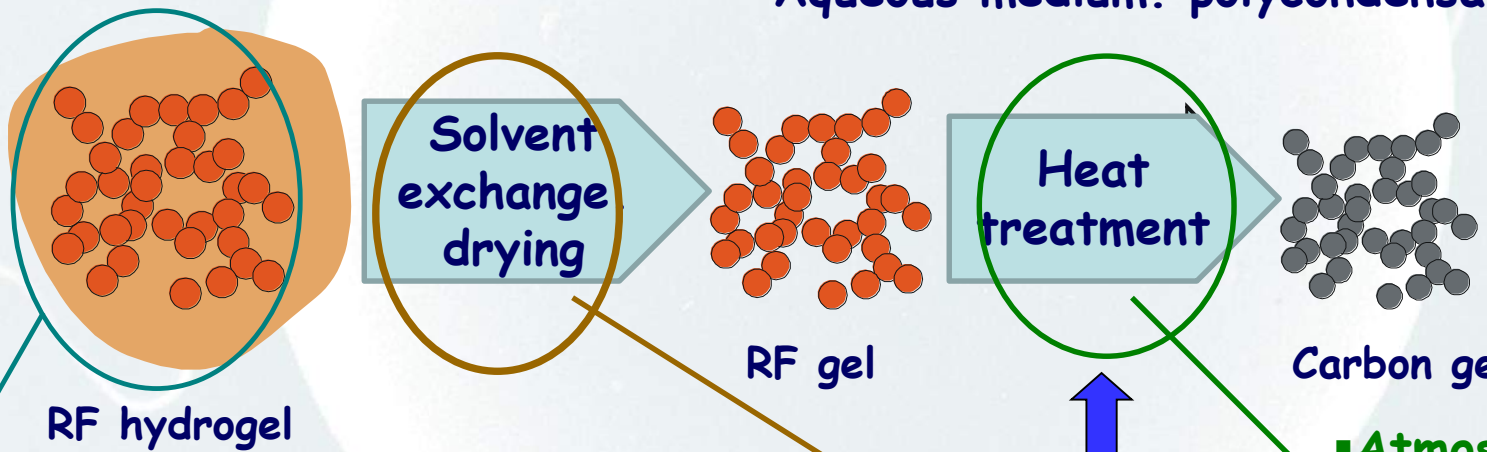




Nagy et al: Carbon, 106, 142-151 (2016)
Nagy et al: Carbon, 112, 103-110, 2017
Domán et al: Appl Surf Sci, 434, 1300–1310 (2018)

3) METAL (Mo, Cu), METAL OXIDE (TiO_2)



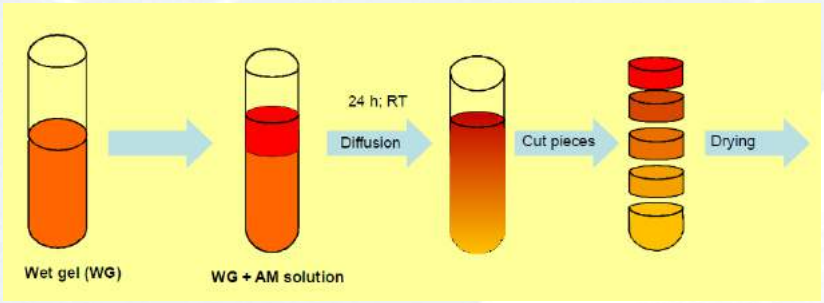


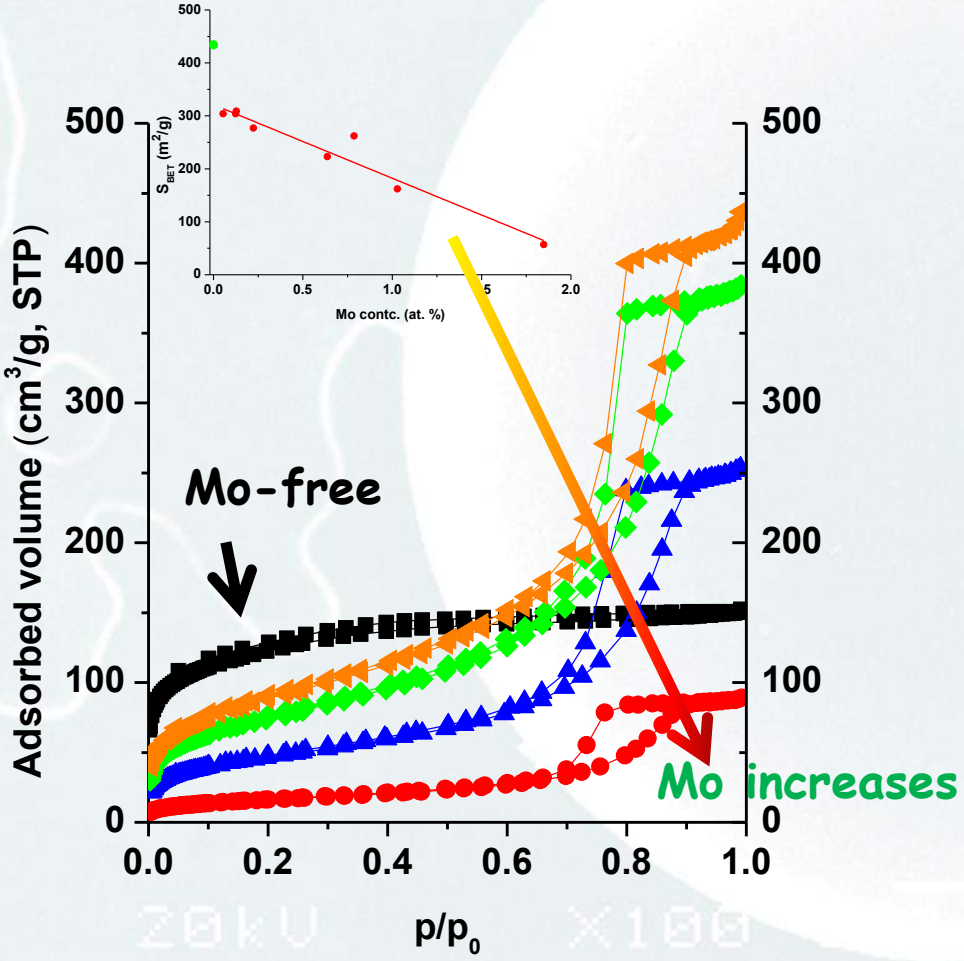
- pH (6.0)
- Catalyst C (Na_2CO_3)
- Stoichiometry (R/C=50;R/F=0.5;c=5 wt/v%)
- T (85°C)
- Time (1 week)

- Heat treatment
- Freeze drying
- Supercritical extraction

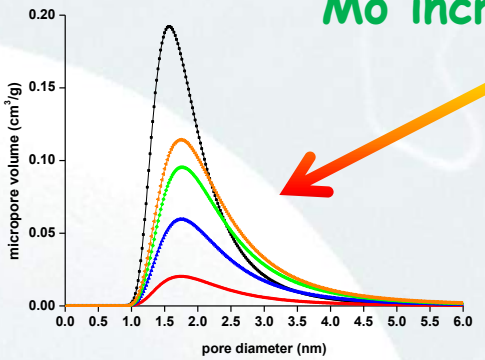
- Atmosphere (N_2)
- T (900 °C)
- Time (1h)

Mo may tune the POROSITY

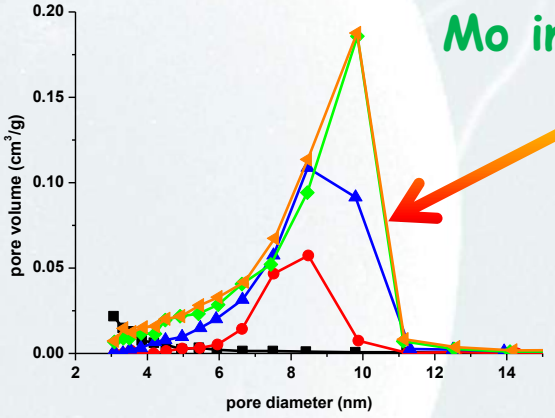


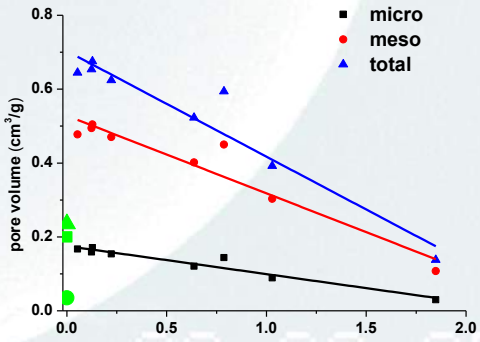


Mo increases



Mo increases





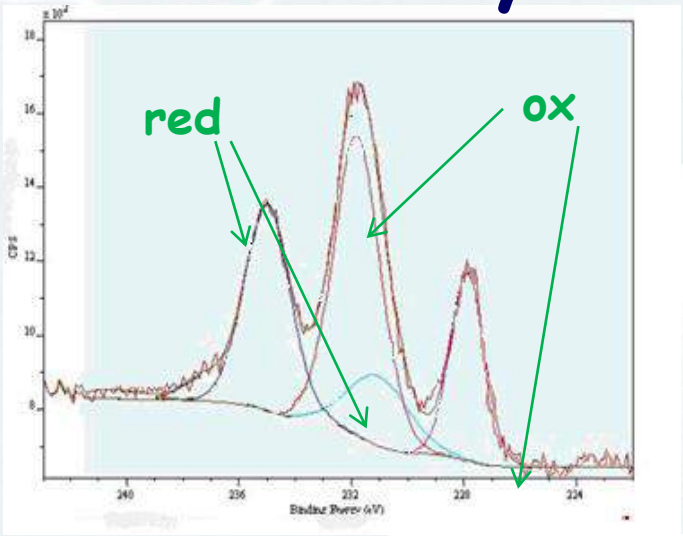
Pore size distribution is conserved, pore volume can be tuned

Samples:

POLYMER		N_2, 900 °C, 1h	CARBON
RF	original polymer aerogel		RF-carb
MoRF	Mo in monomer solution		MoRF-carb
RFMo	RF impregnated		RFMo-carb

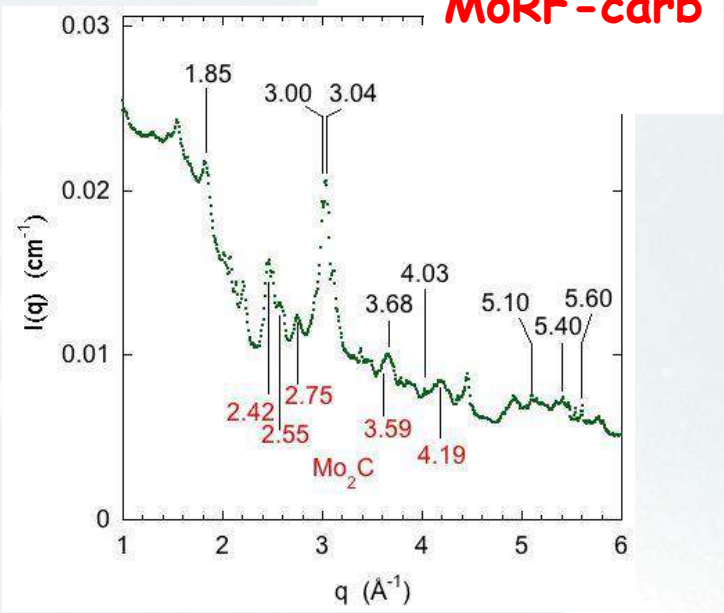
Czakkel et al: Micropor Mesopor Mater, 126 (2009) 213-221
Czakkel et al: J. Coll Interface Science, 337, 513-522 (2009)
Czakkel et al: J. Chem. Phys., 136, 234907 (2012)
Czakkel et al: Nanomaterials and the Environment. 1, 23-30, (2013)
Nagy et al: Micropor Mesopor Mater,, 185, 66-71 (2014)

Mo-chemistry



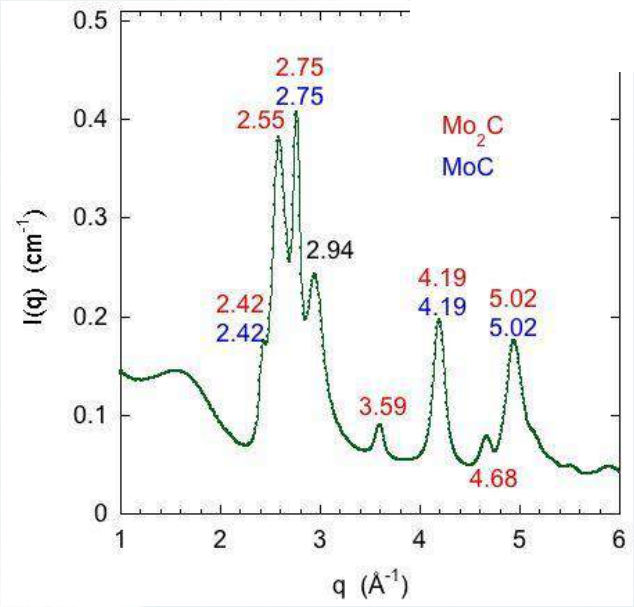
Sample	C at%	O at%	Mo at%
MoRF	59	37.5	0.08
RFMo	54.6	44.1	1.1
MoRF-carb	80.8	19	0.11
RFMo-carb	82	16.5	1.1

MoRF-carb



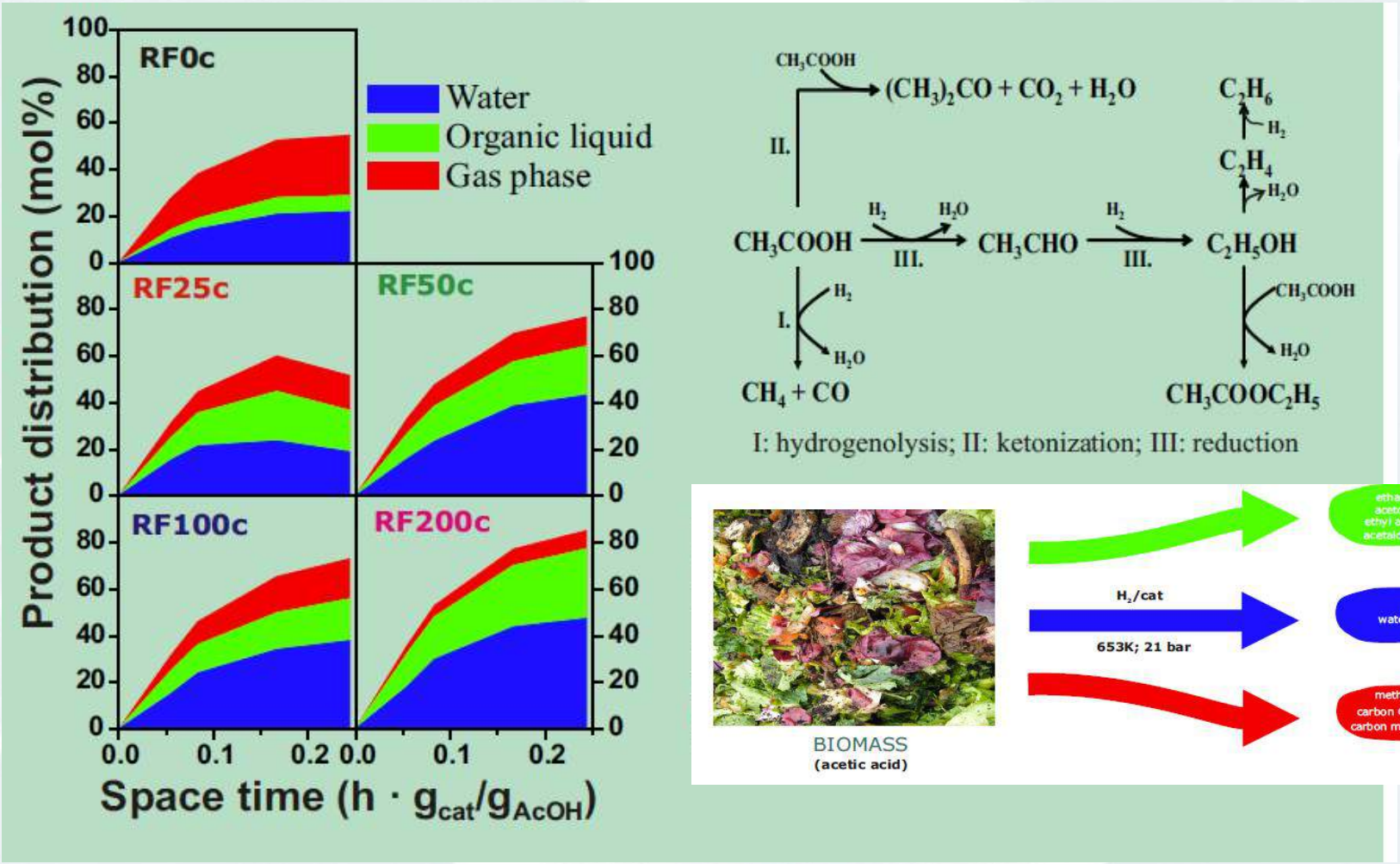
MoC
Mo_2C
ordered C ?

RFMo-carb



Nagy et al: Carbon, 66, 210-218 (2014)

Catalytic activity of RFMo-carb in biomass conversion



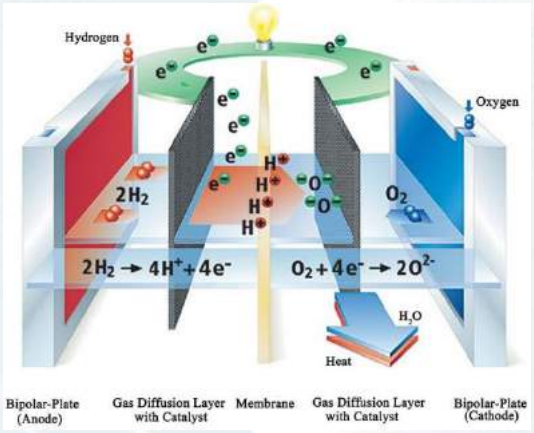
Ábrahám et al: Micropor Mesopor Mater, 190, 46-53 (2014)

CA as electrocatalyst

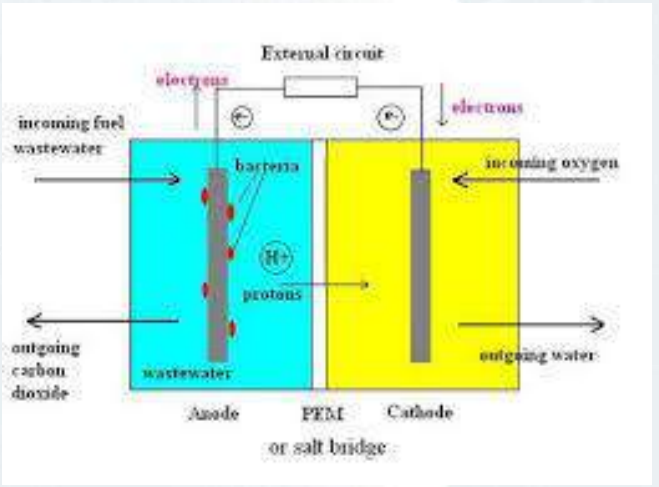
S, N, RGO

Electrode for fuel cells (FCs)

Proton-exchange membrane FC (PEMFC)



Microbial fuel cell (MFC)



Seredych et al: ChemCatChem 7(18) SI 2924-2931 (2015)

Seredych, László, Rodríguez-Castellón, Bandosz: S-doped carbon aerogels/GO composites as oxygen reduction catalysts. Journal of Energy Chemistry 2016, 25(2), 236-245

Nagy, Villar-Rodil, Tascón, Bakos, László: Nitrogen doped mesoporous carbon aerogels and implications for electrocatalysis. Micropor. Mesopor. Mater., 230, 2016, 135-144

Tardy, Lóránt, Lóka, Nagy, László: Enhancing substrate utilization and power production of a microbial fuel cell with nitrogen doped carbon aerogel as cathode catalyst. Biotechnology Letters, 39(7), 993-999 (2017)

Nagy, Bakos, Bertóti, Domán, Menyhárd, Mohai, László: Synergism of melamine and GO in the electrocatalytic behaviour of resorcinol - formaldehyde based carbon aerogels. Carbon 139, (2018) 872-879

http://file.scirp.org/Html/2-6401059_4954.htm

The oxygen reduction reaction (ORR) ON THE CATHODE:

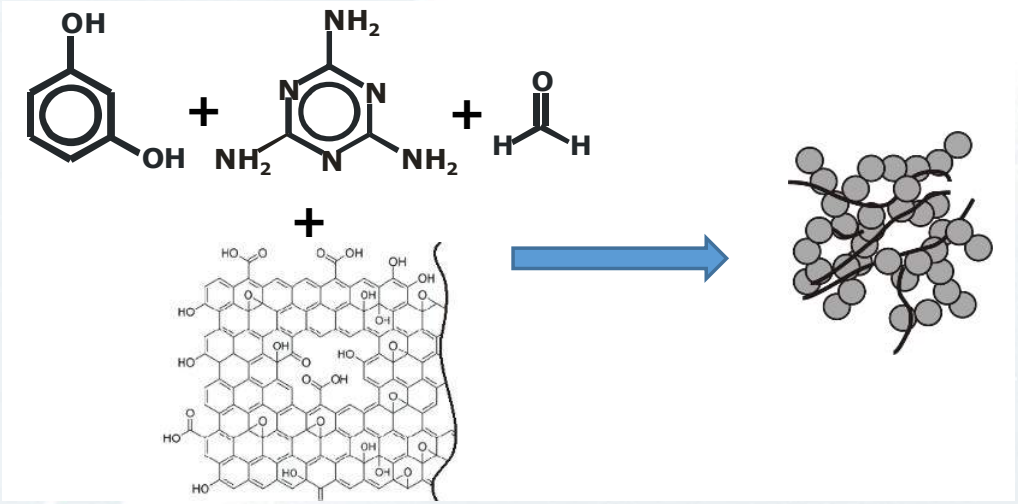
$$O_2 + 4H^+ + 4e^- = 2H_2O$$ faster

$$O_2 + 2H^+ + 2e^- = H_2O_2$$

$$H_2O_2 + 2H^+ + 2e^- = 2H_2O_2$$ slower

Present state of art: noble metal

Double doping: N and RGO



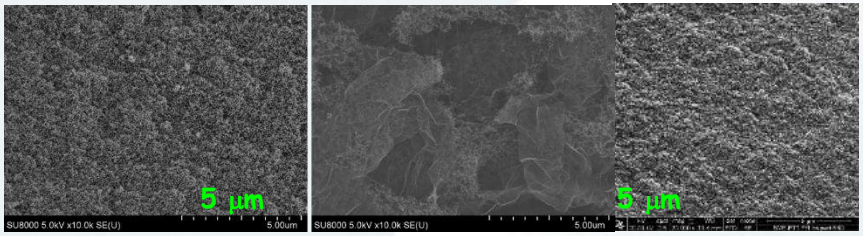
Sample	M/R (molar)	GO/R (mass)
RF + GO	0	0.1
RMF	0.2	-
RMF + GO	0.2	0.1

Nagy et al: Carbon 2018

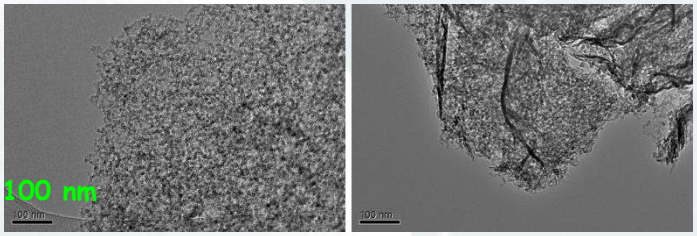
Morphology (SEM, TEM, N_2/77 K)

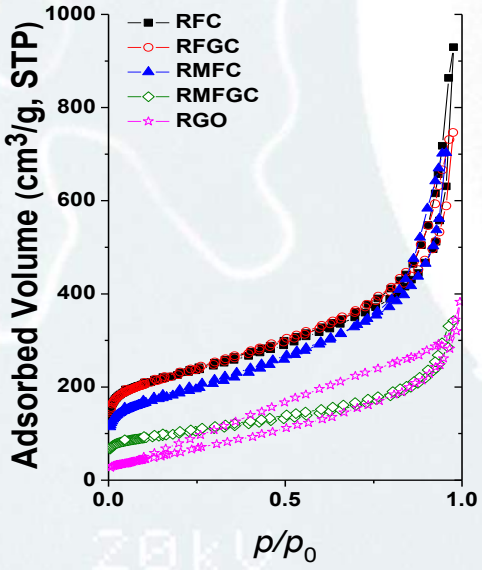


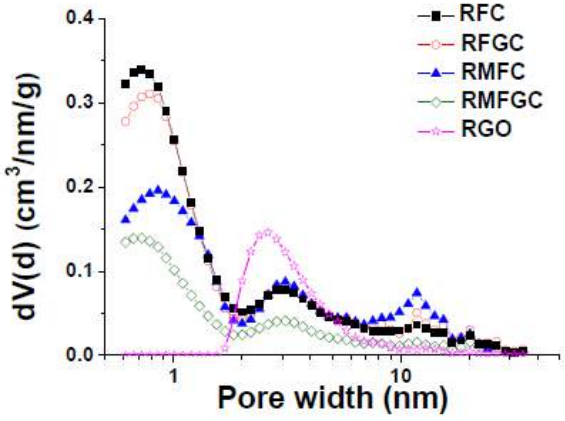
RFC RFGC RMFC



RFC RFGC





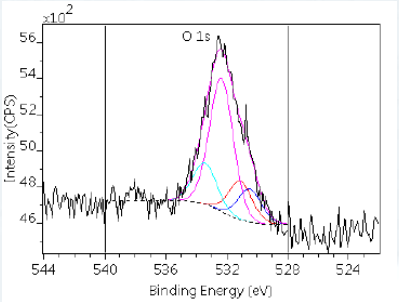


Minta	S_{BET}, m^2/g
RFC	823
RFGC	812
RMFC	645
RMFGC	358

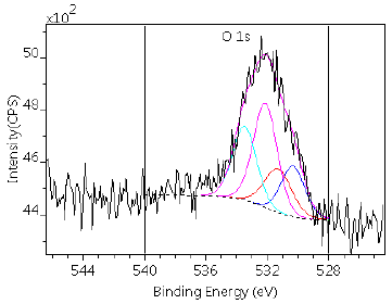
GO is well distributed
PSD retained
GO acts differently in RF and RFM

Surface chemistry

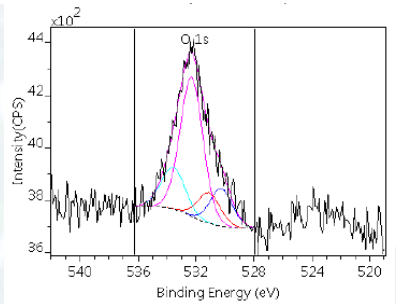
RFC



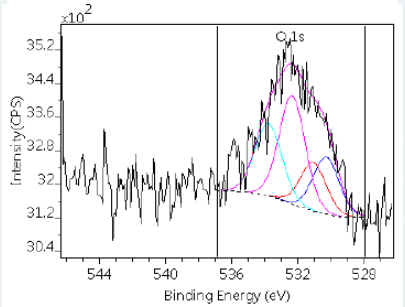
RFGC



RMFC



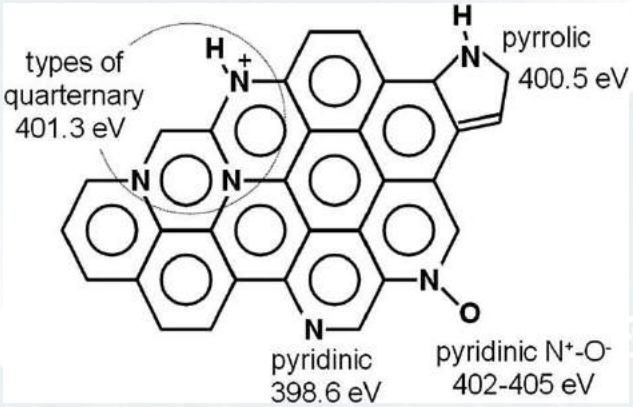
RMFGC



XPS, at %

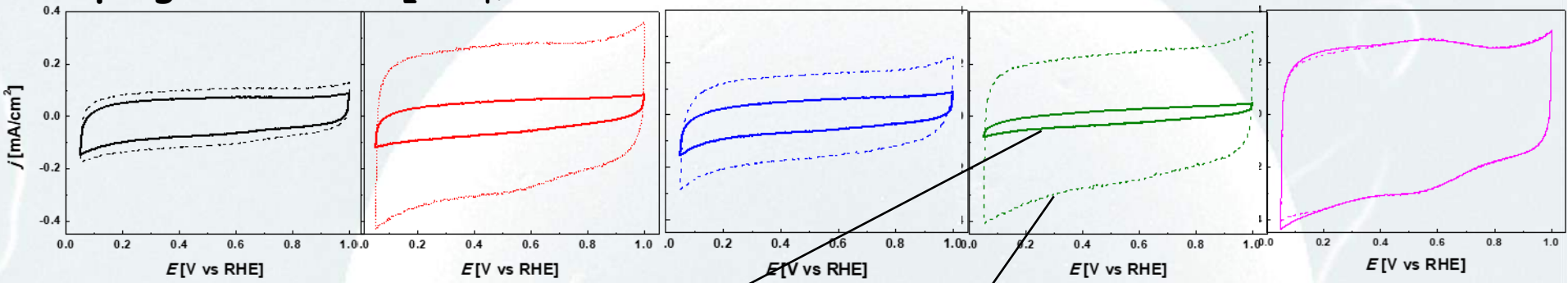
Carbon sample	O	C	N1	N2
RFC	1.7	98.3	-	-
RFGC	2.2	97.8	-	-
RMFC	1.5	97.5	0.3	0.7
RMFGC	1.6	97.8	0.2	0.5
RGO	16.9	83.1	-	-

Complex chemistry
N2 (quaterneric N) is the dominant

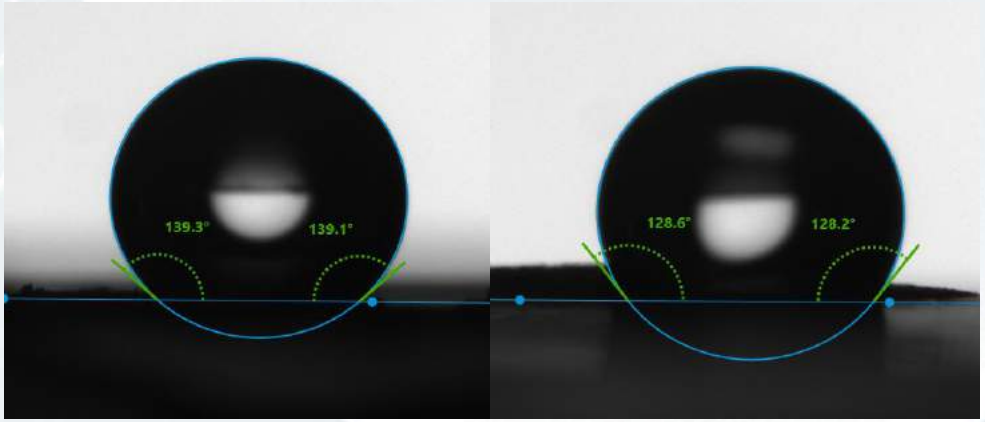


Electrocatalytic test 1: cyclic voltammetry

Ar-purged 0.5 M H_2SO_4, scan rate 50 mV/s



RFC **RFGC** **RMFC** **RMFGC** **RGO**



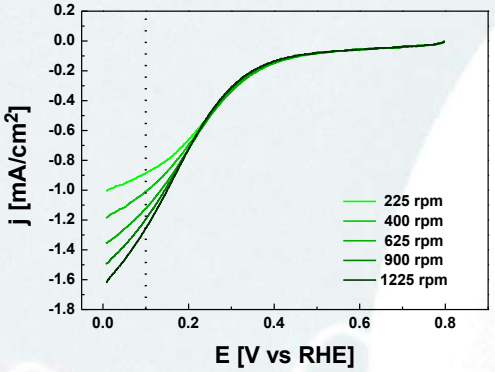
Before **after**

ORR test

As S_{BET} constant the in-situ H_2O_2 improves wetting and thus the access of the electrolyte

Electrocatalytic test 2: linear sweeping voltammetry (LSV)

O_2-saturated 0.5 M H_2SO_4, scan rate 10 mV/s

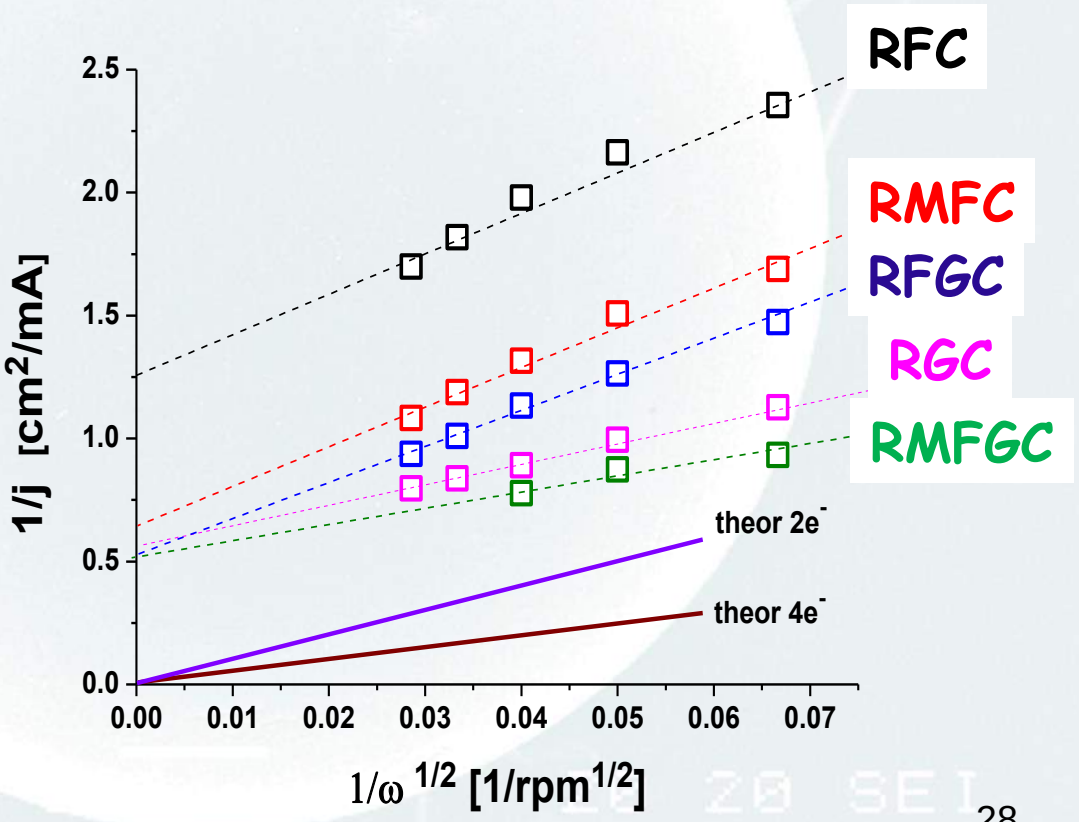


RGO, rotating disc electrode

Neither N nore RGO doping alone is not sufficient but together:

4e⁻ mechanism

Koutecky-Levich (K-L) plot



Confirmation: rotating ring and disc electrode

Summary

The family of carbon aerogels is a fascinating and versatil group of materials

There is still a lot to discover

Go ahead

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Thank you for your attention

