Charakterizace pevných materiálů pro výrobu baterií a katalyzátorů

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Surface and Powder Analysis

SURFACE AREA

POROSITY

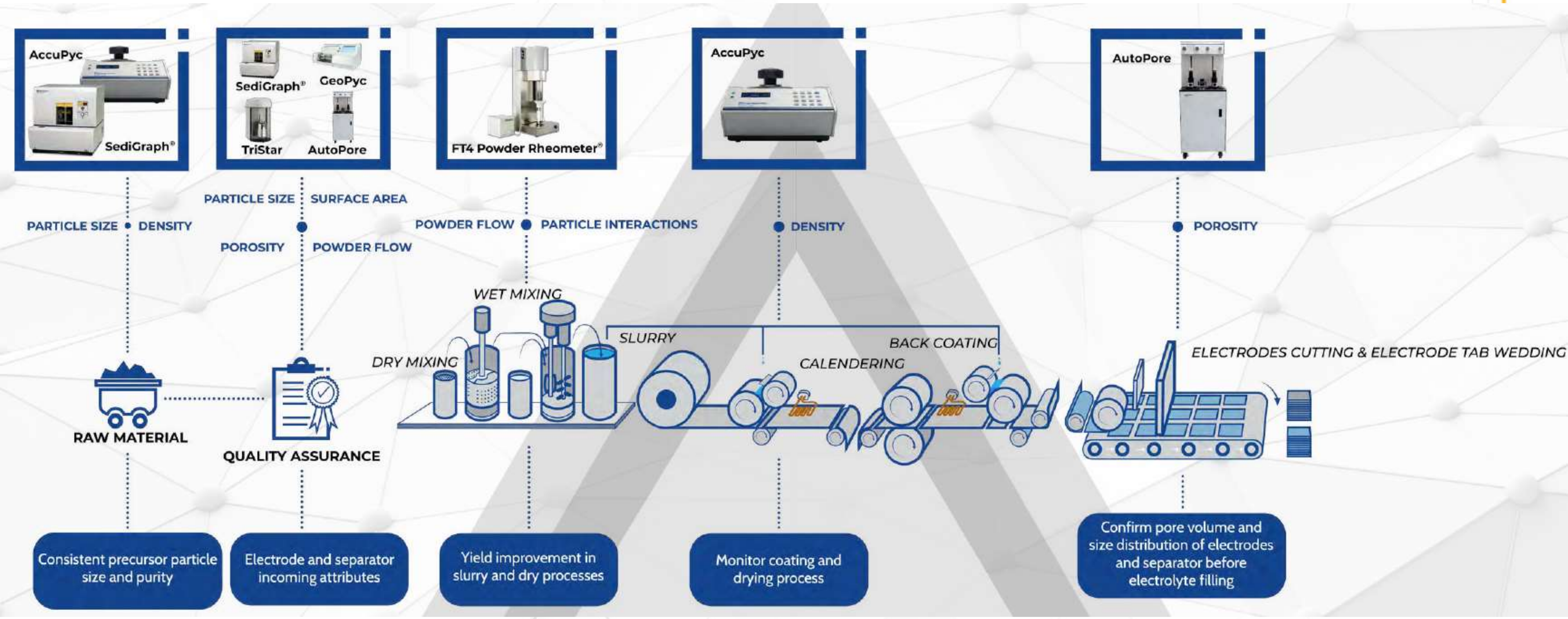
SOLID DENSITY

PARTICLE INTERACTIONS

POWDER FLOW

PARTICLE SIZE

Surface and Powder Analysis



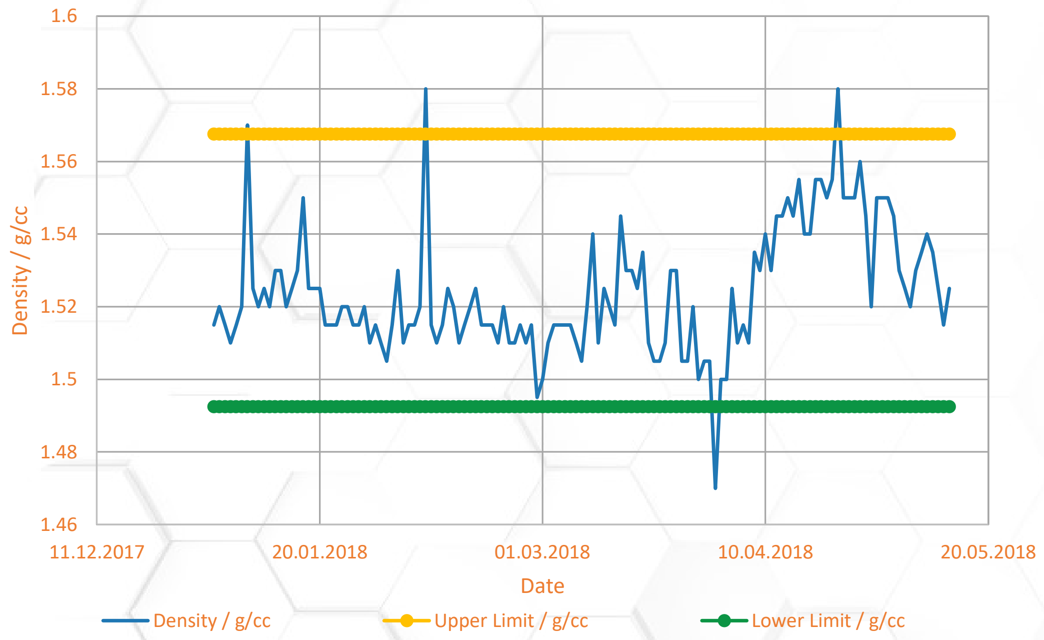
Density A Simple QC Check

Raw Materials

Product

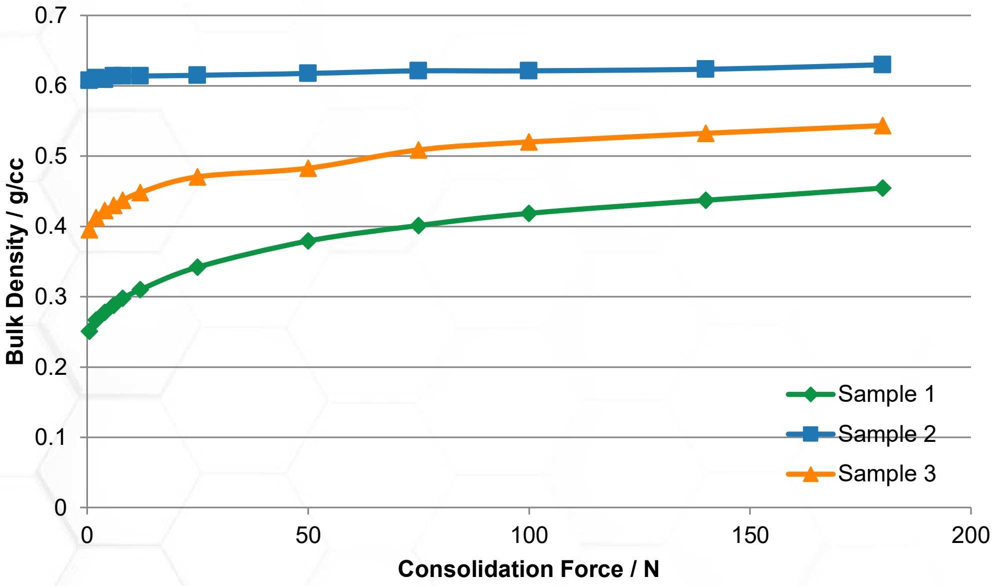
AccuPyc 1345

Density – gas pycnometry
Inherent material property = 1.532 g/cc +/- 0.004 g/cc

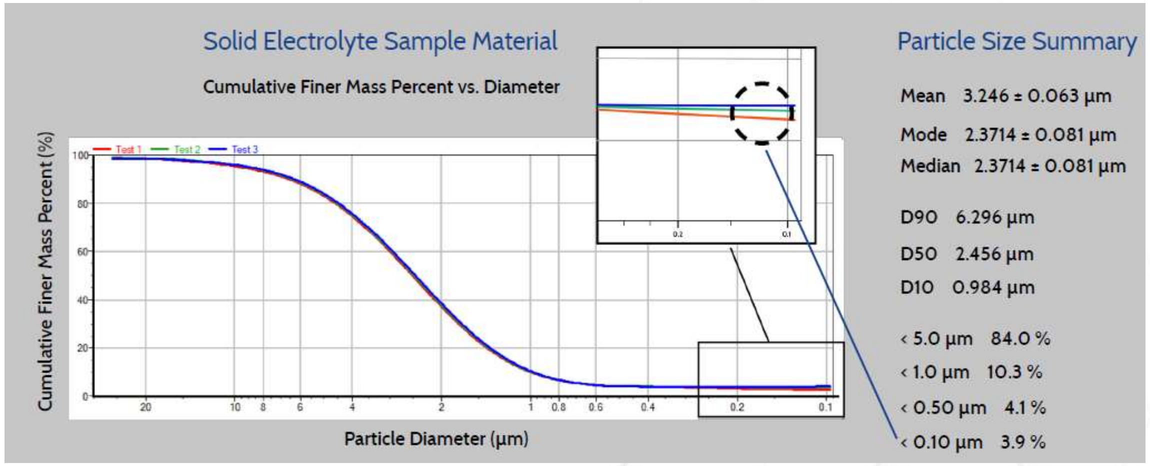


Binder Bulk Density Characteristics

- Profiling Bulk Density
  - Storage
  - Processing
  - Choice of grade
- Influence of other properties
  - Particle size
  - Shape
  - Porosity



Particle Size



SediGraph III 5125

- Sedimentation uses well understood physical laws and easy to measure properties that do not require trial and error modelling
- Provides complete sample mass accountability and quantifies the fine content outside the measurement range
- Uses higher material concentration than many other techniques ensuring a representative sample

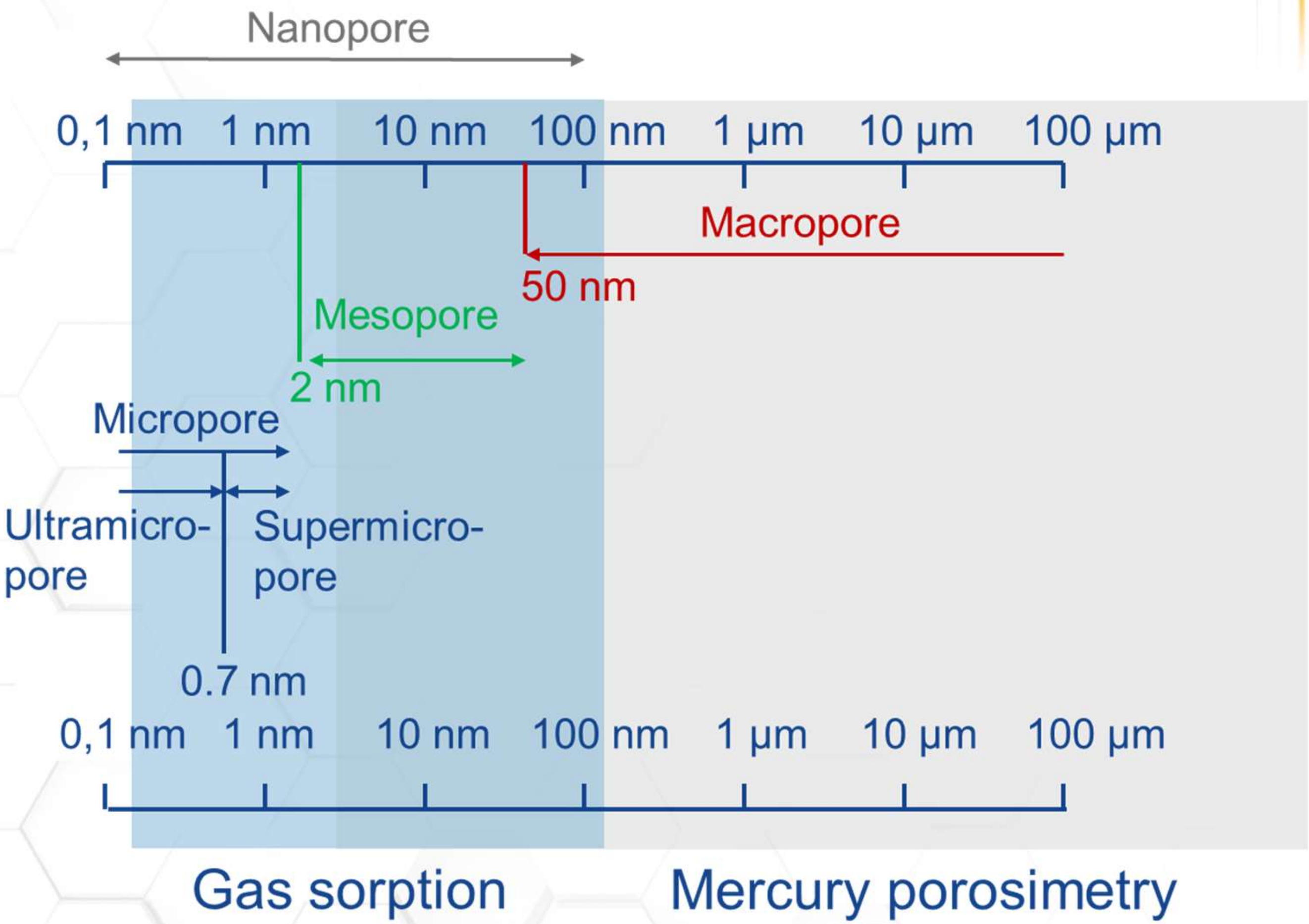
Porosimetry: Gas & Mercury

Gas Adsorption

- BET surface area
- micropore
- mesopore
- 0.35 nm – 300 nm

Mercury Intrusion

- mesopore
- macropore
- 3 nm – 400 µm



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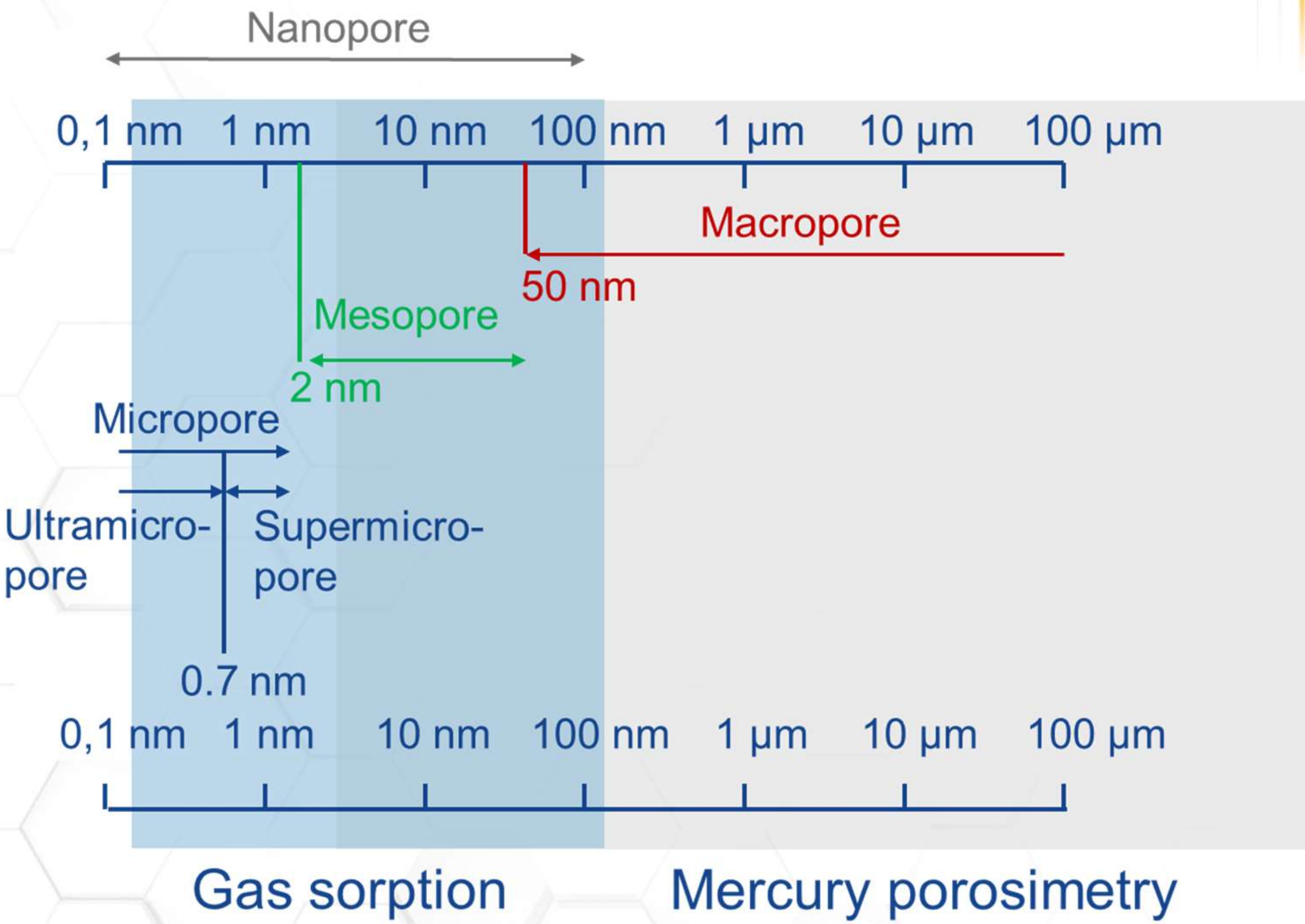

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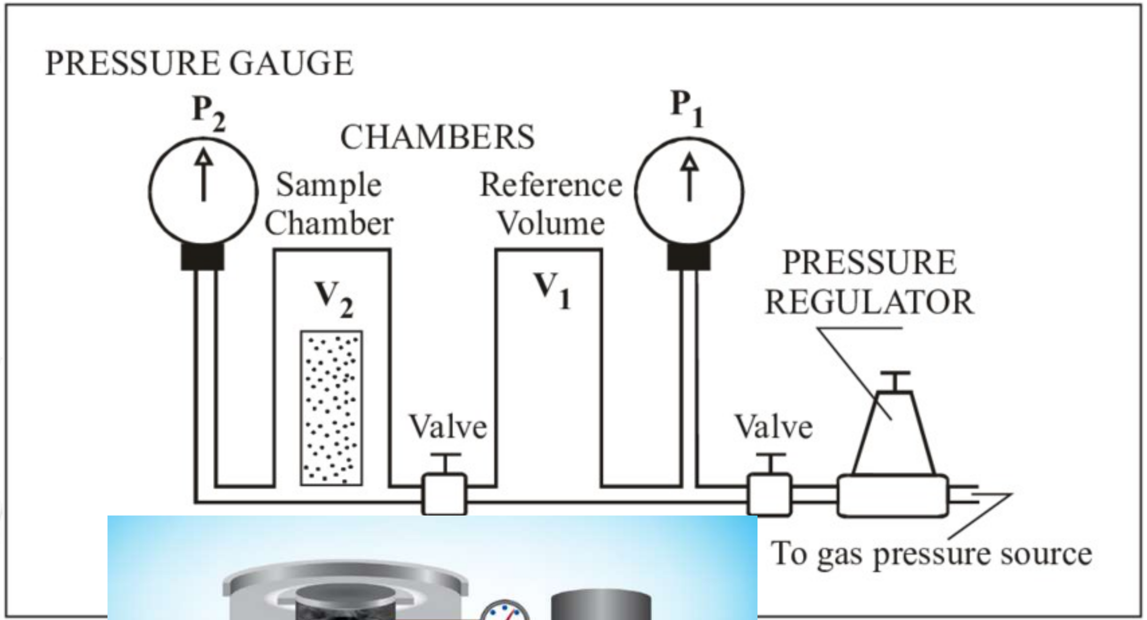
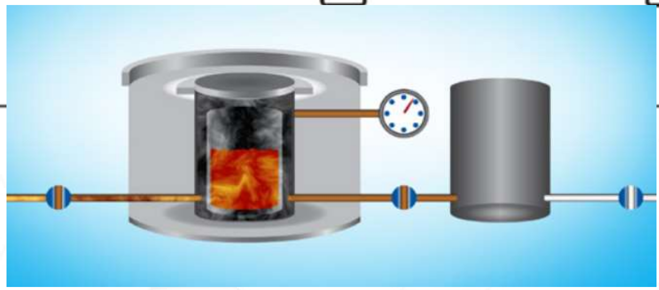
Gas Porosimetry





Physisorption vs. Chemisorption

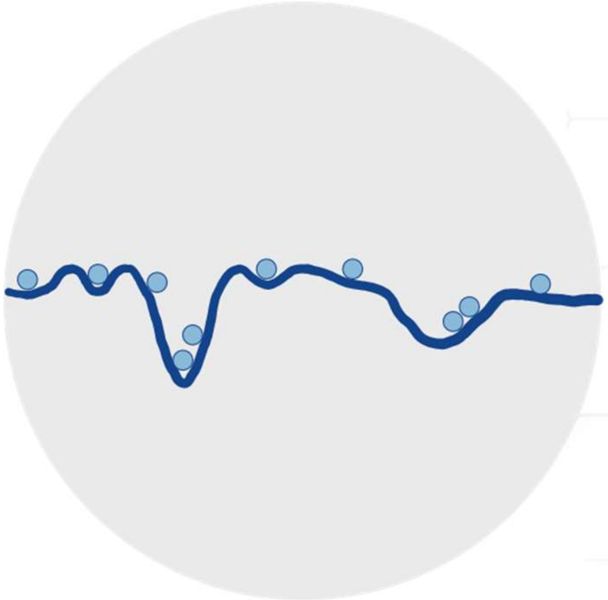
Physisorption

- forces correspond to those of condensation and deviation from the ideal behavior
- general phenomenon with relatively low specificity
- normally multilayers

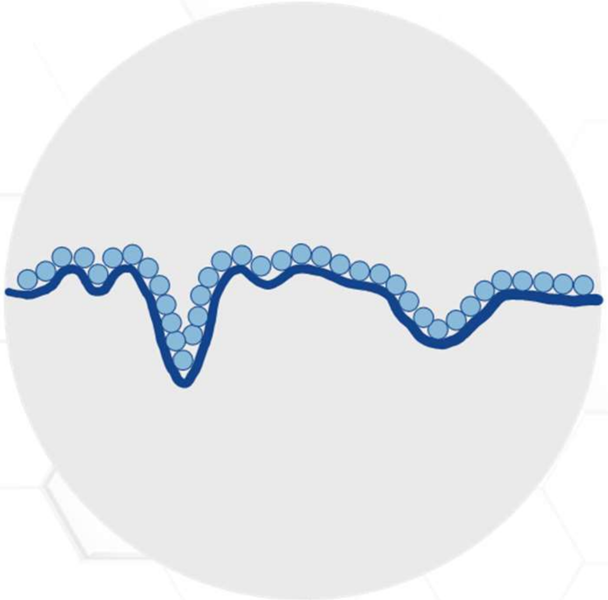
Chemisorption

- forces correspond to those in the formation of chemical compounds
- depending on the reactivity of the adsorbent and the surface
- only monolayers (chemisorbed molecules are bound to reactive areas of the surface)

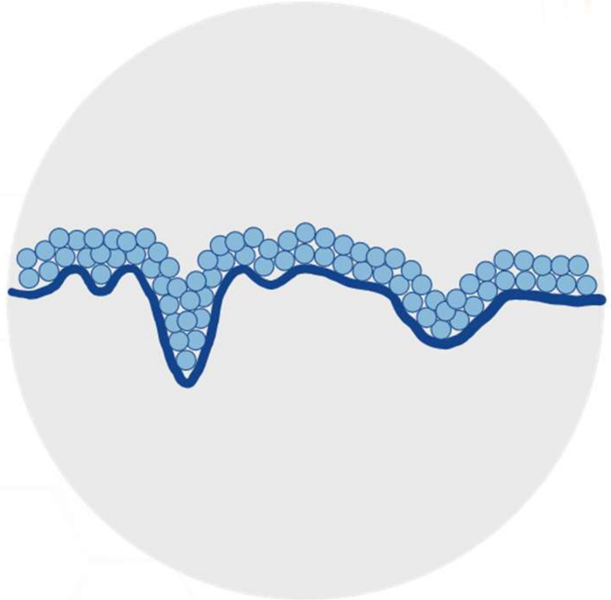
Adsorption Process



Adsorption at isolated sites



Monolayer surface area



Multilayer formation

Increasing pressure

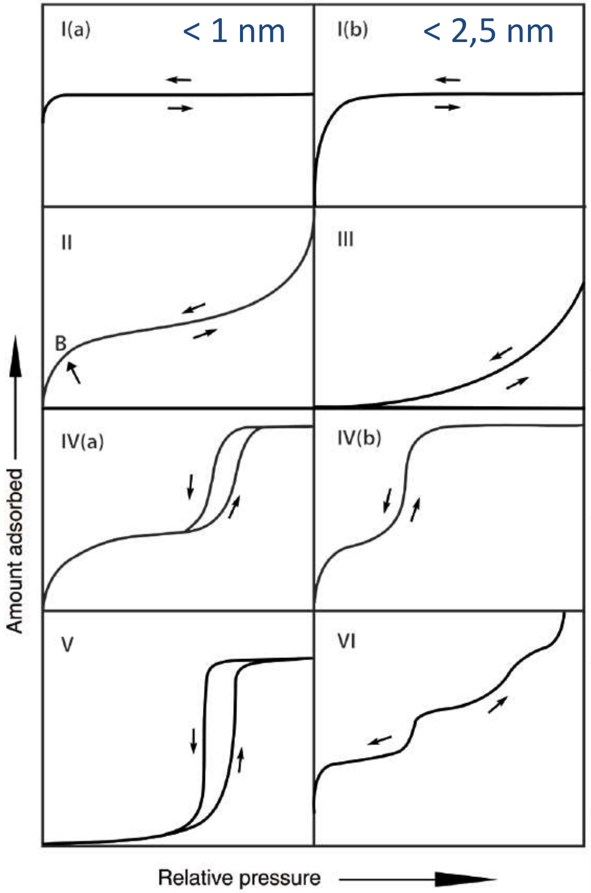
Types of isotherms (IUPAC)

Micro

Non/Macro
B: mono → multilayer

Capillary condensation, Meso > 4 nm

Water on hydrophobic, Micro + Meso



Micro/ small Meso

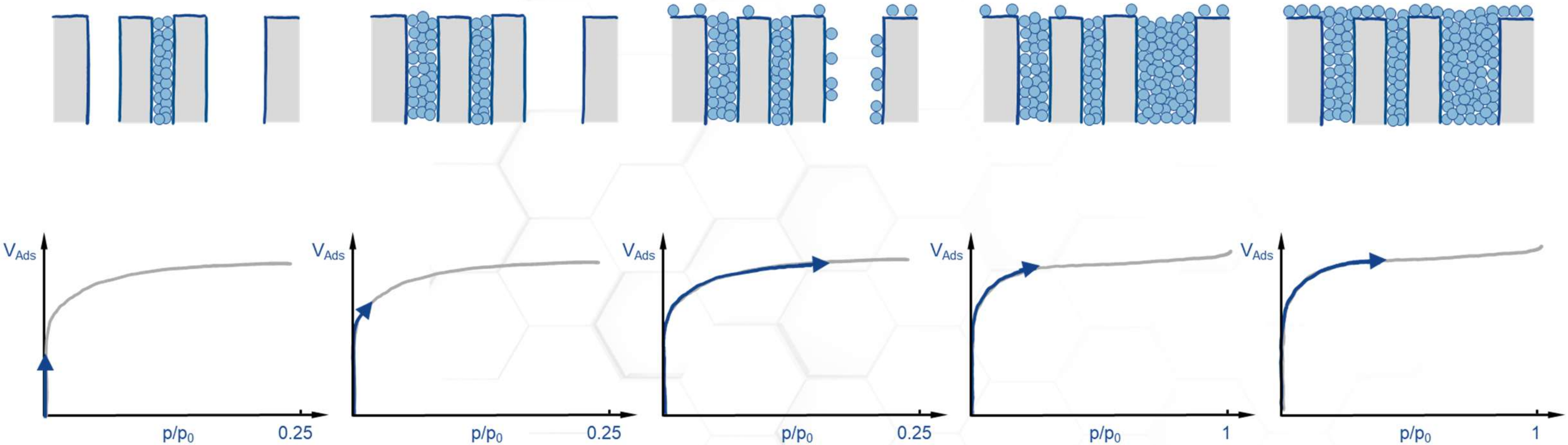
Non/Macro, weak interaction (water on hydrophobic surface)

Capillary condensation, Meso < 4 nm,

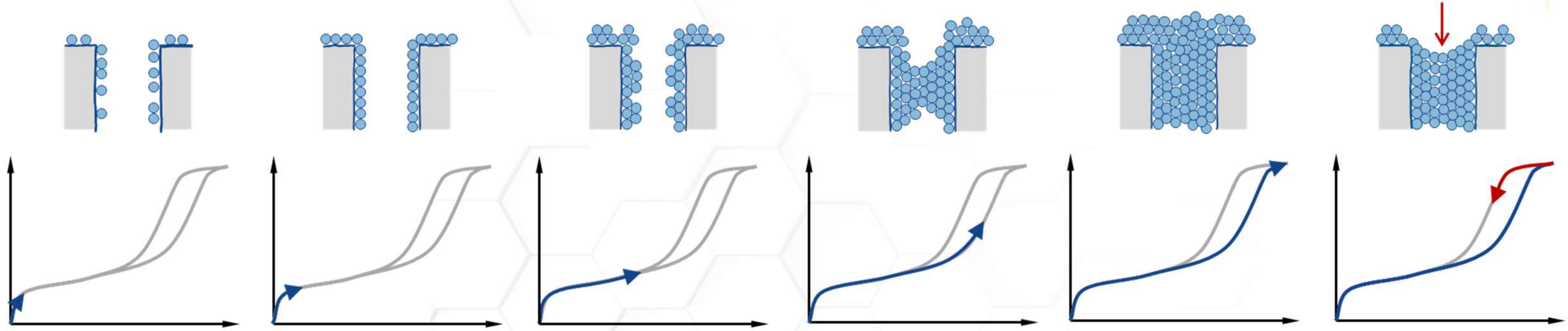
Layers on uniformly, nonporous surface

Pure Appl. Chem. 2015; M. Thommes*, K. Kaneko, A. V. Neimark, J. P. Olivier, F. Rodriguez-Reinoso, J. Rouquerol and K.S.W. Sing;
Physisorption of gases, with special reference to the evaluation of surface area and pore size distribution (IUPAC Technical Report)

Type-I Isotherm



Type-IV Isotherm



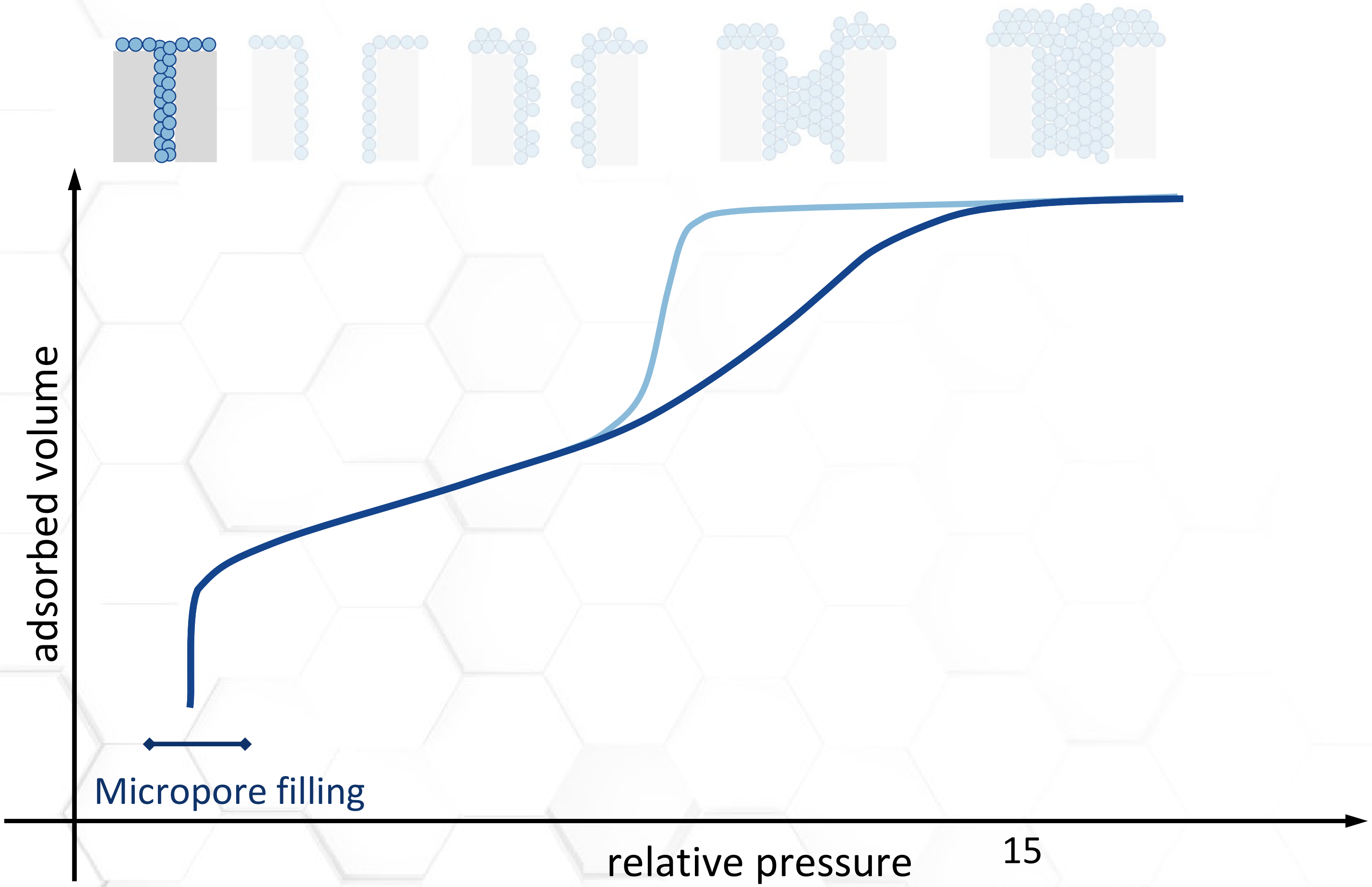
- There are several explanations why hysteresis loops are built
- One explanation assumes a metastable adsorption process, while the desorption occurs from an equilibrium

Data collection

Information from Gas Adsorption

- Surface Area (BET)
- External Surface Area (t-Plot)
- Pore Volume
- Pore Size Distribution

Complete isotherm:
p/p_0: 10^{-9} - 0.999
(for N_2 at 77 K)



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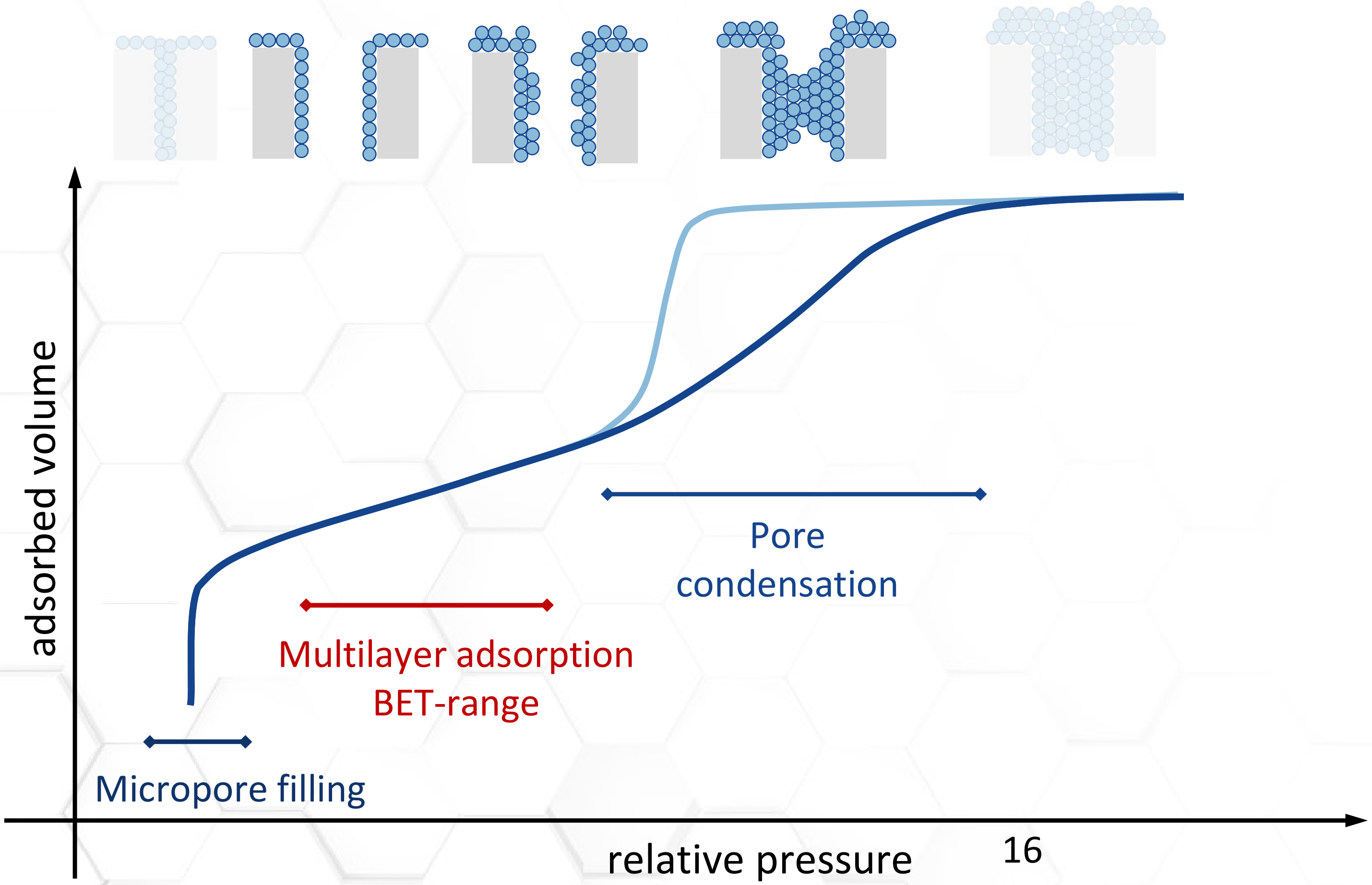

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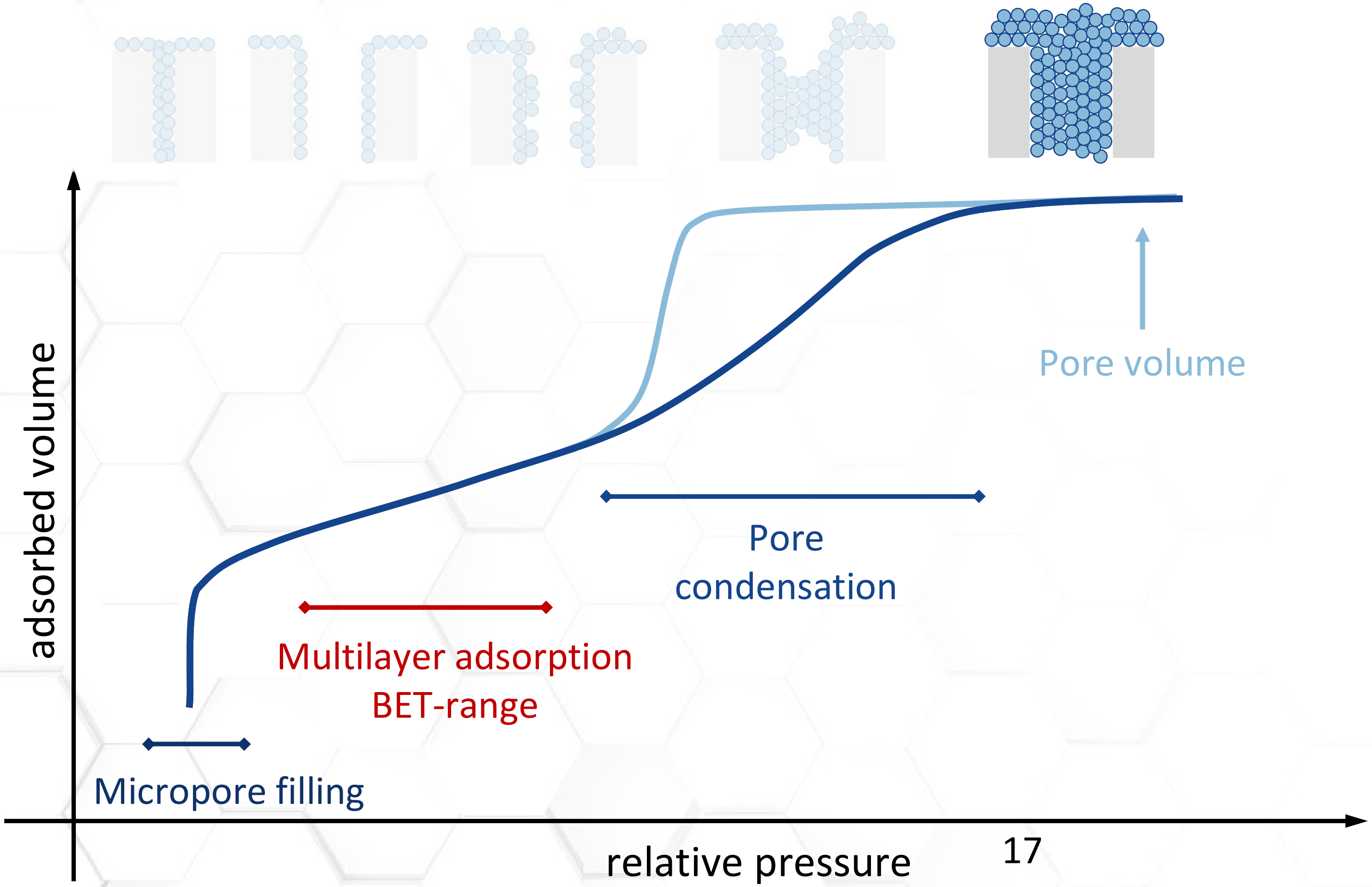

Anode Material

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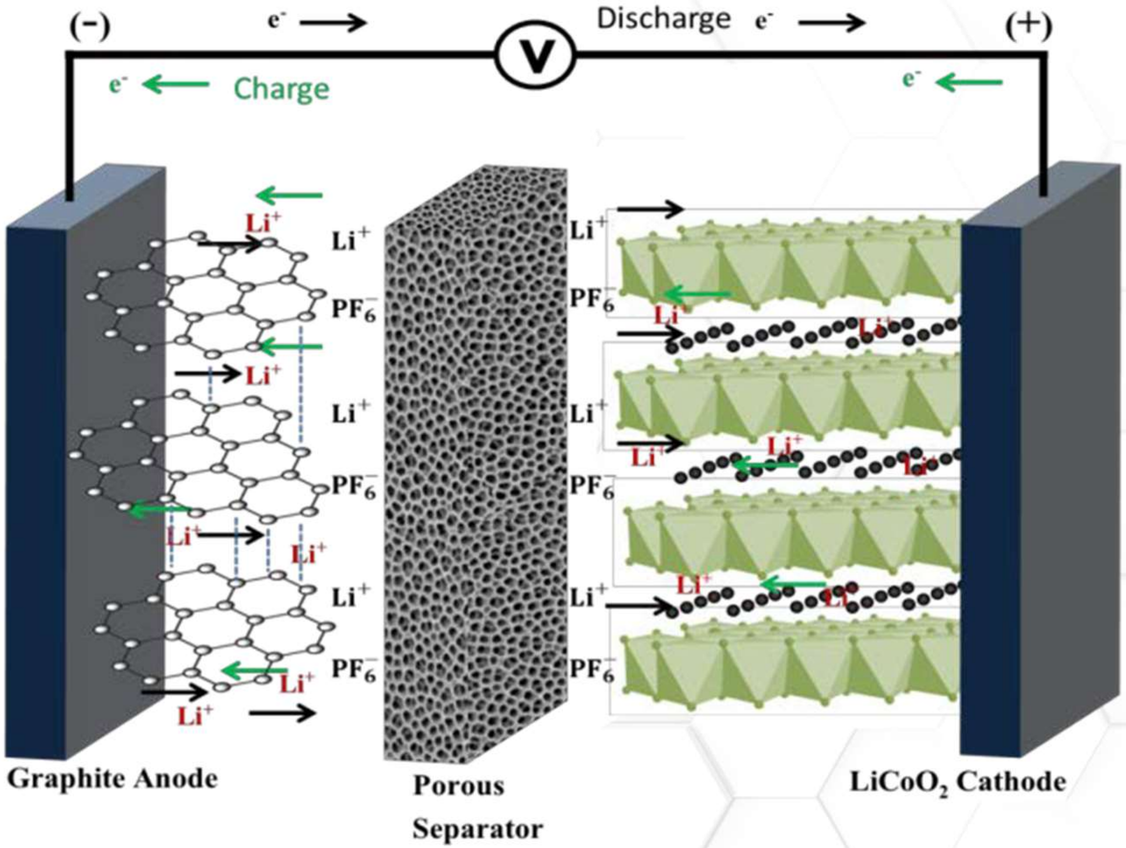

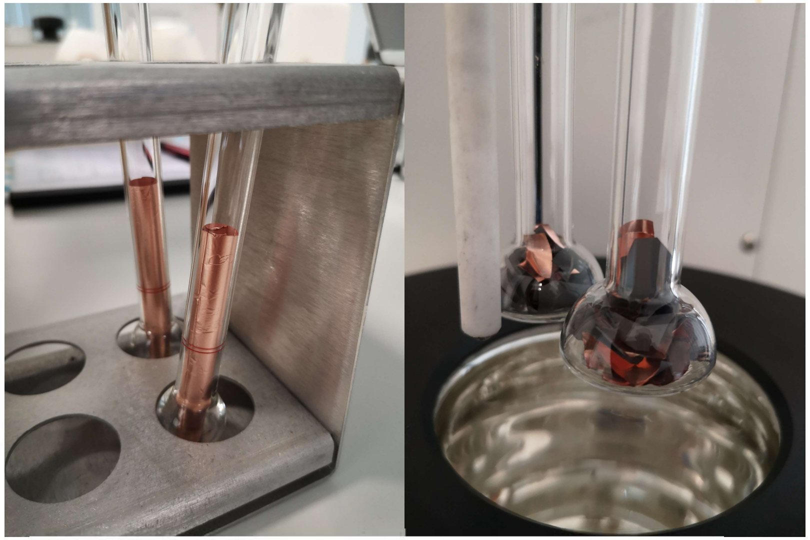

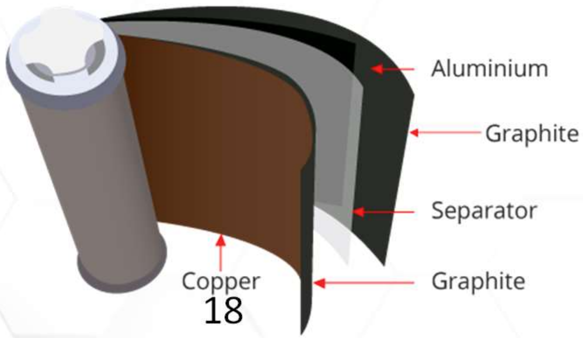

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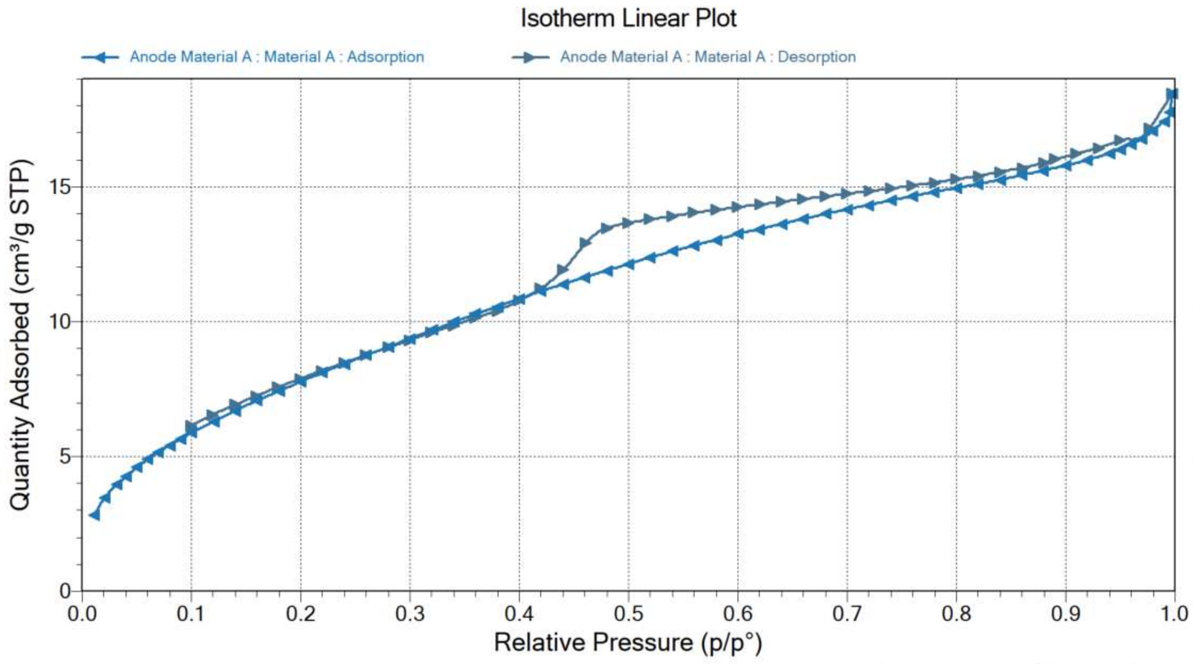
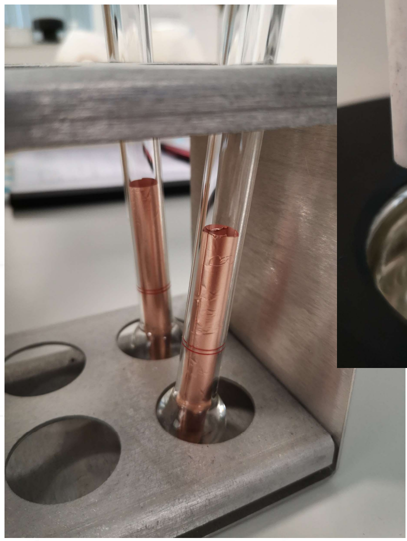
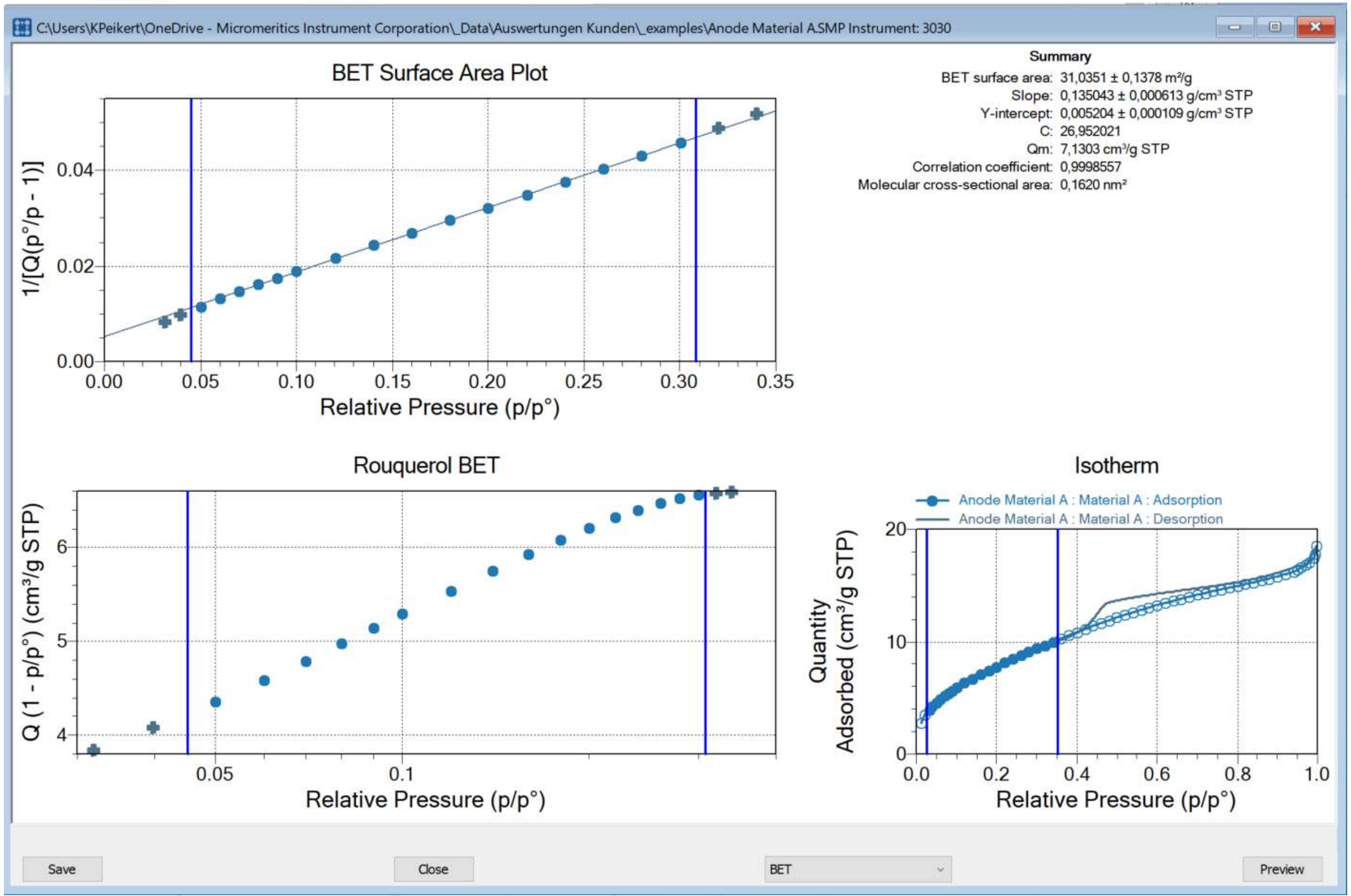
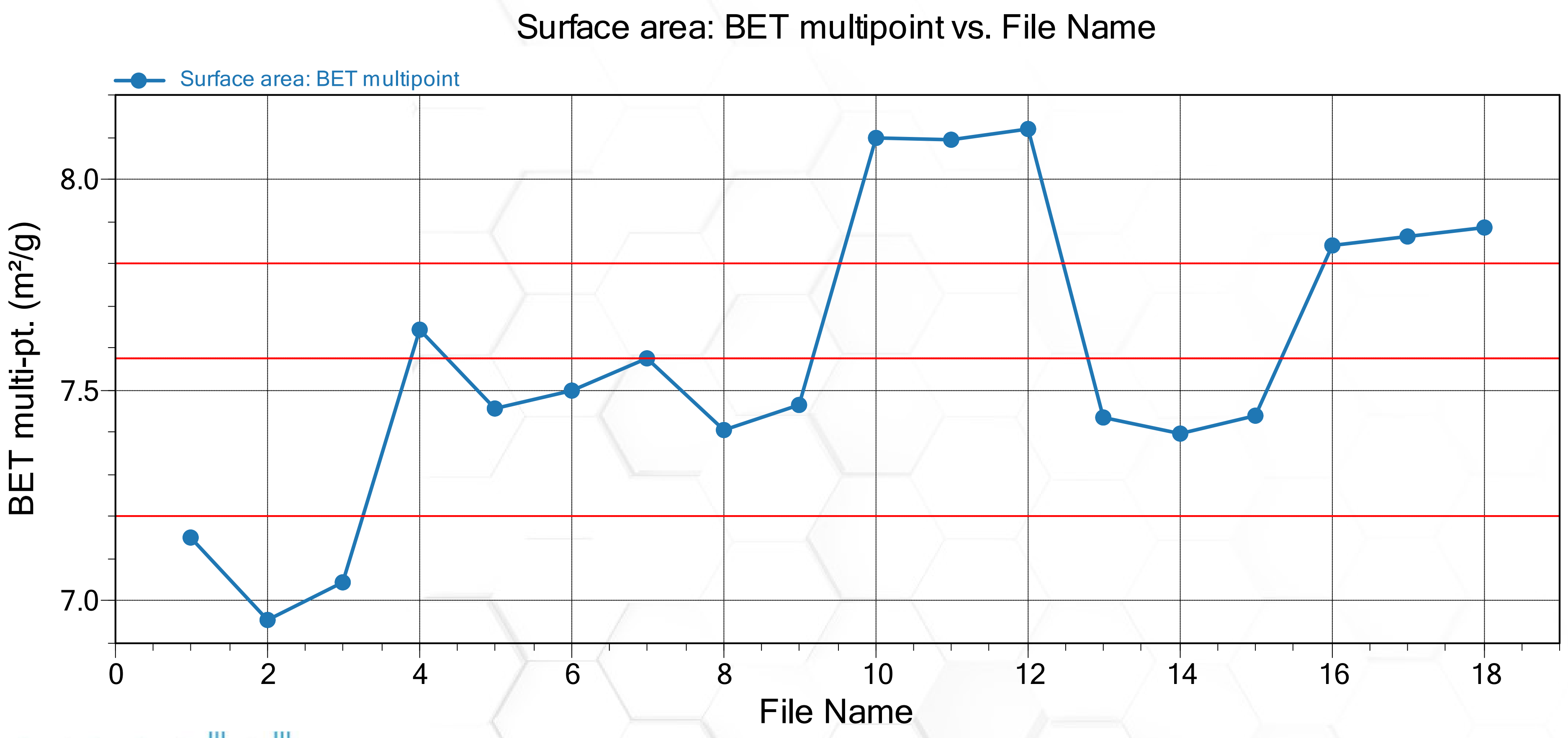




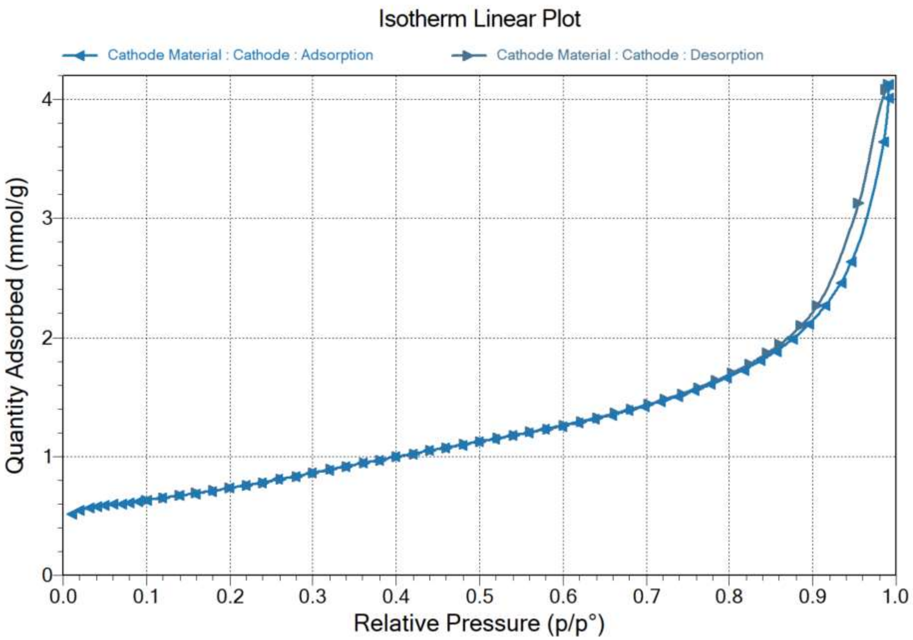
BET Calculation

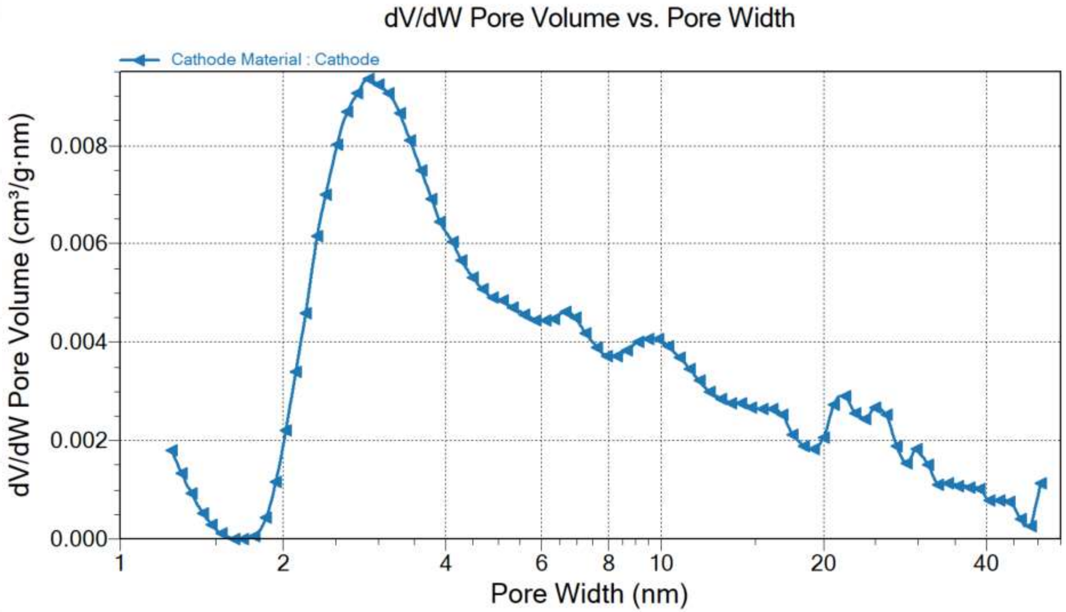


Process Control



Cathode Material





Gas Adsorption – data reduction

p/p_0	mechanism	model
10^{-9} - 0.02	Micropore filling	DFT, HK, DA, DR
0.01 - 0.3	Sub-monolayer formation	DR
0.05 - 0.3	Monolayer developed	BET, LM
> 0.1	Multilayer Formation	t-Plot (de-Boer, FHH)
> 0.35	Capillary condensation	BJH, DH, DFT

DFT - Density Functional Theory
HK - Horvath Kawazoe
DA - Dubinin Astakhov
DR - Dubinin Radushkevic
BET - Brunauer, Emmett & Teller

LM - Langmuir
t-plot - statistical Thickness method
BJH - Barrett, Joyner & Halenda
DH - Dollimore Heal

Gas Adsorption – BET Isotherm

- **Brunauer–Emmett–Teller**

Specific surface area = number of molecules in monolayer (n_m N_A) * space required by one molecule (σ) normalized for sample mass (g)

$$S_{BET} = n_m \cdot N_A \cdot \sigma \cdot g^{-1}$$

$$V_a = \frac{V_m C p}{(p_0 - p)\left(1 + (C-1)\dfrac{p}{p_0}\right)}$$

V_a	adsorbed volume @ p
V_m	adsorbed volume of monolayer
C	empirical constant
p	pressure
p_0	saturation pressure

$$\frac{p}{V_a(p - p_0)} = \frac{1}{V_m C} + \frac{C-1}{V_m C}\left(\frac{p}{p_0}\right)$$

Linear Equation:
Intersection with y-axis
Slope

Extensive range of gas adsorption analyzer QC/QA applications

FlowSorb III

Gemini VII

Tristar II Series

ASAP 2425

ASAP 2460

High resolution gas adsorption analyzers
In-depth porosity investigation

ASAP 2020 Plus
Physi and Chemi

ASAP 2050

3 Flex series
Physi – Chemi - TCD

Micromeritics 3 Flex Gas Analyzer

micromeritics®

- High resolution, high-throughput, physisorption and chemisorption instrument
- Ultra low-pressure data collection for accurate results with a resolution to 10^{-5} mmHg
  - Pneumatic valves
  - Hard seals, VCR
- Servo valve for dosing and evacuation
- Analyze up to three separate probe gases simultaneously
- Enhanced Chemical Resistance (ECR) as option

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Adsorptives Used With The 3Flex

1-butene	chlorine	isooctane	n-Octane
1-hexene	cis-2-butene	isopentane	n-pentane
1-propanol	cyclohexane	isopropanol	octanal
2 2 dimethylbutane	cyclopropane	krypton	oxygen
2 3 dimethylbutane	deuterium	m-xylene	o-xylene
333trifluoropropene	dimethyl methylphosphonate	methane	phosphine
acetaldehyde	dimethylamine	methanol	propane
acetic acid	ethane	methyl acetate	propylene
acetone	ethanol	methyl ethyl ketone	p-xylene
acetylene	ethanolamine	methylamine	pyridine
air	ethylamine	n-butane	styrene
ammonia	ethylbenzene	n-decane	sulphur dioxide
argon	ethylene	neon	sulphur hexafluoride
arsine	formaldehyde	neopentane	toluene
benzaldehyde	helium	n-heptane	trans-2-butene
benzene	hexafluoropropene	n-hexane	trifluoroiodomethane
boron triflouride	hydrogen	nitric oxide	vinylidene fluoride
carbon dioxide	hydrogen sulphide	nitrogen	water
carbon disulfide	isobutane	nitrogen trifluoride	xenon
carbon monoxide	isoheptane	nitrous oxide	
CF4-R14	isohexane	n-nonane	

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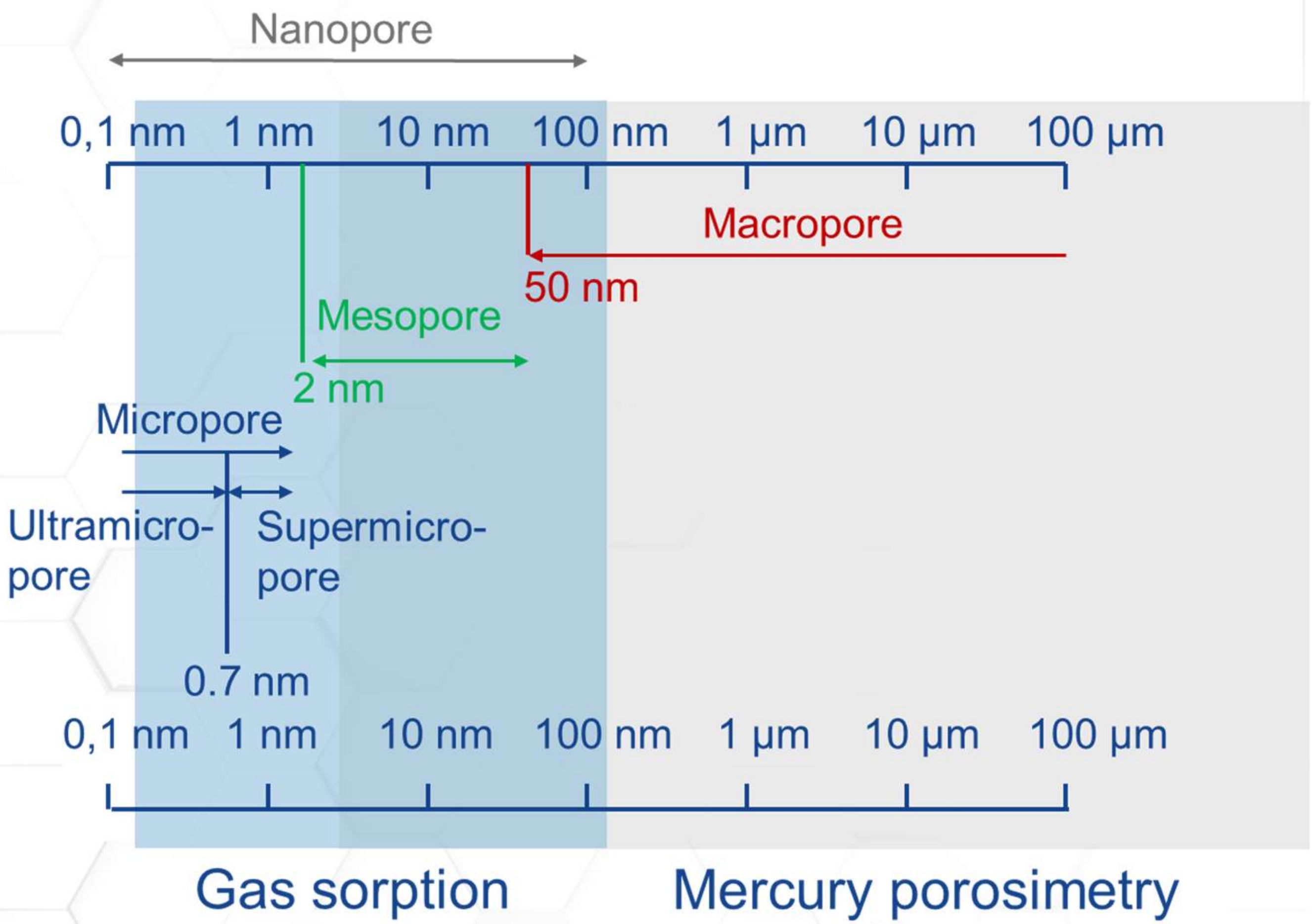

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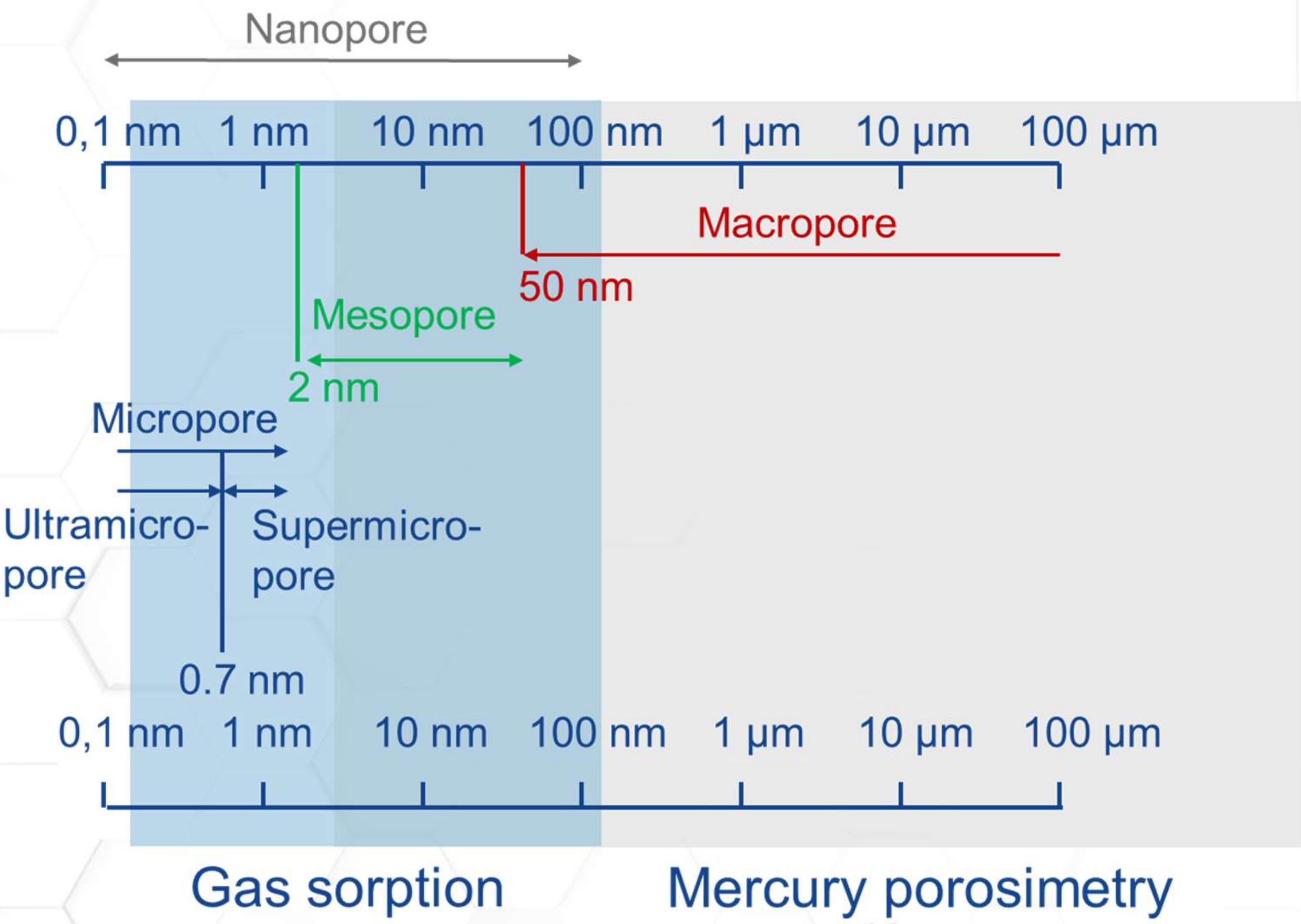

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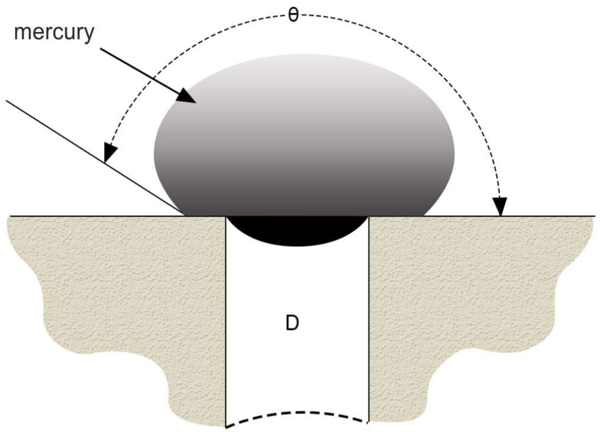
Mercury Porosimetry

AutoPore V

Measure

- Pressure – pore size
- Capacitance – volume intruded

- Study and optimize separator pore size distribution, a key safety consideration.
- Quality control of final electrodes and separator.



Autopore V: Pore Size-Volume Distribution

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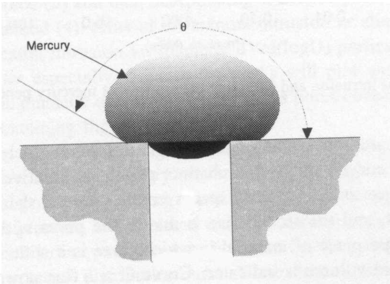

Mercury Intrusion Porosimetry

Pressurized mercury is forced into the cavities of the porous material. The penetration pressure allows to calculate the pore dimensions.

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A widely used technique

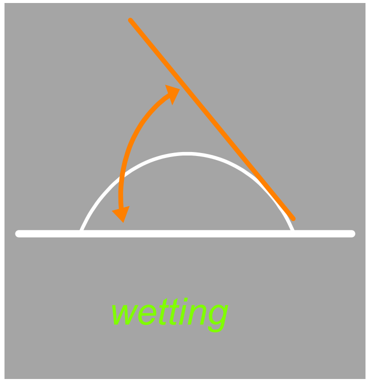
Performance of porous solids is strongly related to the pore structure, thus the wide applicability of mercury porosimetry technique to test industrial products:

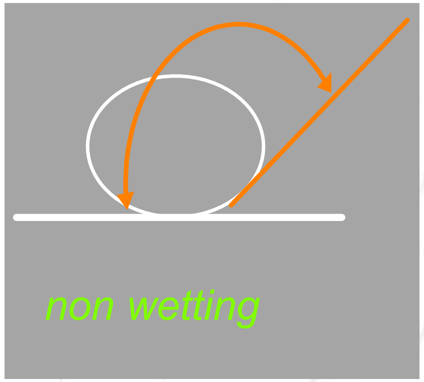
- Catalysts
- Pharmaceuticals (controlled drug release, tablets)
- Gas separation (columns for GC and LC, molecular sieves)
- Filtration, polymers, ceramics
- Building materials, reservoir rocks, geology
- Car industry (batteries, brake pads, etc)

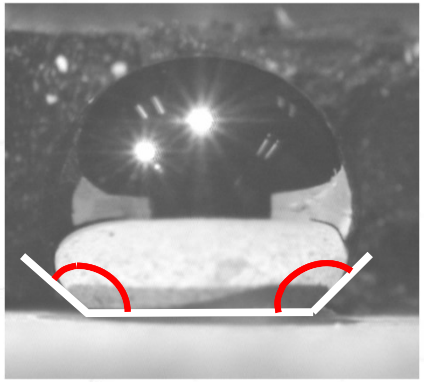
Facts about mercury porosimetry

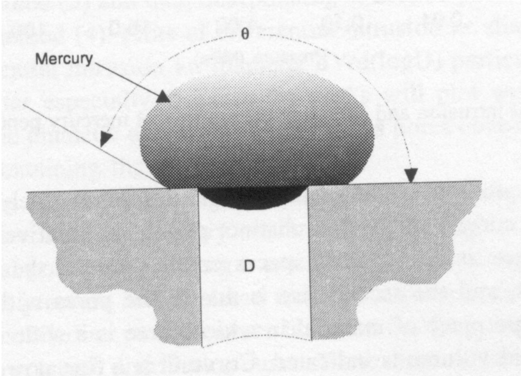
- Suitable to study all porous materials and powders which are not wetted by mercury, except some metals producing amalgams (metallic gold, aluminum, copper, nickel, silver, etc.)
- Not recommended for compressible or fragile materials
- Based on properties of non-wetting liquids which need a pressure to be forced into a porous structure
- Penetration pressure into pores is related to access pore size through the Washburn equation (d = - 4 g cos [q] / P)
- Mercury porosimetry can measure pores ranging from about 0.003 to 900 microns (depending on instrument type and sample nature)
- Other information are total pore volume in the range, bulk and apparent densities, porosity and particle size distribution

Basics of mercury porosimetry



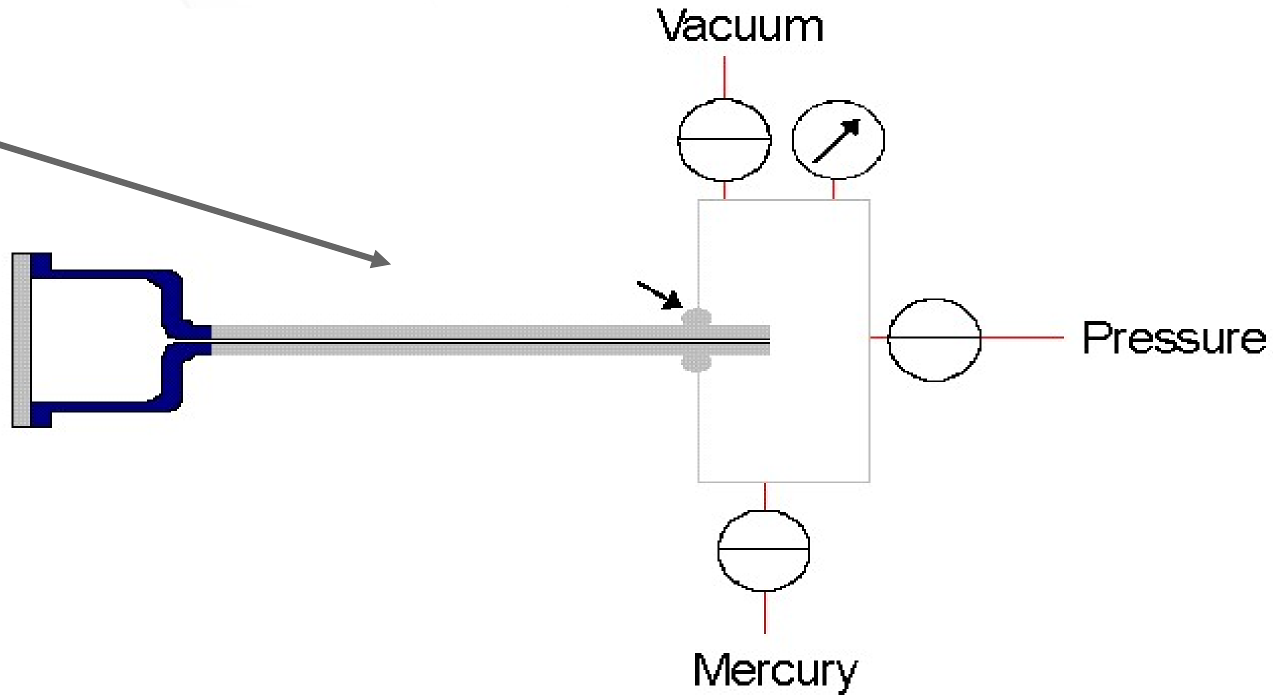






- Hg is a non-wetting liquid for many solids
- Hg must be forced to penetrate pores
- Penetration pressure is related to pore radius
- Volume of Hg is related to pore volume

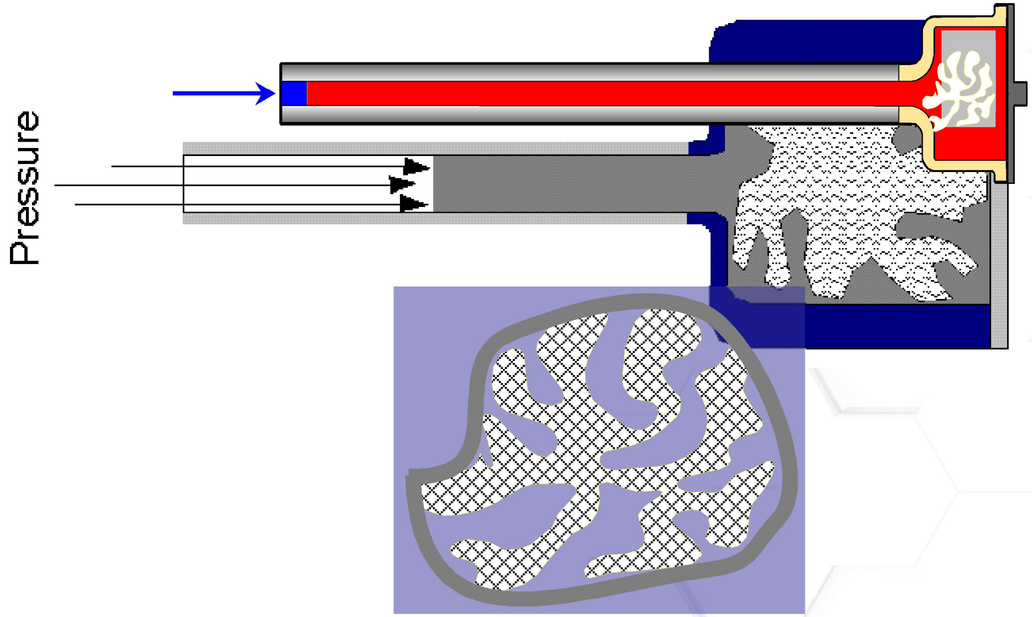
Low Pressure Analysis

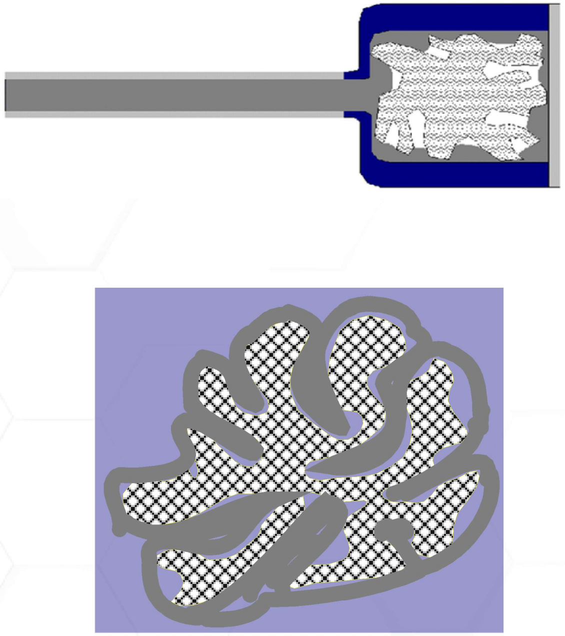


Hg penetration under pressurization

Hg cannot enter pores under vacuum (bulk density calculation)

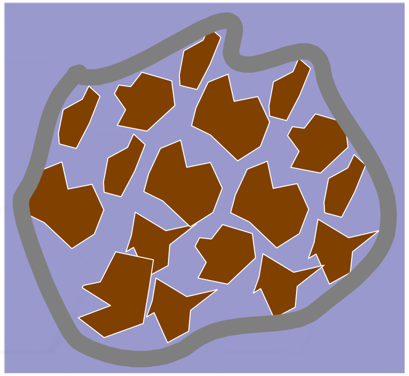
An increasing pressure forces Hg to penetrate all accessible pores (apparent density, pore size and volume)



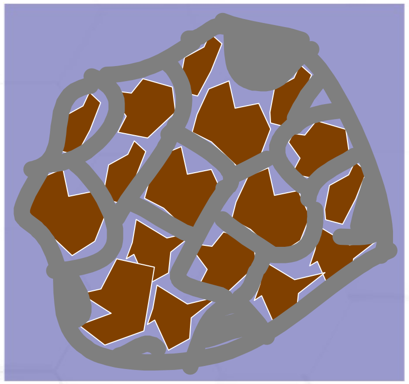


Hg can also measure particle size

First pressurization: Hg penetrates inter-particle voids and breaks aggregates (aggregation degree of powders)



Second pressurization: Hg penetrates only the inter-particle voids (particle size distribution)



MIP: AutoPore V 9600 Series

micromeritics®

- Four models, 2 or 4 low pressure ports and 1 or 2 high pressure ports
- Pressure ranges up to 227 MPa and 414 MPa
- Available results
  - Pore Volume Distribution - The volume of pores as a function of diameter or applied pressure
  - Pore Area Distribution - The area of pore walls as a function of diameter or applied pressure
  - Density and Porosity - Apparent Skeletal and Bulk Density
  - Extended Materials Characterization
    - Tortuosity
    - Permeability
    - Compressibility
    - Fractal Dimensions
  - Particle Size Distribution - Mayer and Stowe
  - Pore Throat and Cavity Distribution - Reverberi Intrusion/Extrusion cycling
  - Pore Number Report - Incremental and Cumulative

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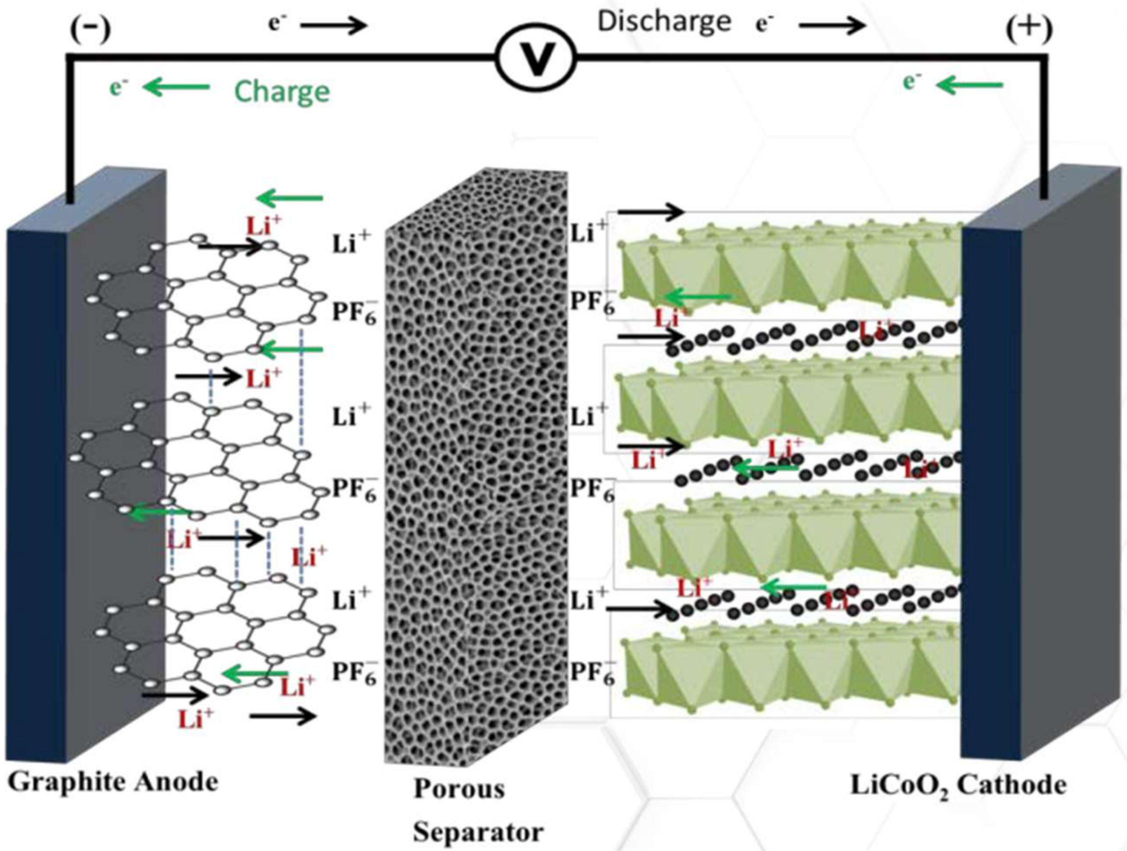
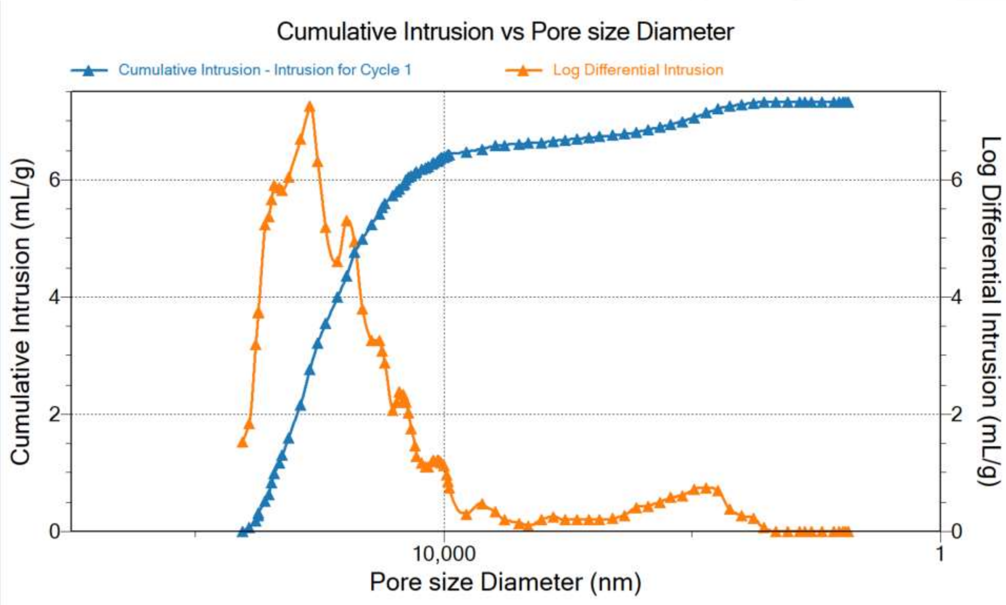
Separator Porosity

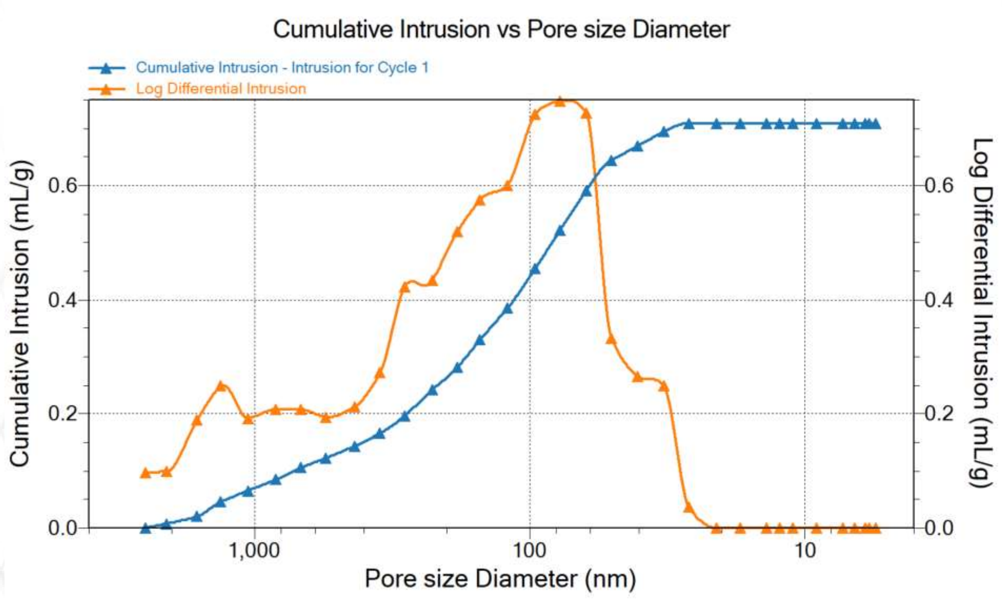


Separator:

- PE, PP, Multilayers of porous thin film
- Separate cathode and anode and Li-ion flow through

Separator Porosity





- Specific pore volume: 0.7 cm^3/g
- Median Pore size: 132 nm
- Percent posority: 40 %

Děkuji za pozornost

www.pragolab.cz

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kolejka@pragolab.cz