COVALENT METROLOGY

Welcome

CHARACTERIZATION OF CLIMATE BENEFICIAL MATERIALS BY GAS SORPTION

SPEAKER:

Martin Thomas, PhD

Lead Scientist,
Anton Paar Quantatec

May 19, 2022 | 11am PT

Anton Paar

COVALENT METROLOGY

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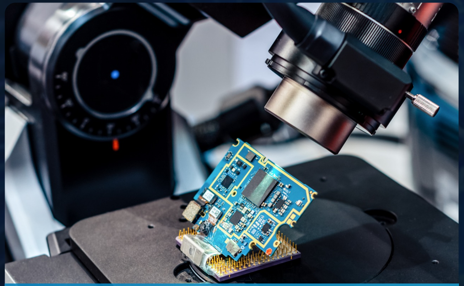
Silicon Valley-based analytical labs and platform delivering quality data and expert analysis for advanced materials and device innovation



Comprehensive Solutions Stack

- 50+ cutting-edge instruments, offering 100+ techniques
- Analytical Services
- Advanced Modeling
- Method Development
- Temporary Staffing Solutions

Affordable and Fast

- Fast Turnaround Times, No Expedite Fees
- Volume Savings
- Instant Access to Data and Reports in Secure Portal

Flexible Business Model

- Custom Consulting Solutions and Certified On-site Support
- Training and Certification on Instrumentation
- Co-op and Tool-Share Opportunities
- Laboratory Audits

Rigaku
JEOL Solutions for Innovation
ThermoFisher SCIENTIFIC
Anton Paar
Asylum Research an Oxford Instruments company
HORIBA Scientific
KEYENCE
TELEDYNE CETAC TECHNOLOGIES Everywhereyoulook
J.A. Woollam
PVA TePla
Digital Surf

Rich Network of Partnerships

- Partner to the World's Leading Instrument Manufacturers and Labs
- Expanding Instrumentation, Lab Connections, and Learning

Who We Are, Who We Serve

- 500+ Clients, 40 – 60 Added / Quarter
- 60+ Employees, 14 PhDs
- Cutting-edge Analytical Capabilities
- Silicon Valley Lab located in Sunnyvale, CA

Covalent Technical Groups & Organization

COVALENT METROLOGY

PCBA, Semiconductor, and Electronic Device Metrology & Failure Analysis

- DPA / Mechanical Cross-section
- Dye & Pry Test
- EBIC / OBIC failure analysis
- Hot Spot Detection
- IR Imaging / Emission Microscopy
- NIR Imaging
- Root-Cause Failure Analysis

Electron Microscopy and Scanning Probe Microscopy

- AFM & Advanced AFM Modes (EFM, KPFM, MFM, PFM)
- Scanning Acoustic Microscopy (SAM)
- SEM (+ EDS)
- FIB-SEM (+ EDS)
- S/TEM (+ EDS / + EELS)
- Nano-indent / Nano-scratch

Optical Microscopy & Spectroscopy

- Chromatic Aberration
- Digital Optical Microscopy
- FTIR and ATR-FTIR
- Laser Scanning Confocal Microscopy
- Spectral Ellipsometry
- UV-Vis-NIR Spectroscopy
- White Light Interferometry

X-Ray Characterization

- X-Ray Diffraction (XRD)
- X-Ray Reflectometry (XRR)
- Micron-spot ED-XRF
- WDXRF
- Micro-computed X-ray Tomography (Micro-CT)
- 2D X-ray Inspection & X-ray Radiography

Elemental / Chemical Composition Analysis

- EPMA
- GD-OES
- GC-MS
- ICP-MS and LA-ICP-MS
- Raman Microscopy & Spectroscopy
- NMR (1D or 2D; solid / liquid)

Particle Analysis

- Dynamic Light Scattering (DLS)
- Laser Diffraction Particle Size Analysis (PSA)
- Particle Zeta Potential

Material Property Characterization

- DSC
- DMA & TMA
- Rheometry
- TGA
- Surface Zeta Potential
- Porometry / Porosity
- Gas Adsorption
- Gas Pycnometry
- Foam Density
- Tap Density

Surface Spectroscopy Analysis

- Dynamic-SIMS
- ToF-SIMS (Static-SIMS)
- Ion Scattering Spectroscopy (ISS)
- Ultraviolet Photoelectron Spectroscopy (UPS)
- X-ray Photoelectron Spectroscopy (XPS)

Covalent Partners

Anton Paar

- **Partnership with Anton Paar initially announced in May, 2020**
  - Established new Anton Paar Demonstration Facility in Covalent's Silicon Valley Laboratory to expand industry access and develop new analytical applications
  - **Initial instruments installed include:** MCR702 Rheometer / DMA, SurPASS 3, and Litesizer 500; STeP 6 Nanoindentation platform added in Fall 2021
- Anton Paar and Covalent later expanded partnership to **deliver industry-leading porous materials and powders analysis throughout the West Coast**
  - Anton Paar acquired Quantachrome in 2018 and in 2021 added new instrumentation to the shared Demo Facility at Covalent
  - **Instruments include:** Autosorb iQ C-XR-XR with CryoSync accessory, Ultrapyc 5000 Micro, Porometer 3G, and DualAutoTap system
  - **NEW Upgraded Nova 800 BET (Gas Adsorption) Analyzer** - for true surface area measurement and pore size distribution

Other Covalent Partners

Rigaku

JEOL Solutions for Innovation

ThermoFisher SCIENTIFIC

KEYENCE

PVA TePla

TELEDYNE CETAC TECHNOLOGIES Everywhereyoulook™

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Introducing...

COVALENT METROLOGY

Martin Thomas, PhD

Lead Scientist
Anton Paar Quantachrome

- Product Manager
- 30 Years with Quantachrome QuantaTec
- Obtained 10 patents in the field of porous materials analysis
- Co-author of "*Characterization of Porous Solids and Powders Surface Area, Pore Size, and Density*" (Springer)

Anton Paar

CHARACTERIZATION OF CLIMATE BENEFICIAL MATERIALS BY GAS SORPTION

WHICH MATERIAL PROPERTIES CAN GAS SORPTION BE USED TO MEASURE?

WHY IS GAS SORPTION ANALYSIS ADVANTAGEOUS FOR PRODUCT RESEARCH RELEVANT TO CLIMATE CHANGE AND SUSTAINABILITY?

HOW DOES GAS SORPTION ANALYSIS WORK?

WHAT ARE SOME ADVANCED MODES OF GAS SORPTION ANALYSIS THAT HAVE EMERGED RECENTLY?

WHICH MATERIAL PROPERTIES CAN GAS SORPTION BE USED TO MEASURE?

- Surface Area
- Pore Volume
- Pore Size Distribution
- Absorption Capacity

FOR WHAT TYPES OF MATERIALS?

- Battery cathode and anode powders
- Adsorbents for air and water purification
- Catalysts for pollution control
- Greenhouse gas storage materials
- Hydrogen storage materials

WHY IS GAS SORPTION ANALYSIS ADVANTAGEOUS FOR PRODUCT RESEARCH RELEVANT TO CLIMATE CHANGE AND SUSTAINABILITY?

- Surface area is the quantitative expression of the extent of the interface between a solid and its surrounds… be it an adsorber of a toxic gas, or the electrodes of a lithium battery

WHY IS GAS SORPTION ANALYSIS ADVANTAGEOUS FOR PRODUCT RESEARCH RELEVANT TO CLIMATE CHANGE AND SUSTAINABILITY?

- Surface area can further be qualified as catalytically active surface area – essentially exactly how efficient is your emission control catalyst.

WHY IS GAS SORPTION ANALYSIS ADVANTAGEOUS FOR PRODUCT RESEARCH RELEVANT TO CLIMATE CHANGE AND SUSTAINABILITY?

- Pore volume represents the adsorption capacity primarily in high pressure applications where adsorption is not just 2-dimensional (limited to the surface) but 3-dimensional!

CARBON CAPTURE AND STORAGE

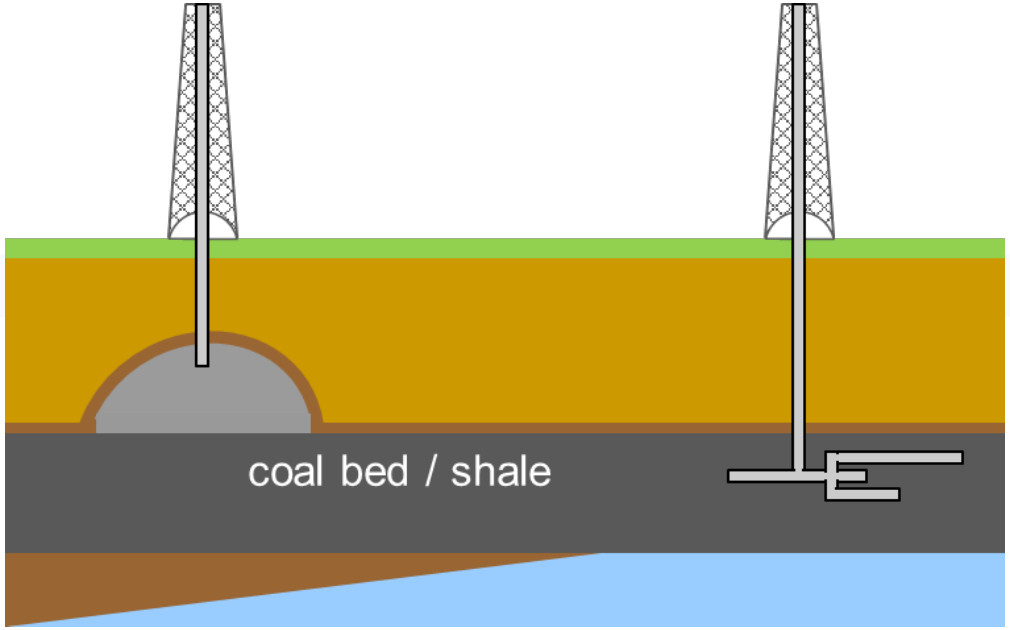
Functional solids for adsorption of CO_2 and CH_4:

Geostores:

- Oil/gas bearing rock (shale)
- Coal

Synthetic carbons

Metal organic frameworks (MOFs)



WHY IS GAS SORPTION ANALYSIS ADVANTAGEOUS FOR PRODUCT RESEARCH RELEVANT TO CLIMATE CHANGE AND SUSTAINABILITY?

- Pore size distribution controls diffusion of fluids and reactants in and out of the pore structure, and can impart a molecular sieving effect.

WHY IS GAS SORPTION ANALYSIS ADVANTAGEOUS FOR PRODUCT RESEARCH RELEVANT TO CLIMATE CHANGE AND SUSTAINABILITY?

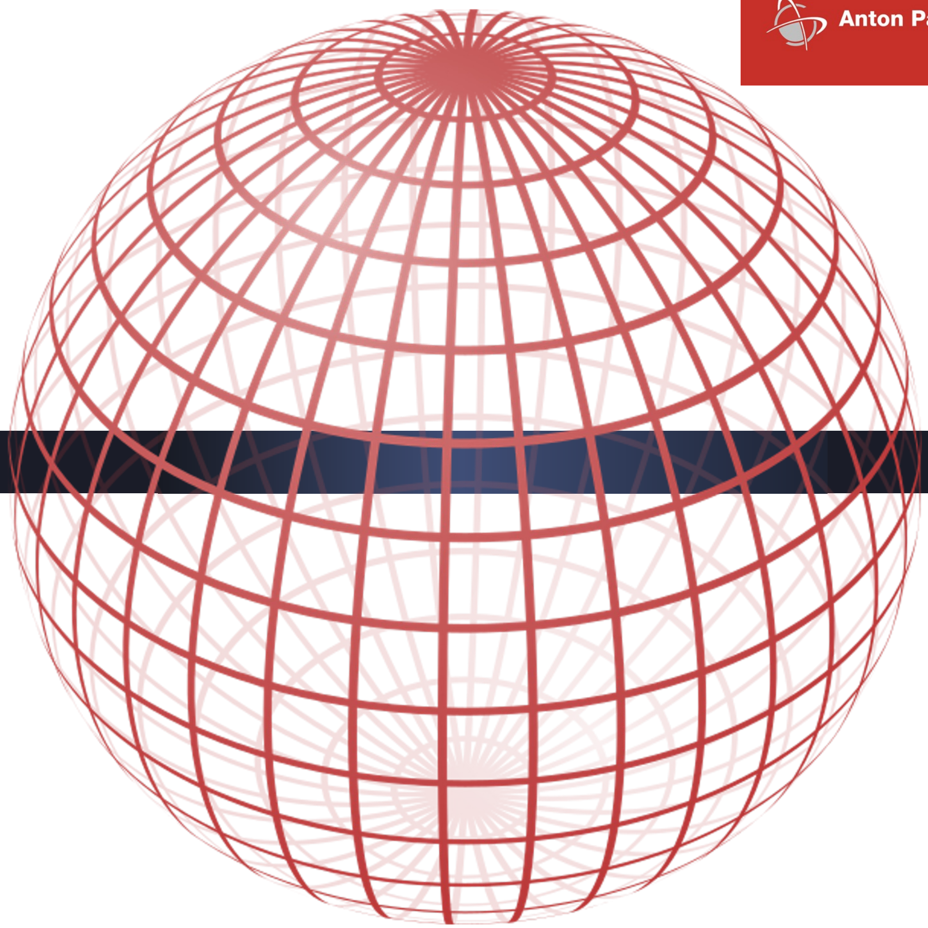
- **Ab**sorption tells us how much hydrogen, for example, can be reversibly stored as a chemical compound in certain hydride forming metals.

CRYOGENIC ANALYSIS FOR CLEAN **BATTERY** MATERIALS

REACTIVE GAS CHEMISORPTION TO ANALYZE **ENVIRONMENTAL CATALYSTS**

HIGH PRESSURE GAS SORPTION TO PROBE **GREENHOUSE GAS SEQUESTRATION** MATERIALS…

…AND **FUEL CELL AND HYDROGEN STORAGE** MATERIALS



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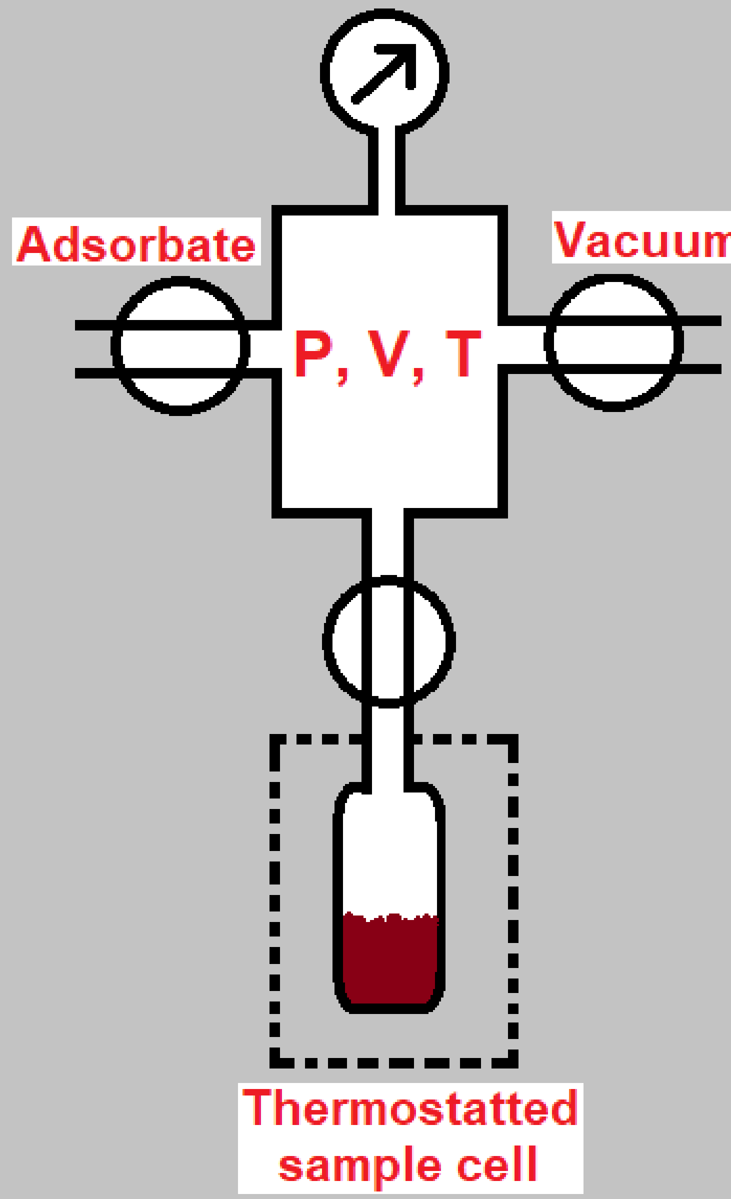
GAS SORPTION ESSENTIALS

HOW DOES GAS SORPTION WORK?

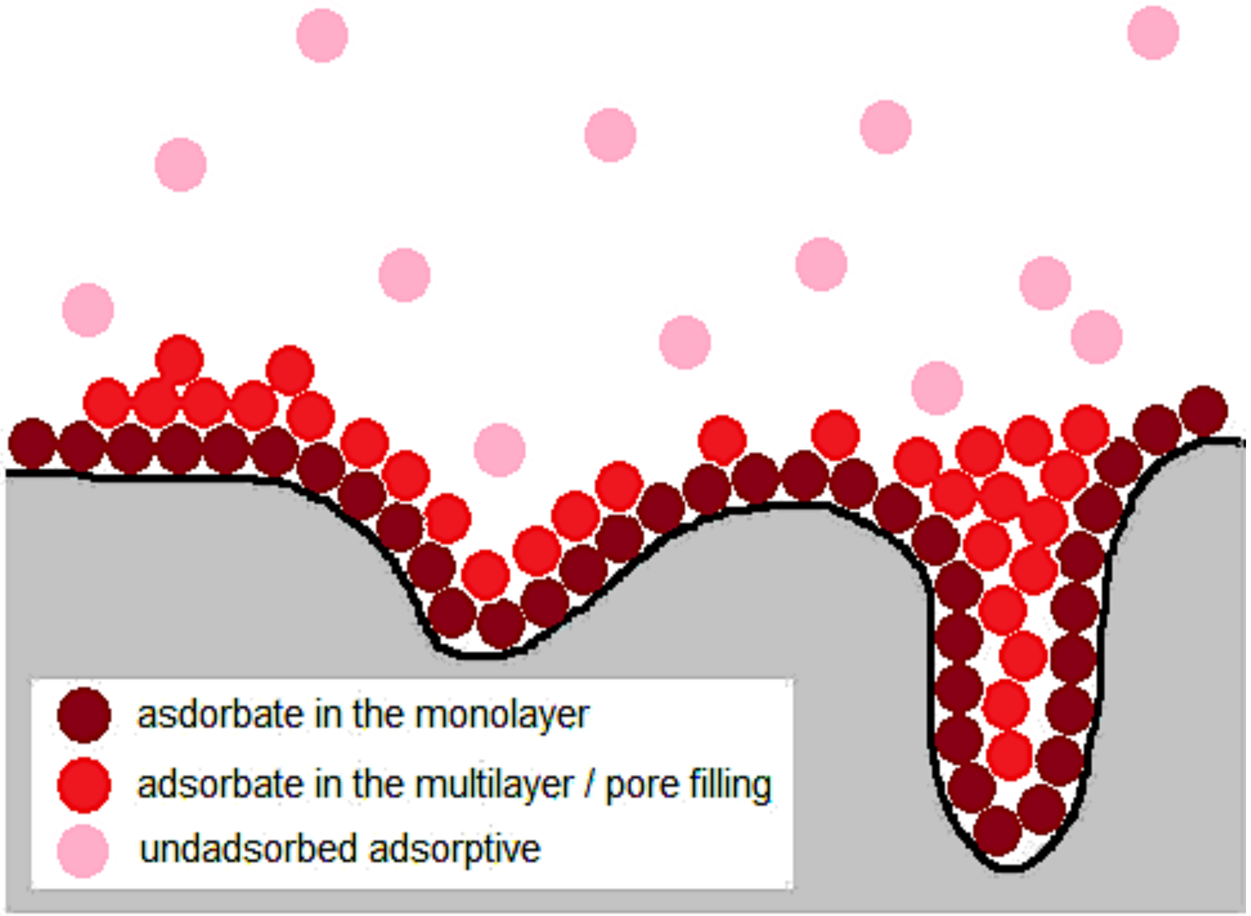
- Physisorption
  (inert gases, low temperatures)
- Chemisorption
  (reactive gases, moderate temperatures)
- Absorption
  (solubility, bulk compound formation)

- Vacuum-volumetric apparatus
- Pressure
- Temperature



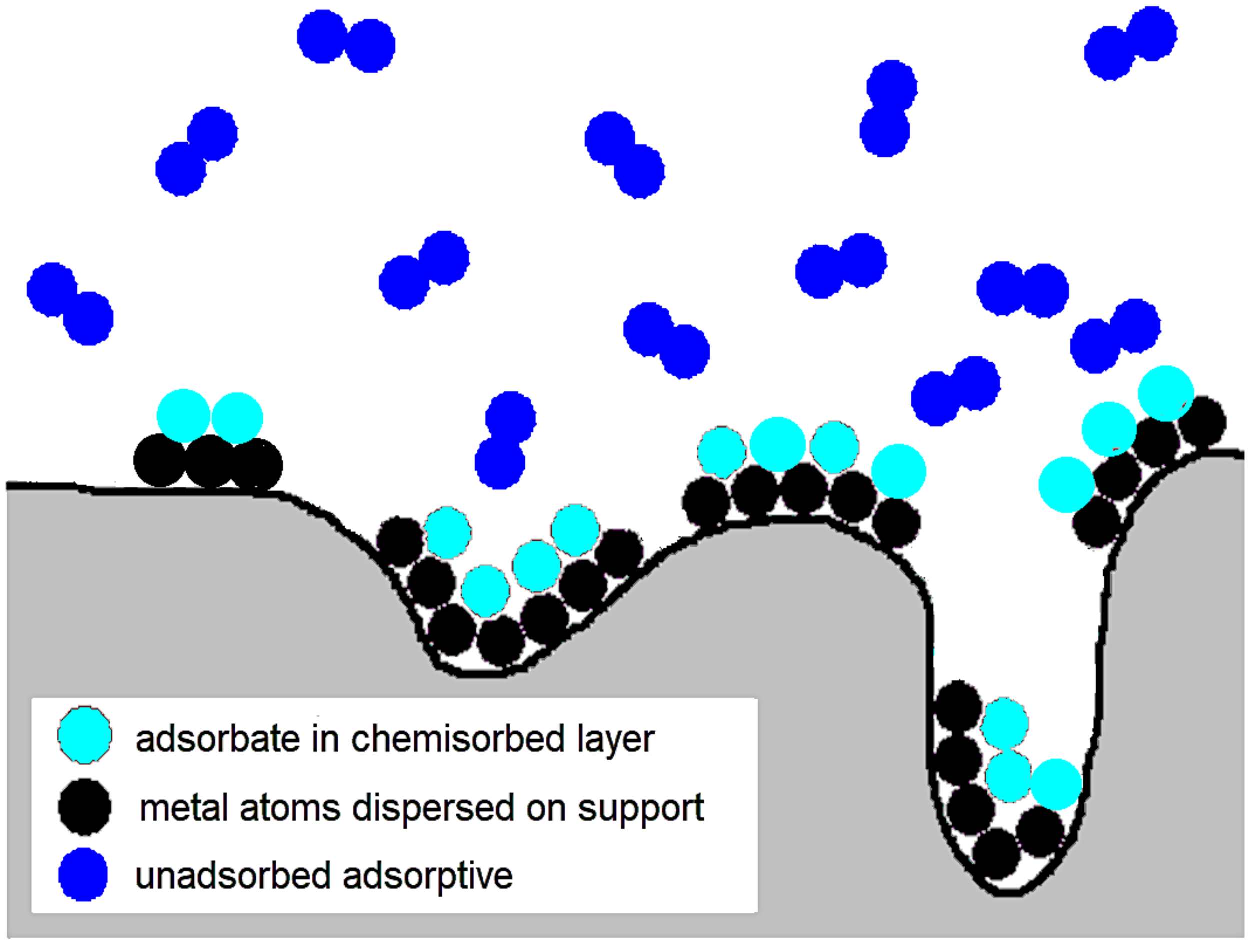
WHAT IS PHYSISORPTION?

- A weak & reversible physical interaction between a solid and an adsorbate (gas or vapor).
- Used to measure surface area, pore size and pore volume.



WHAT IS CHEMISORPTION?

- A strong and largely irreversible reaction between a solid and an adsorbate (gas or vapor).
- Used to measure the extent of catalytically active area

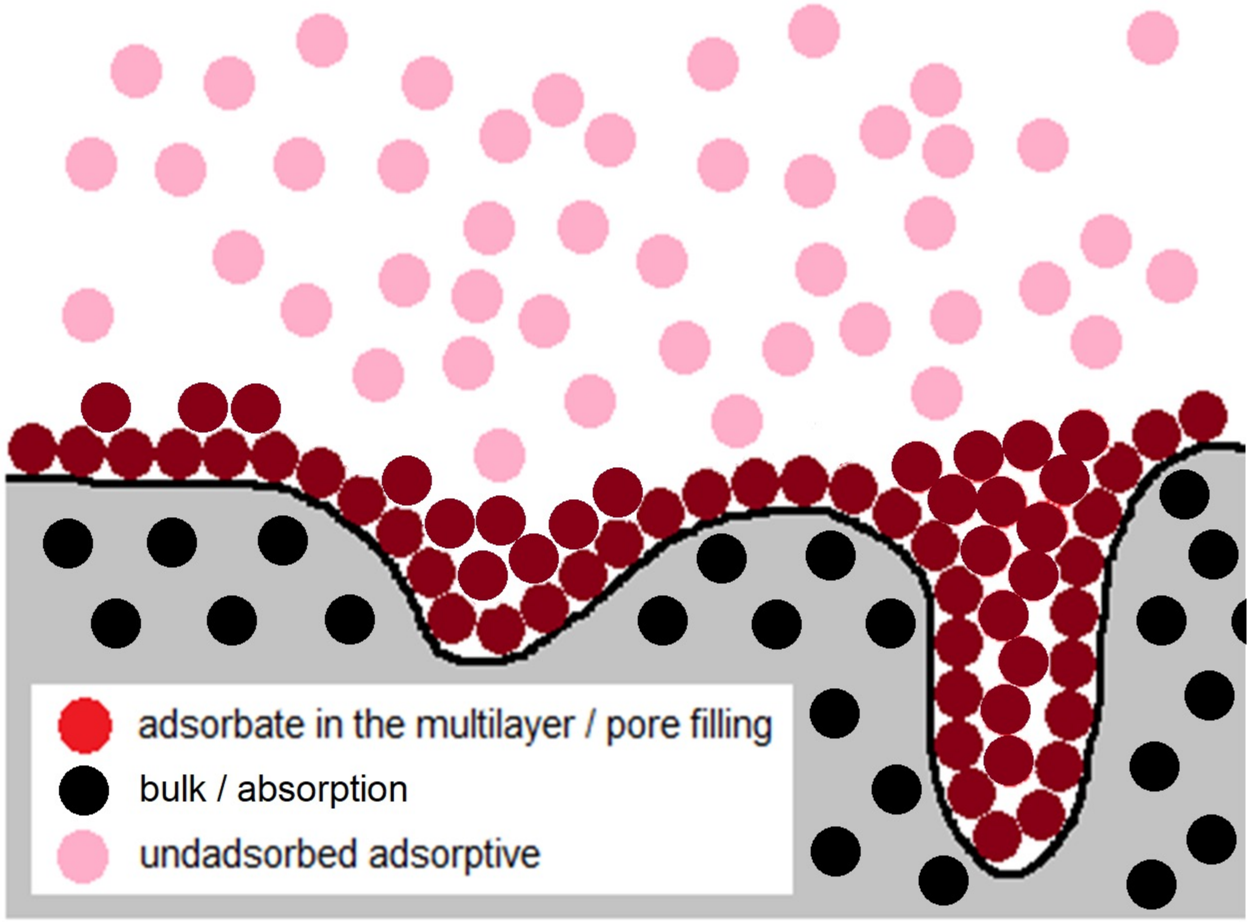


WHAT IS HIGH PRESSURE SORPTION?

- Can be physisorption, can be chemical absorption (bulk compound)

- High pressures needed to overcome super-ambient or supercritical temperatures

- Usually corresponds to process/storage temperatures



RECOMMENDATIONS

Material	Application	Property	Method	Gas
Mixed metal oxides	Battery cathode	Surface area	Physisorption	N_2 @ 77K
Graphite	Battery anode	Surface area	Physisorption	N_2 @ 77K
Activated carbon, zeolites	Gas/water purification	Surface area and micropore size distribution	Physisorption	N_2 @ 77K Ar @ 87K CO_2 @ 273K
Supported metal catalysts	Emission control, pollution control	Active metal area	Chemisorption	H_2, CO ~300K
Coal, shale	Carbon(CO_2/CH_4) sequestration	Micropore volume	High pressure sorption	CO_2/CH_4 >300K
Activated carbons	Hydrogen storage	Micropore volume	High pressure sorption	$H_2 \leq$ 300K
Metals/alloys	Hydrogen storage	Hydride formation	High pressure sorption	H_2 ~300K

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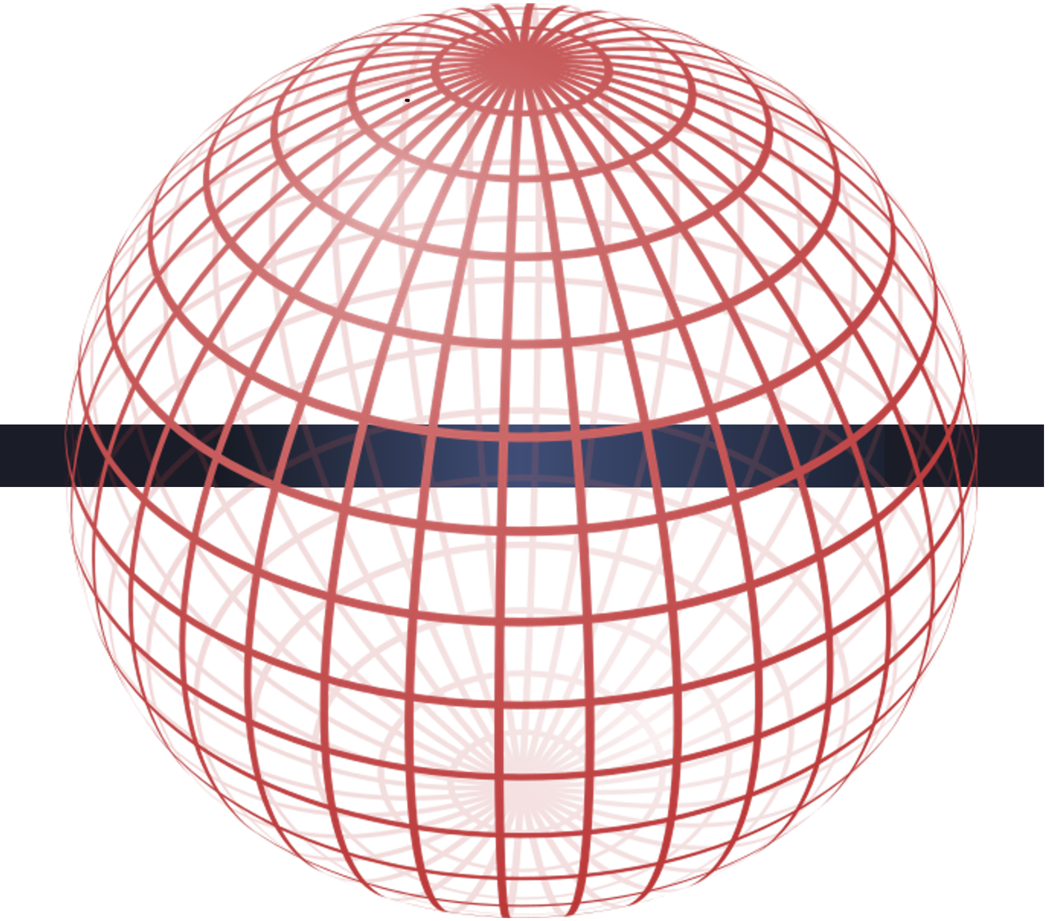


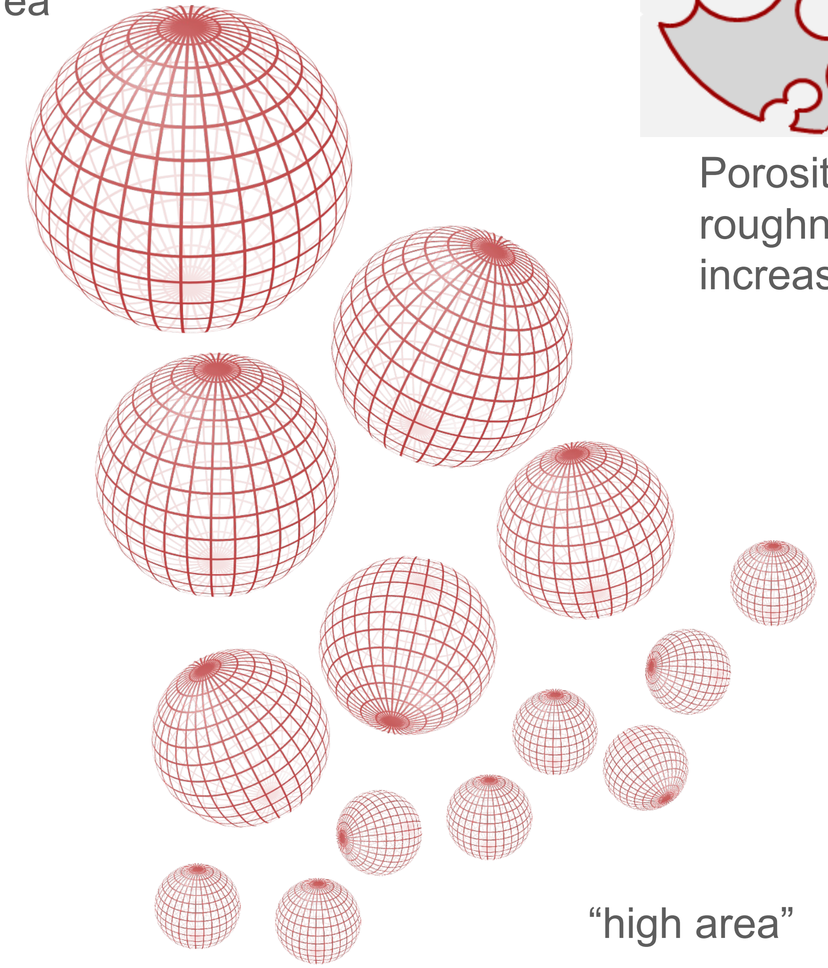
SURFACE AREA AND PORE SIZE ESSENTIALS

SURFACE AREA

- Surface Area is the **extent of the interface** through which a solid quantitatively interacts

- Surface area is **created** by division of particles (size reduction) and the generation of porosity (drying, decomposition).

“low area”



“high area”

Porosity and roughness increase area

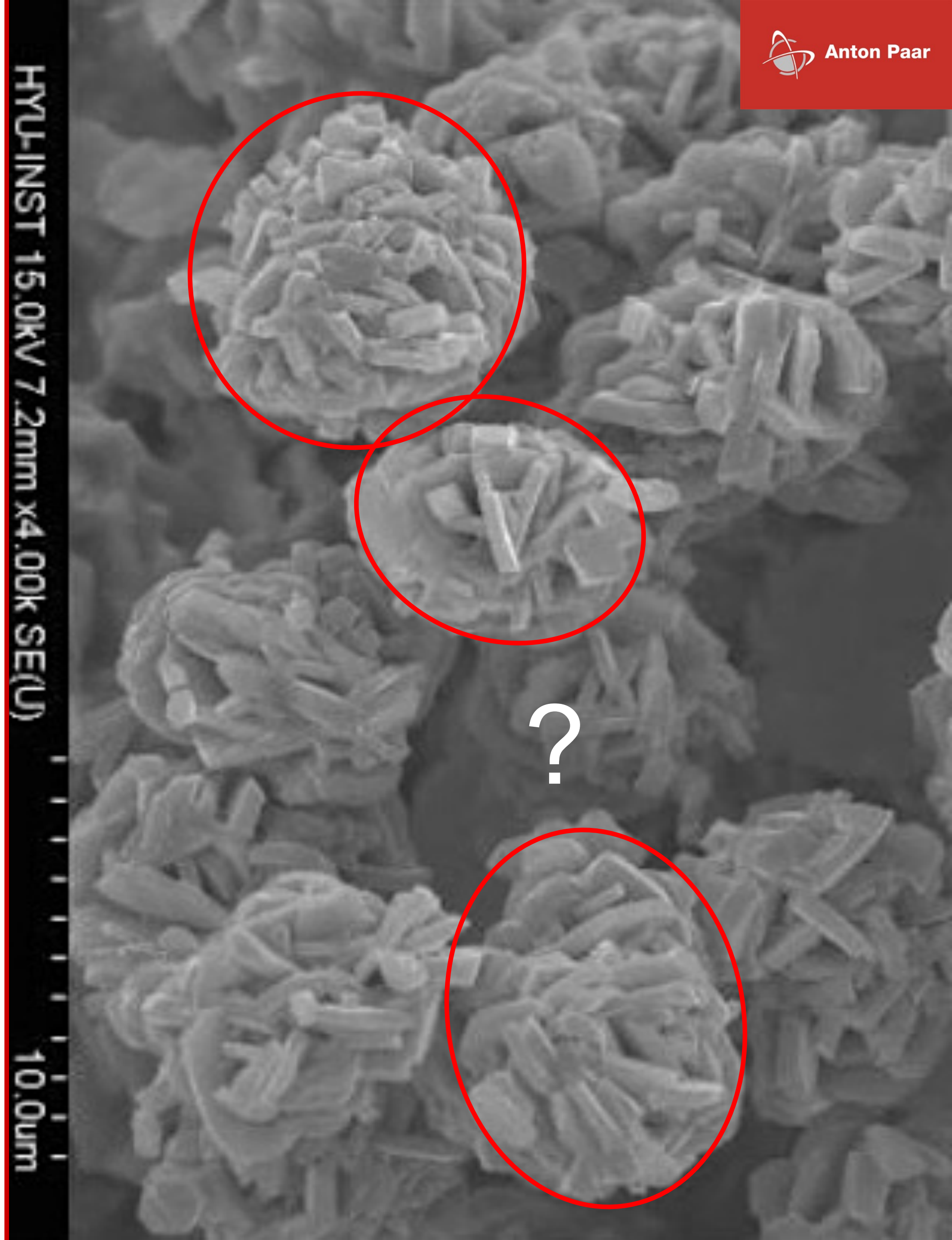
SURFACE AREA BATTERIES, BATTERY MINERALS

- More area = more interfacial current
- More area = more side reactions and ageing

$$S = \frac{6}{\rho D} \quad ?$$

Surface area D of spherical particles calculated from diameter D

Realistic surface area from *gas adsorption*

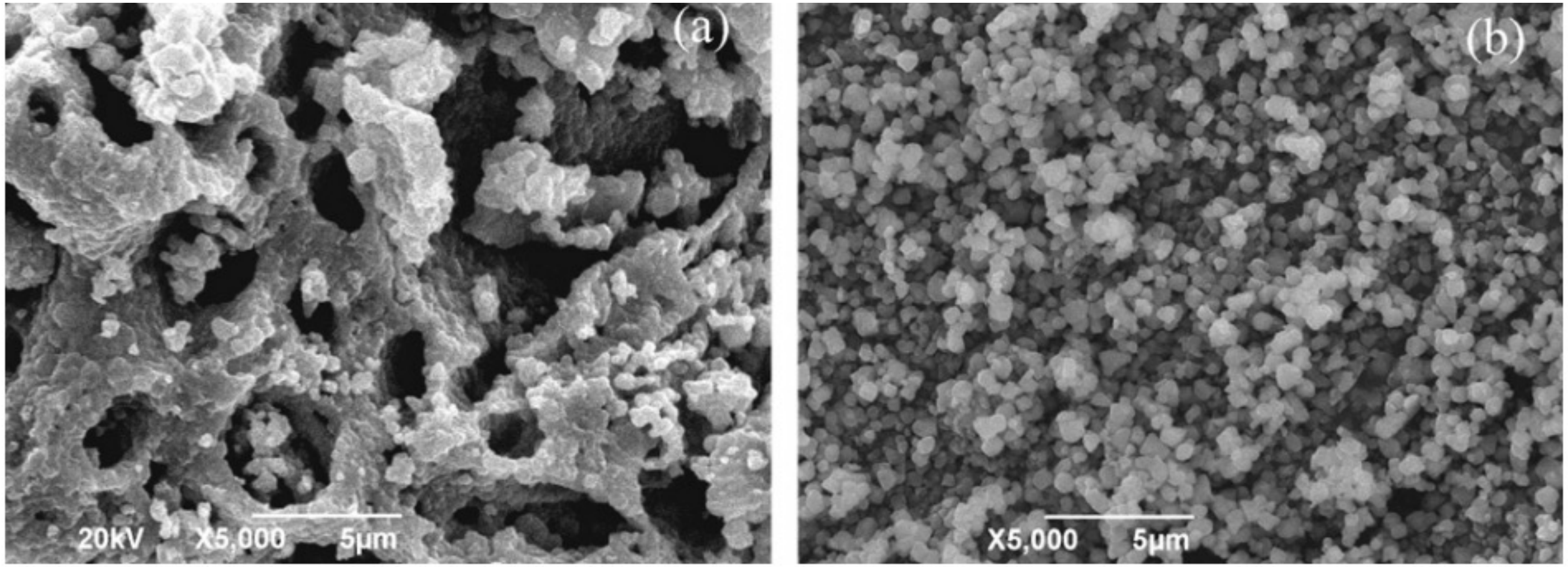


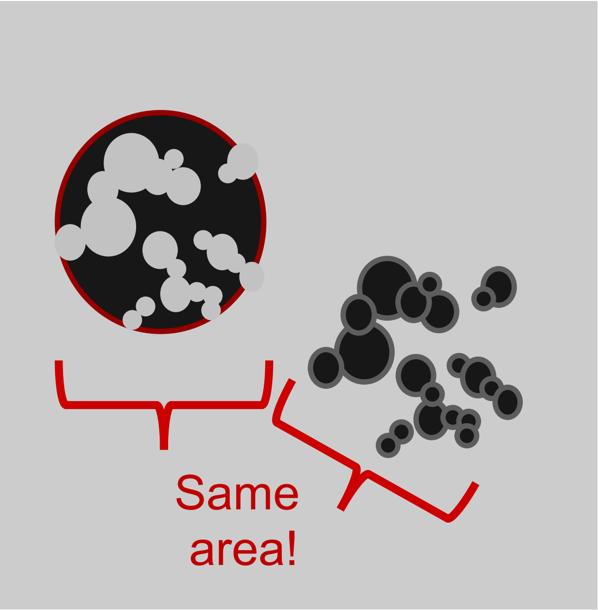
J. Am. Chem. Soc. 2011, 133, 9, 3139–3143 doi.org/10.1021/ja110522x

INTERNAL/EXTERNAL SURFACE AREA

Batteries, Battery minerals

macroporous $LiNi_{0.5}Mn_{0.5}O_2$ (8.87 m^2g^{-1}) from solution vs solid state reaction method (2.93 m^2g^{-1})



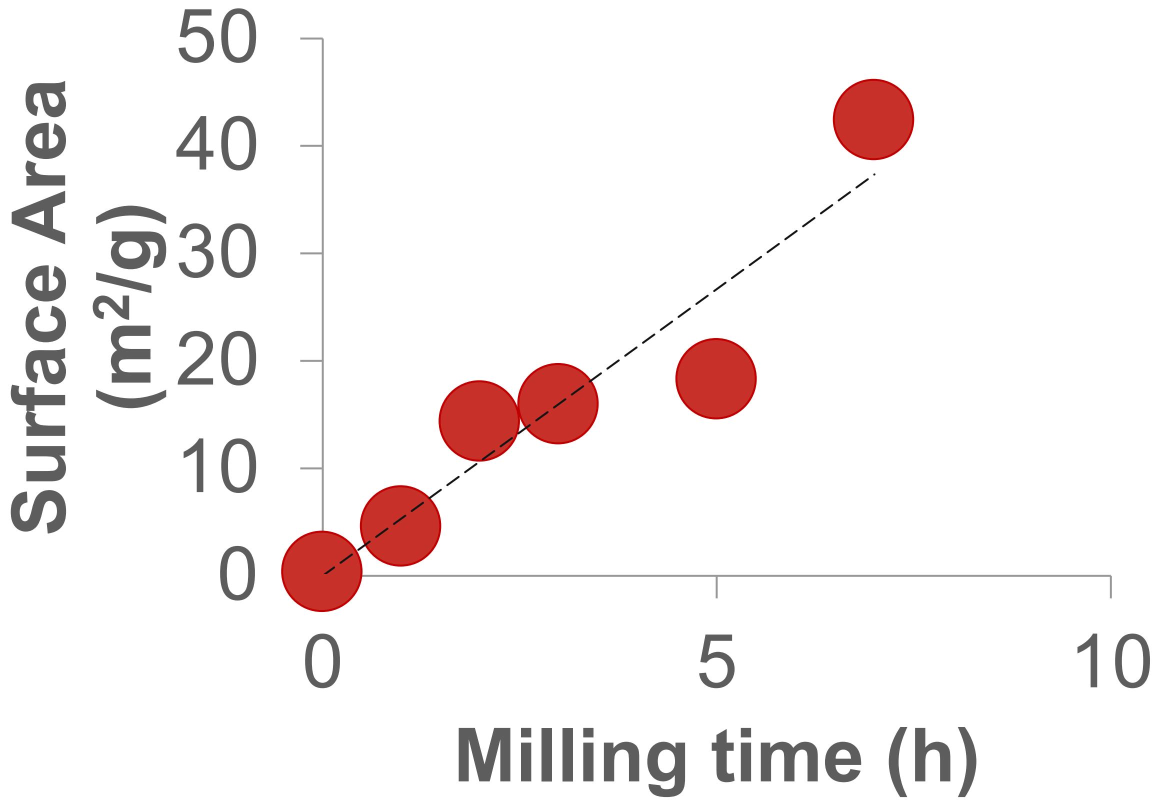


Electrochimica Acta 56 (2011) 4065–4069 doi:10.1016/j.electacta.2010.12.108

CATHODE SURFACE AREA

$LiCoO_2$

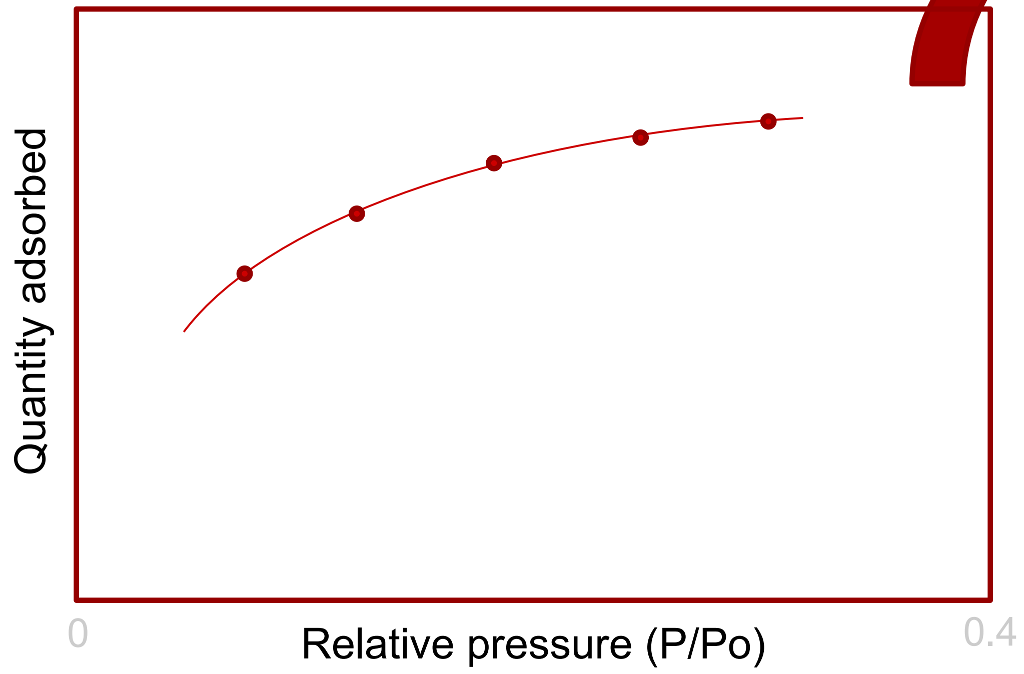
- Higher surface area significantly reduces thermal stability
- Activation energy of cathode decomposition decreases with increasing surface area
- High surface area materials react more exothermally with electrolyte

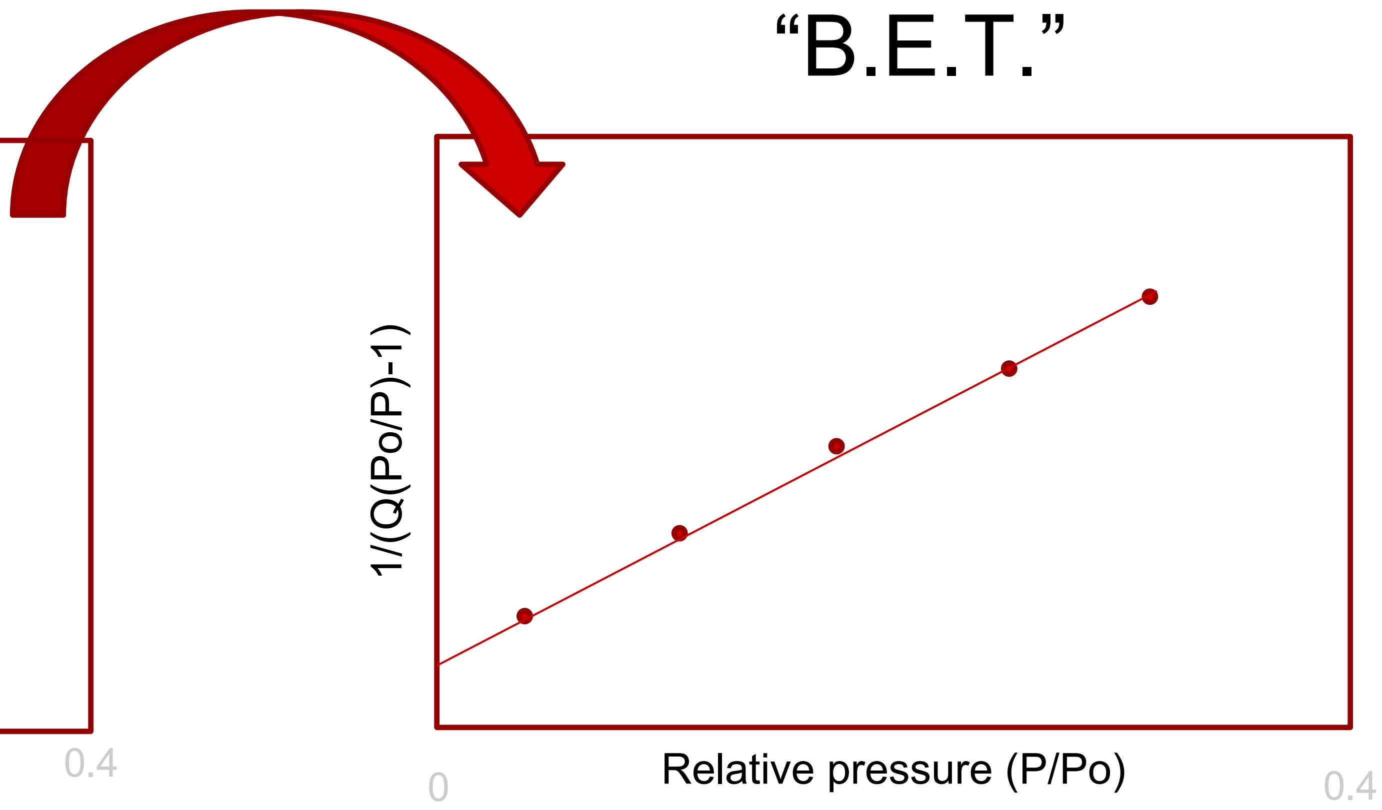


Journal of Power Sources 257 (2014) 286-292 dx.doi.org/10.1016/j.jpowsour.2014.01.116

EXPERIMENTAL DATA – CALCULATION MODEL – B.E.T. AREA

- Isotherm > monolayer > area

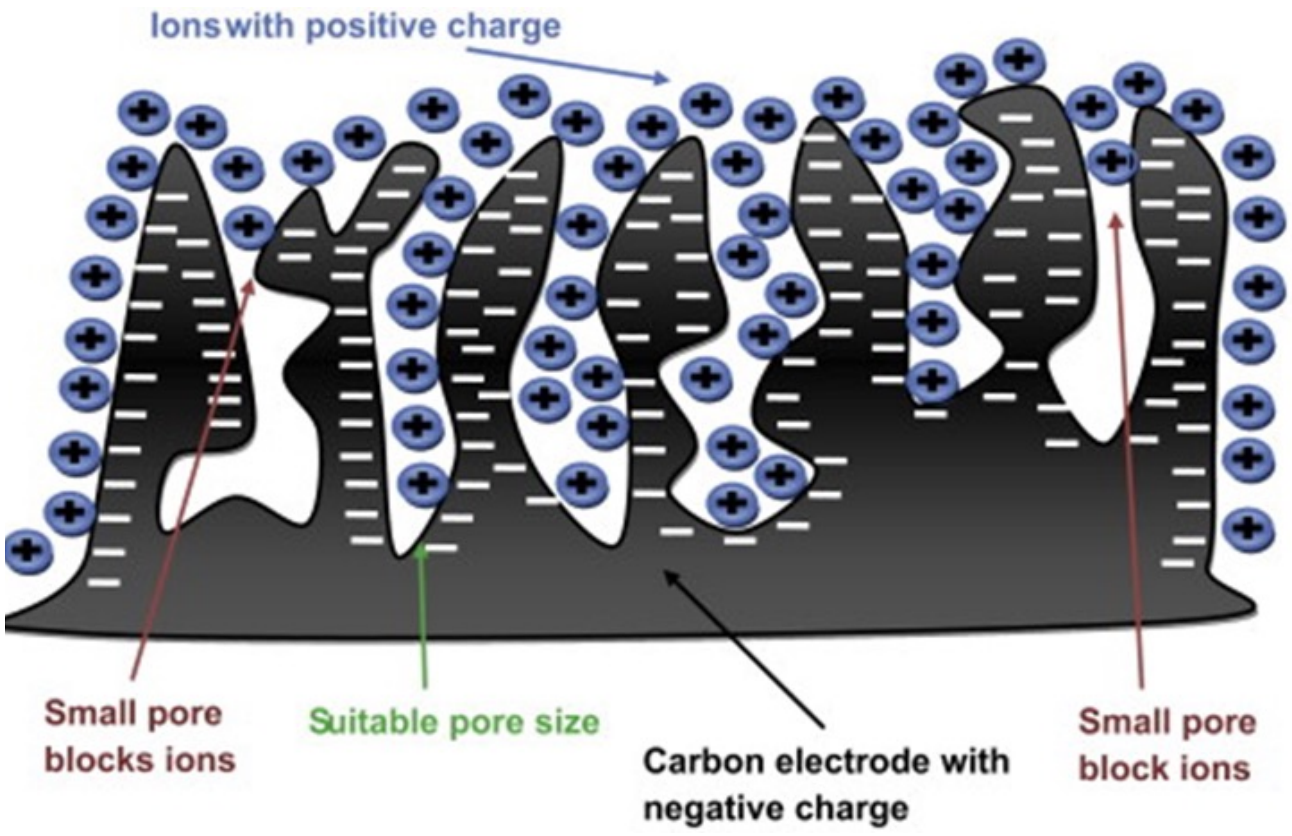




Brunauer, Stephen; Emmett, P. H.; Teller, Edward (1938). *J. Am. Chem. Soc.* **60** (2): 309–319.

WHY PORE SIZE DISTRIBUTIONS?

= Pore volume and how it is distributed amongst pores of different size



- Pores create surface area
- Pore size and network controls fluid migration e.g. *reactants in and products out of a catalyst particle*
- Smaller pores decrease diffusion kinetics
- Smallest pores restrict access completely

XinLia and Bingqing Wei, Nano Energy Volume 2, Issue 2, March 2013, Pages 159-173

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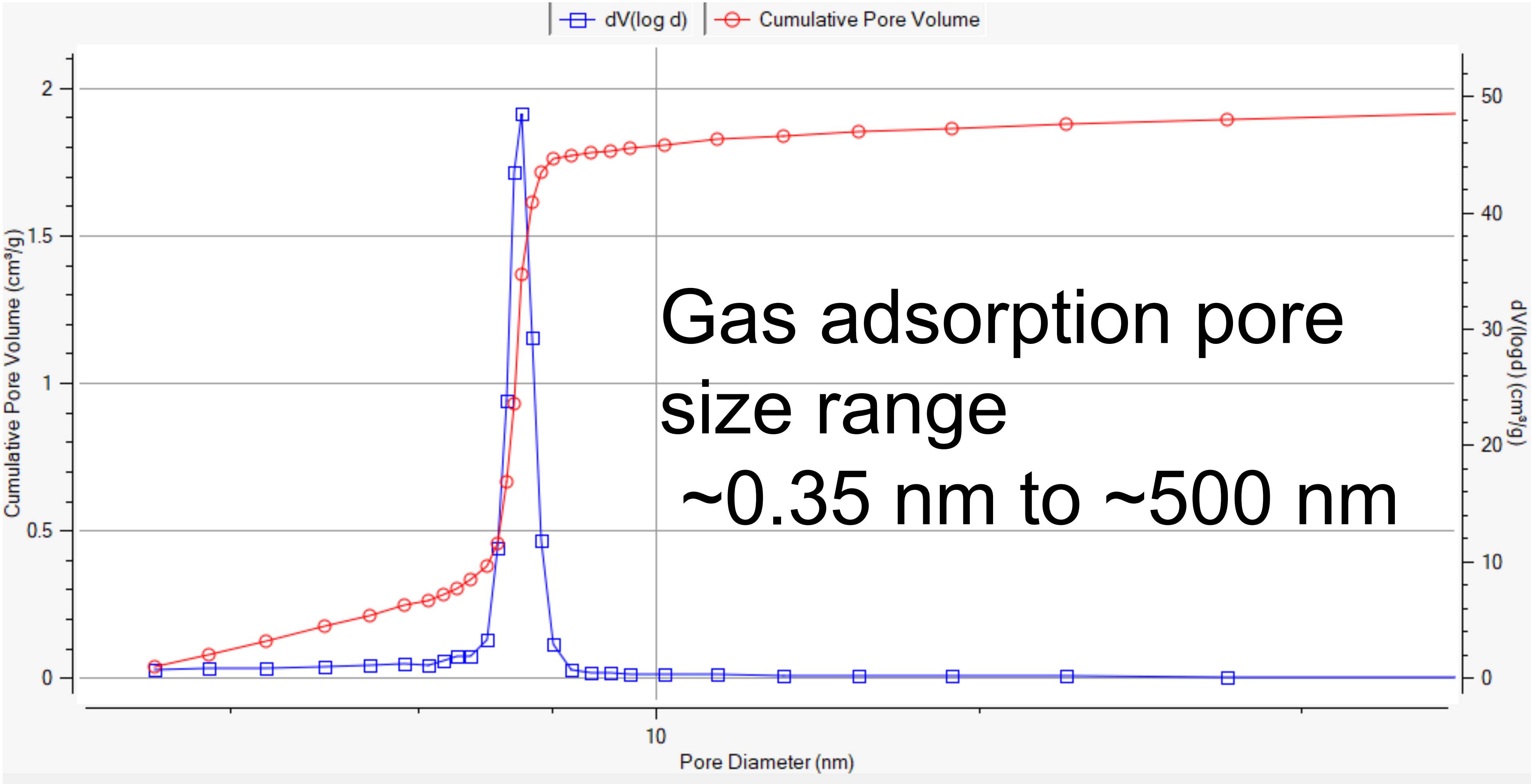
PORE SIZE AND VOLUME

Are expressed both as cumulative and derivative pore size distributions



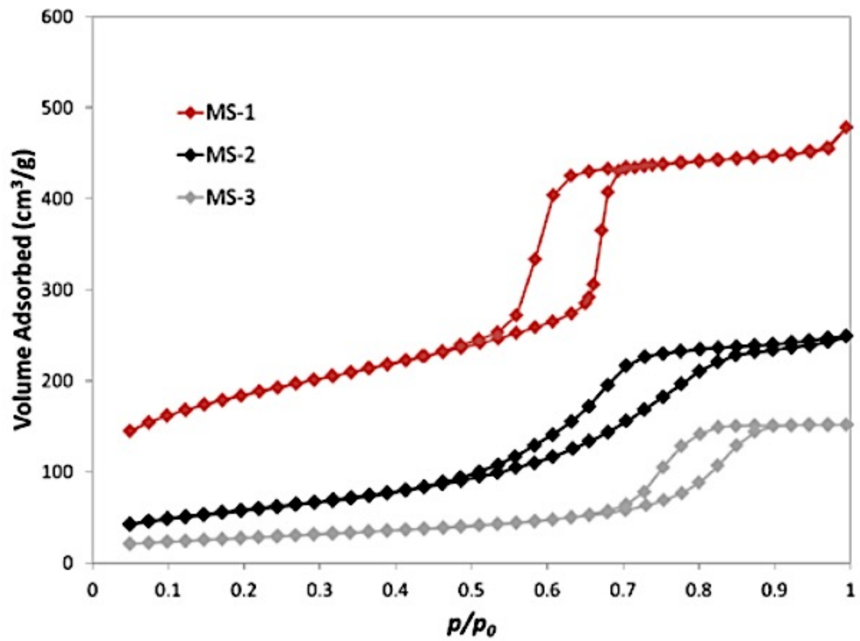
PORE SIZE

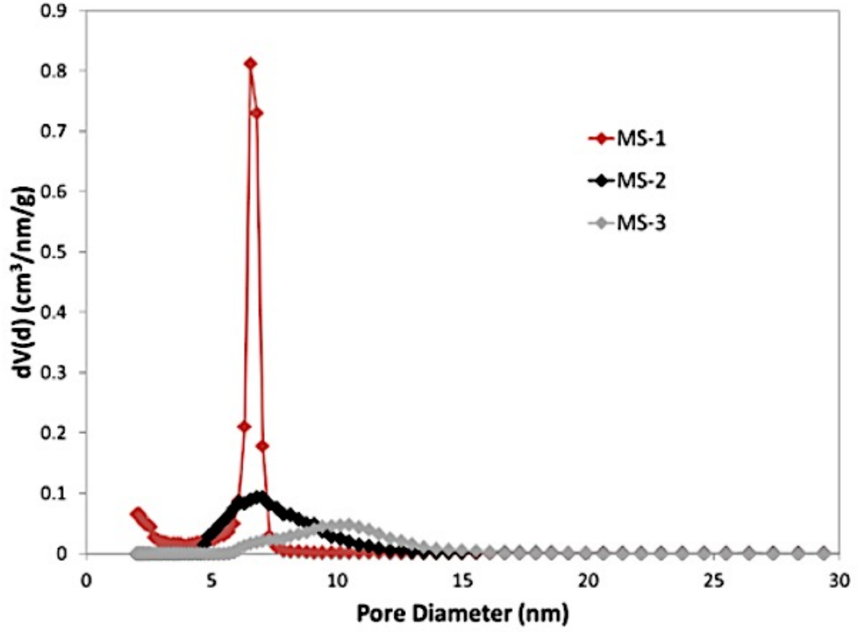
Catalyst supports

- Silica (MS-1)
- Alumina (MS-2)
- Titania (MS-3)

Nitrogen, 77.4K	MS-1	MS-2	MS-3
BET surface area (m^2/g)	662	211	98
Total pore volume (mL/g)	0.705	0.376	0.235

Mesoporous Catalyst Supports – Nova x00 Series, Anton Paar Application Report (2022)





ACTIVATED CARBON

- Micropores
- CO_2, 273K
- NLDFT
- Pore size merge

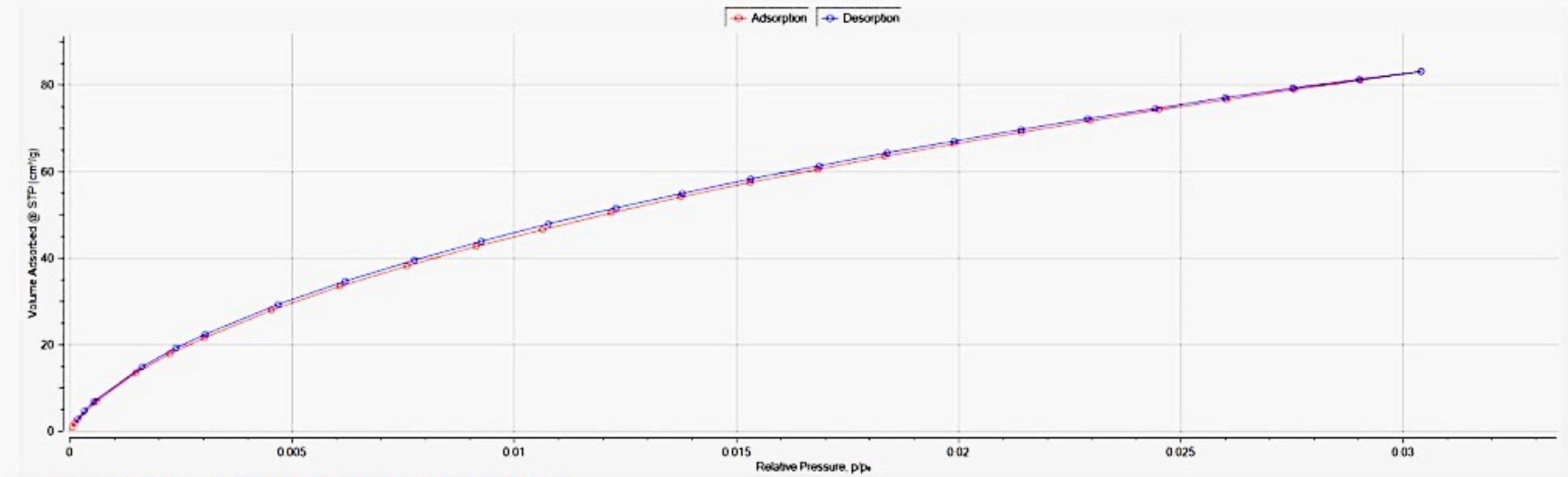


Figure 1: CO_2 (273 K) isotherm on activated carbon

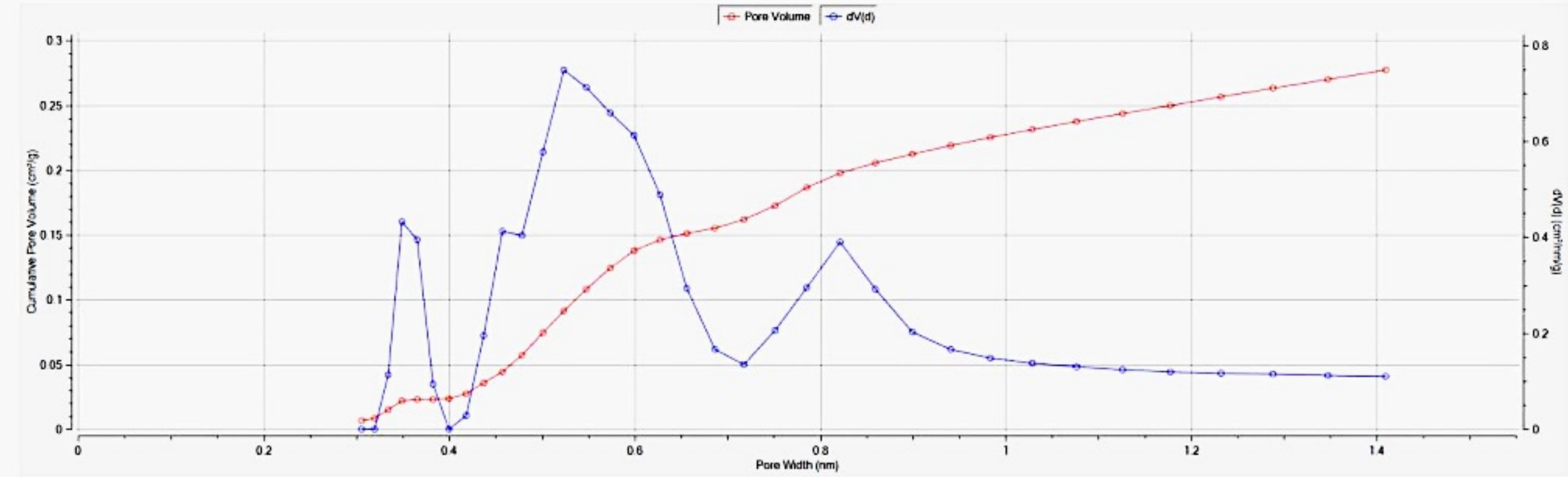
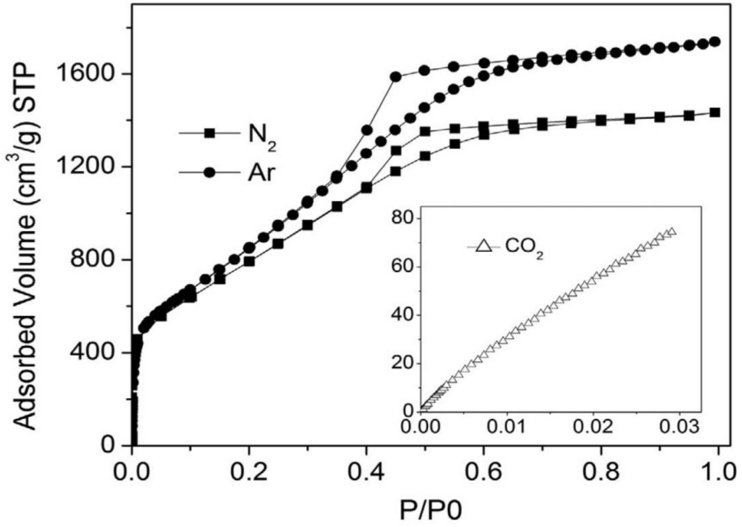
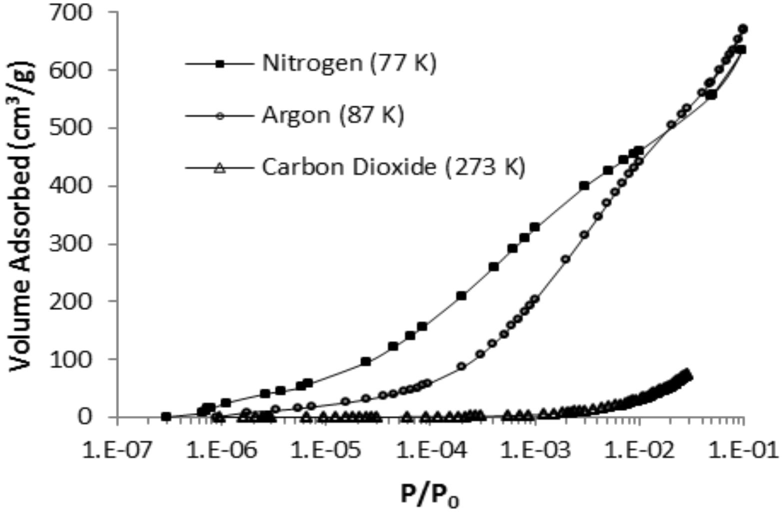


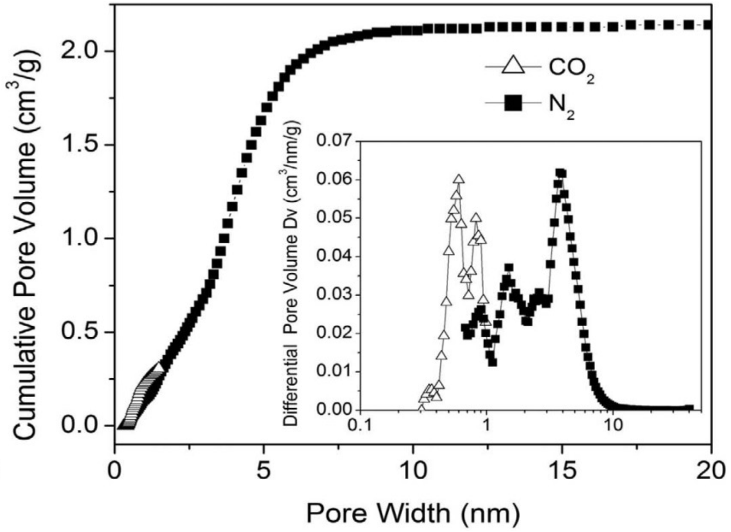
Figure 2: NLDFT pore size distribution calculated from the CO_2 (273 K) isotherm

Activated Carbon – Micropore Size Distribution using CO2 Adsorption – Nova x00 Series, Anton Paar Material Brief (2022)

SUPERCAPACITOR CARBON – GRAPHENE OXIDE: N_2 (77 K) AND CO_2 (273 K) ARE COMPLEMENTARY

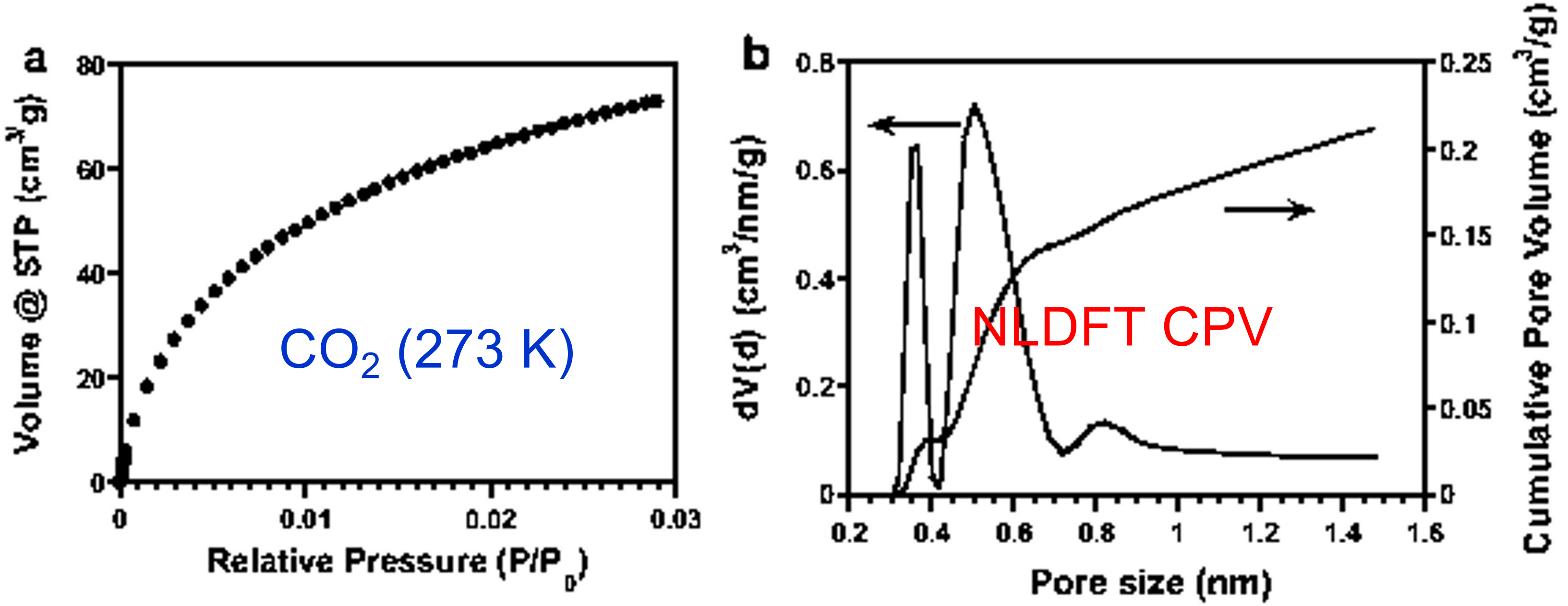






Zhu, Y.; Murali, S.; Stoller, M.D.; Ganesh, K.J.; Cai, W.; Ferreira, P.J.; Pirkle, A.; Wallace, R.M.; Cychosz, K.A.; Thommes, M.; Su, D.; Stach, E.A.; Ruoff, R.S. *Science* **2011**, *332*, 1537-1541

CO_2 MICROPORE ANALYSIS OF LI/S BATTERY SUPPORT



- Microporous carbon support for Li/S batteries
- Only small micropores (< 1 nm) present in this carbon
- Therefore, only S_2 (0.4 nm) can be confined within the pores and larger $S_{4\text{-}8}$ molecules (> 0.5 nm) are excluded

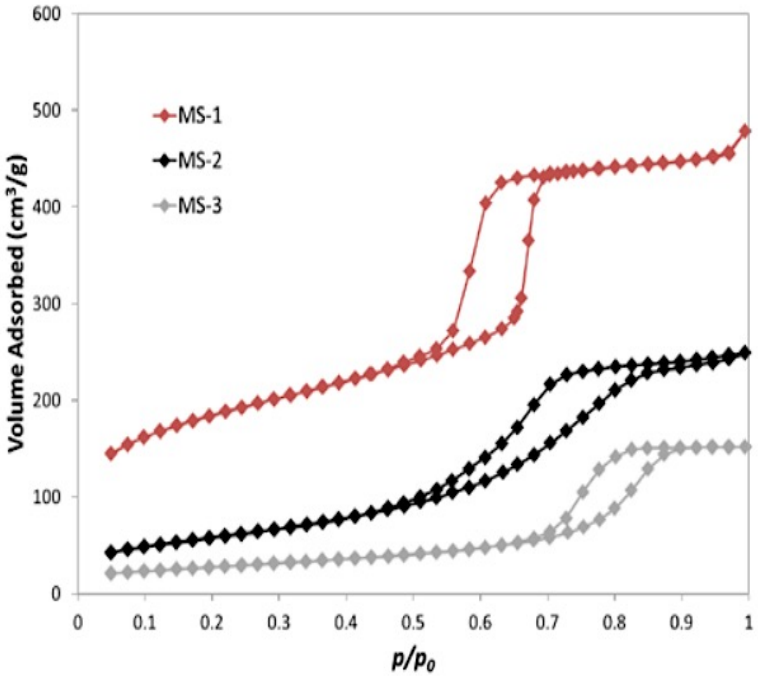
Xu, Y.; Wen, Y.; Zhu, Y.; Gaskell, K.; Cychosz, K.A.; Eichhorn, B.; Xu, K.; Wang, C. *Adv. Funct. Mater.* **2015**, *25*, 4312-4320

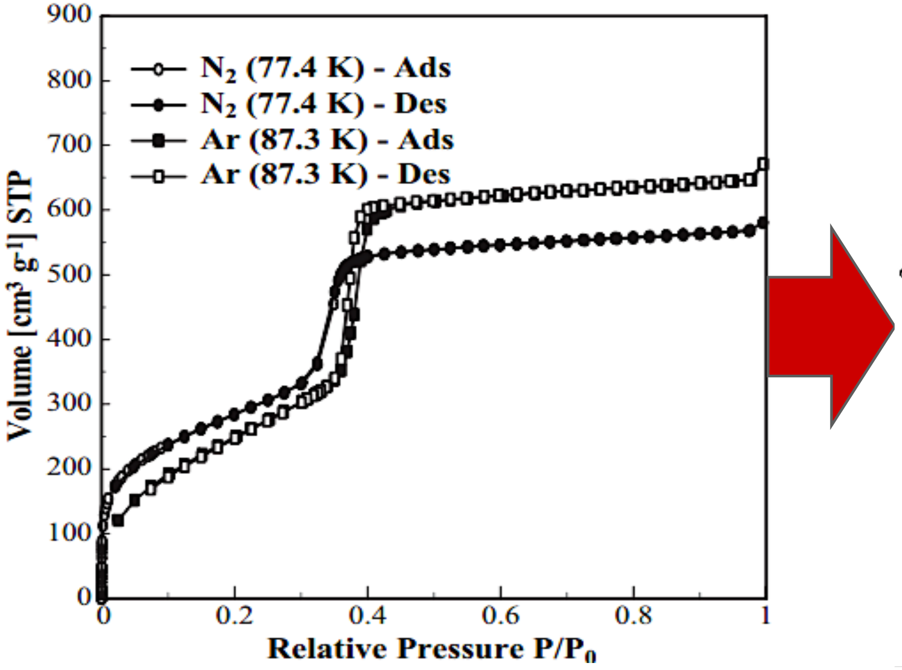
PORE SIZE CALCULATIONS

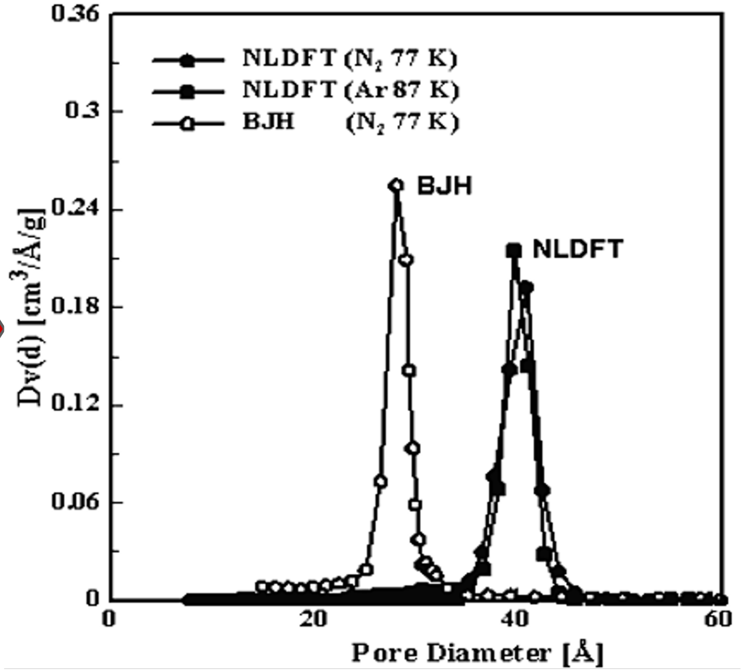
Pore size $\propto p/p_0$

Micropores fill as low as 1×10^{-7} p/p_0, mesopores > 0.3 p/p_0

Traditional: BJH, Modern: DFT, GCMC



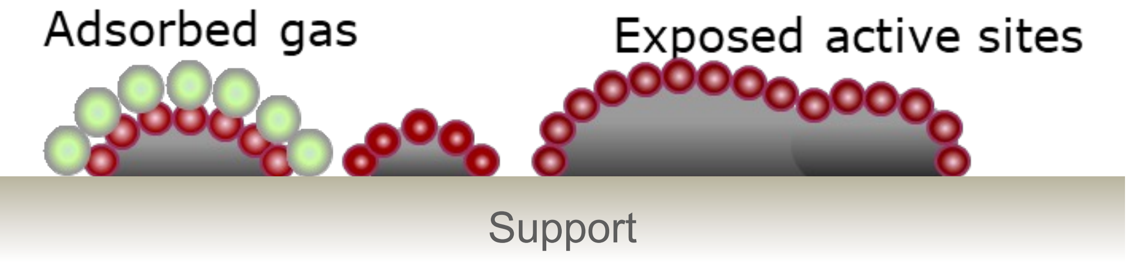




M. Thommes, K.A. Cychosz, A.V. Neimark, “Advanced Physical Adsorption Characterization of Nanoporous Carbons”, in: J.M.D. Tascon, Novel Carbon Adsorbents, Elsevier Ltd, 2012, pp. 107–145.

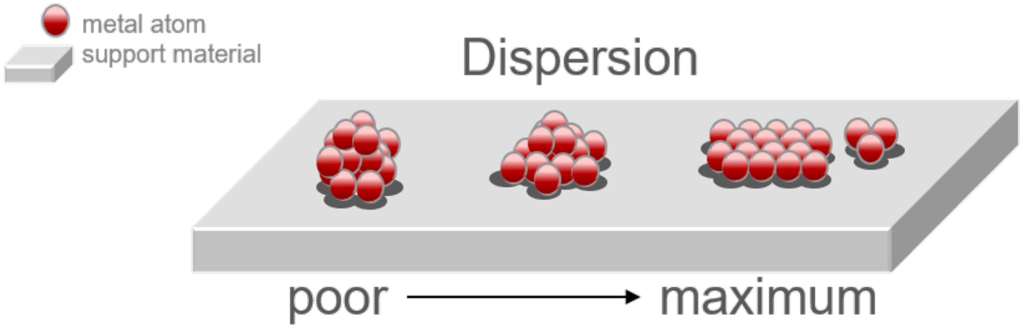
CHEMISORPTION ESSENTIALS

WHAT EXACTLY DOES CHEMISORPTION TELL US?



ACTIVE METAL AREA

- The number of active sites usually expressed as an active metal area



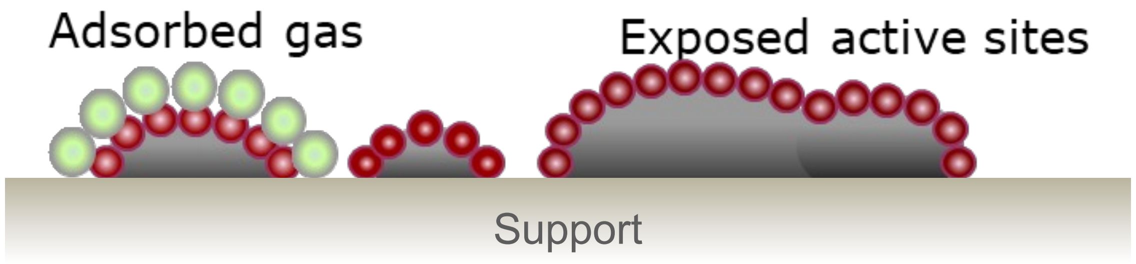
DISPERSION

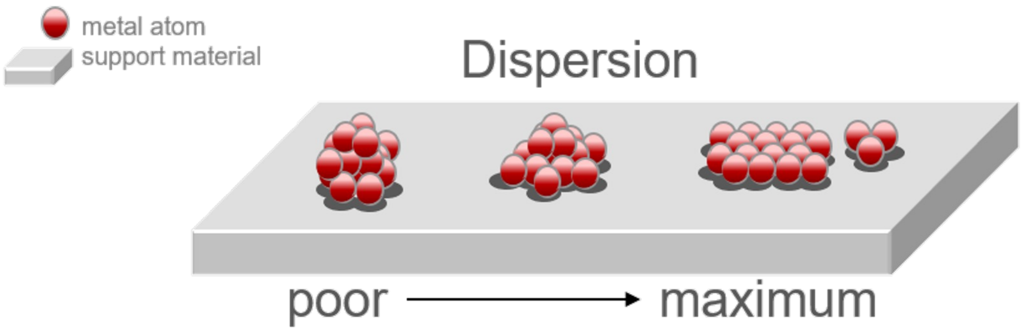
- The number of metal atoms accessible to reactive gases expressed as a percentage of the total in the sample

CRYSTALLITE SIZE

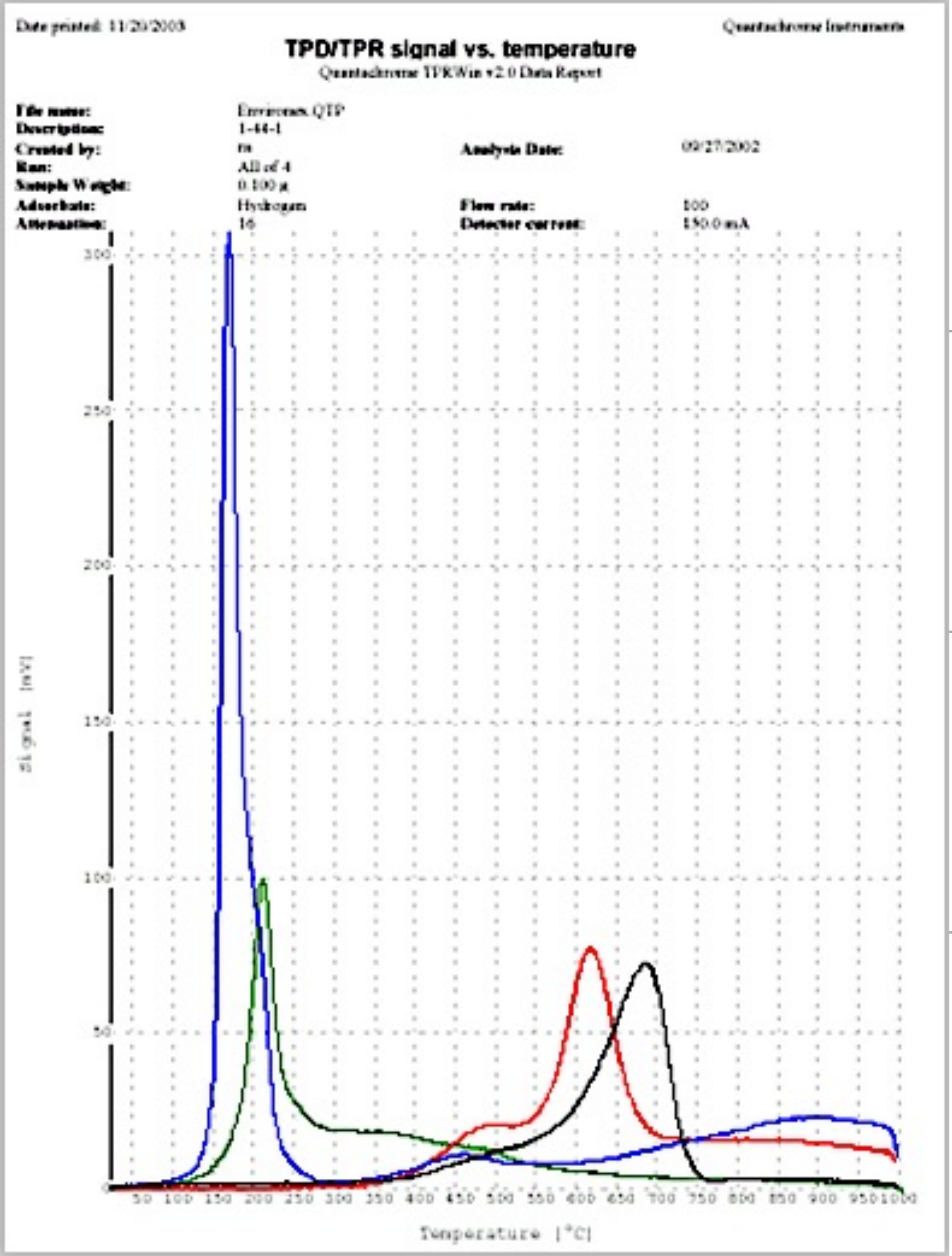
- The approximate size of the metal nanoparticles distributed across the surface of the inert support material

CHEMISORPTION ANALYSES





Property	Method
Metal area	Static Isotherms, Flow Pulse Titration
Dispersion & crystallite size	Static Isotherms, Flow Pulse titration
Spillover (excess chemisorption)	Static Isotherms
Oxide reducibility	TPR (Flow)
Catalyst regeneration (carbon removal)	TPO (Flow)
Zeolite acidity	TPD, ammonia (Flow)



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ANYTHING ELSE?

CATALYST ACTIVATION

› Temperature Programmed Reduction: TPR

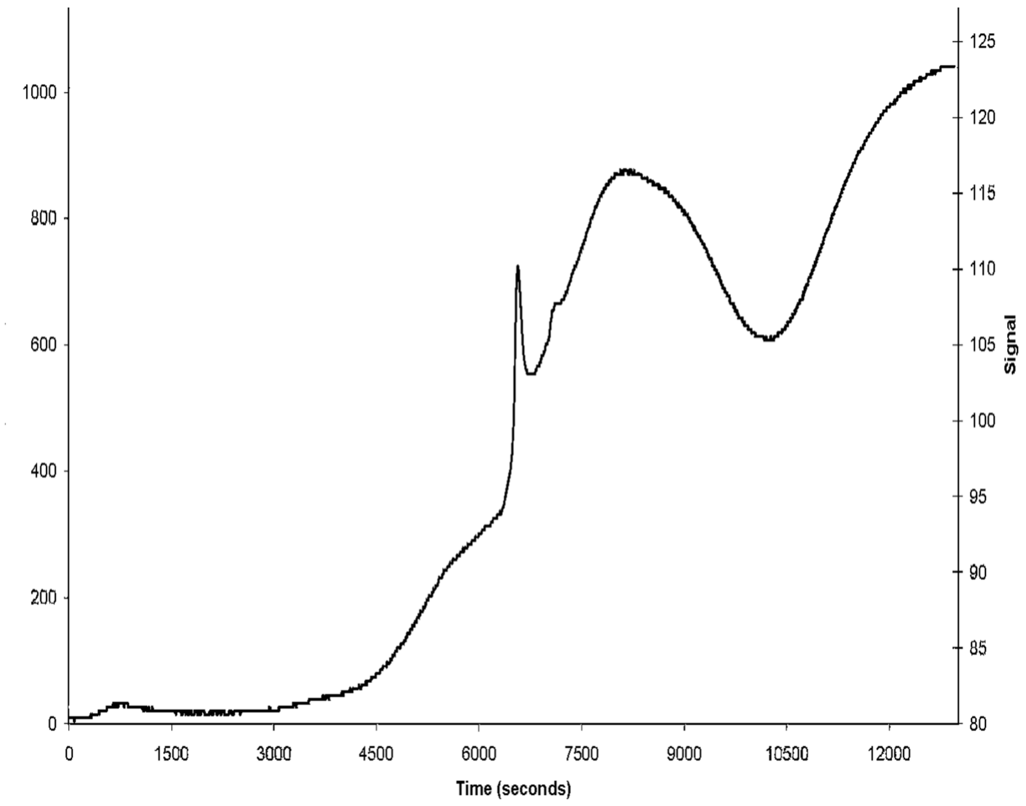
CATALYST REGENERATION

› Temperature Programmed Oxidation: TPO

ACID SITE STRENGTH

› Temperature Programmed Desorption: TPD

ANYTHING ELSE?



CATALYST ACTIVATION

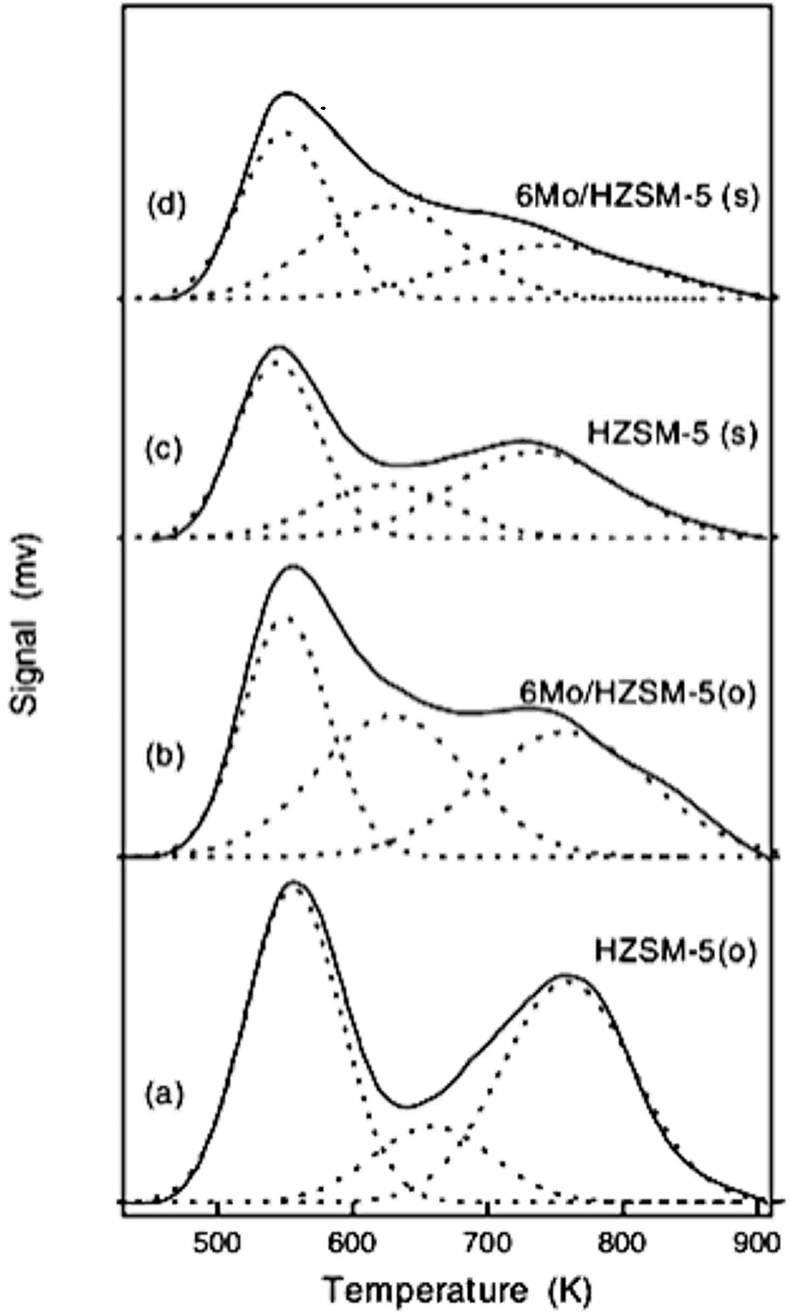
› Temperature Programmed Reduction: TPR

CATALYST REGENERATION

› Temperature Programmed Oxidation: TPO

ACID SITE STRENGTH

› Temperature Programmed Desorption: TPD



H. Liu et al. / Catalysis Today 93–95 (2004) 65–73

ANYTHING ELSE?

CATALYST ACTIVATION

- Temperature Programmed Reduction: TPR

CATALYST REGENERATION

- Temperature Programmed Oxidation: TPO

ACID SITE STRENGTH

- Temperature Programmed Desorption: TPD

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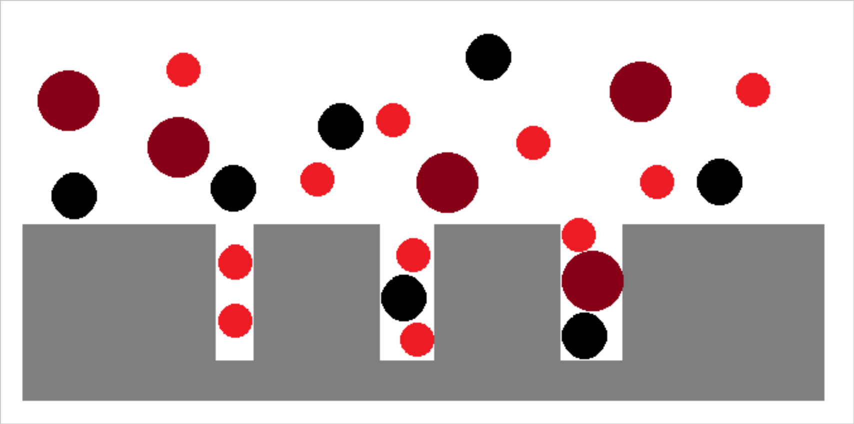
HIGH PRESSURE GAS SORPTION ESSENTIALS

ADSORPTION CHARACTERISTICS

› Capture, Storage, Characterization

- Strong adsorption
  - Capture
  - Retention
  - Micropores
- Selectivity
  - Pore size
  - Adsorption enthalpy



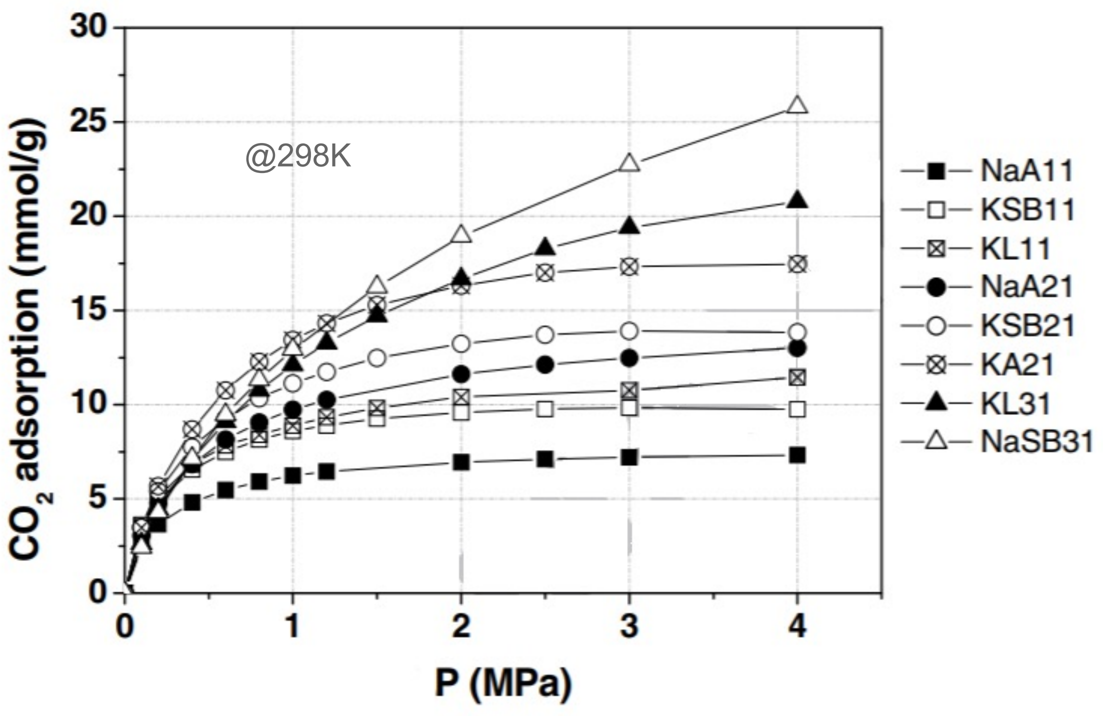
Desirable Properties:

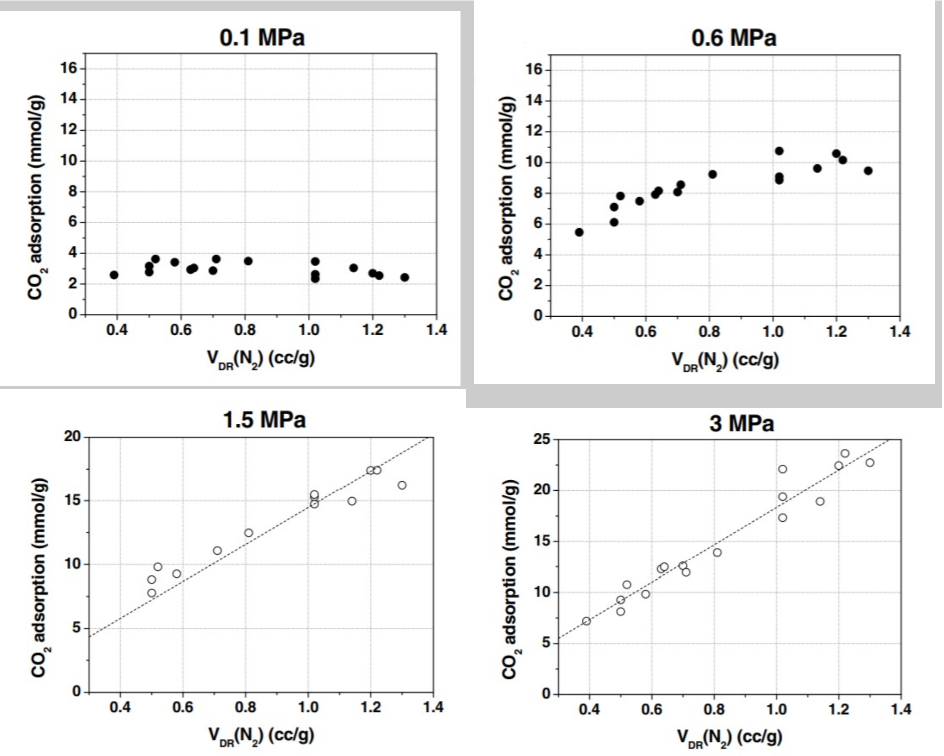
- High adsorption capacity
- Good kinetics
- Recoverable/regenerable

WHY HIGH PRESSURE SORPTION?

Case Study: CO_2 Capture

Activated carbons from anthracite, sub-bituminous coals and lignite





Marco-Lozar, JP; Kunowsky, M; Suárez-García, F; Linares-Solano, A. Sorbent design for CO_2 capture under different flue gas conditions
Carbon 2014, (72) 125-134

CH_4 STORAGE

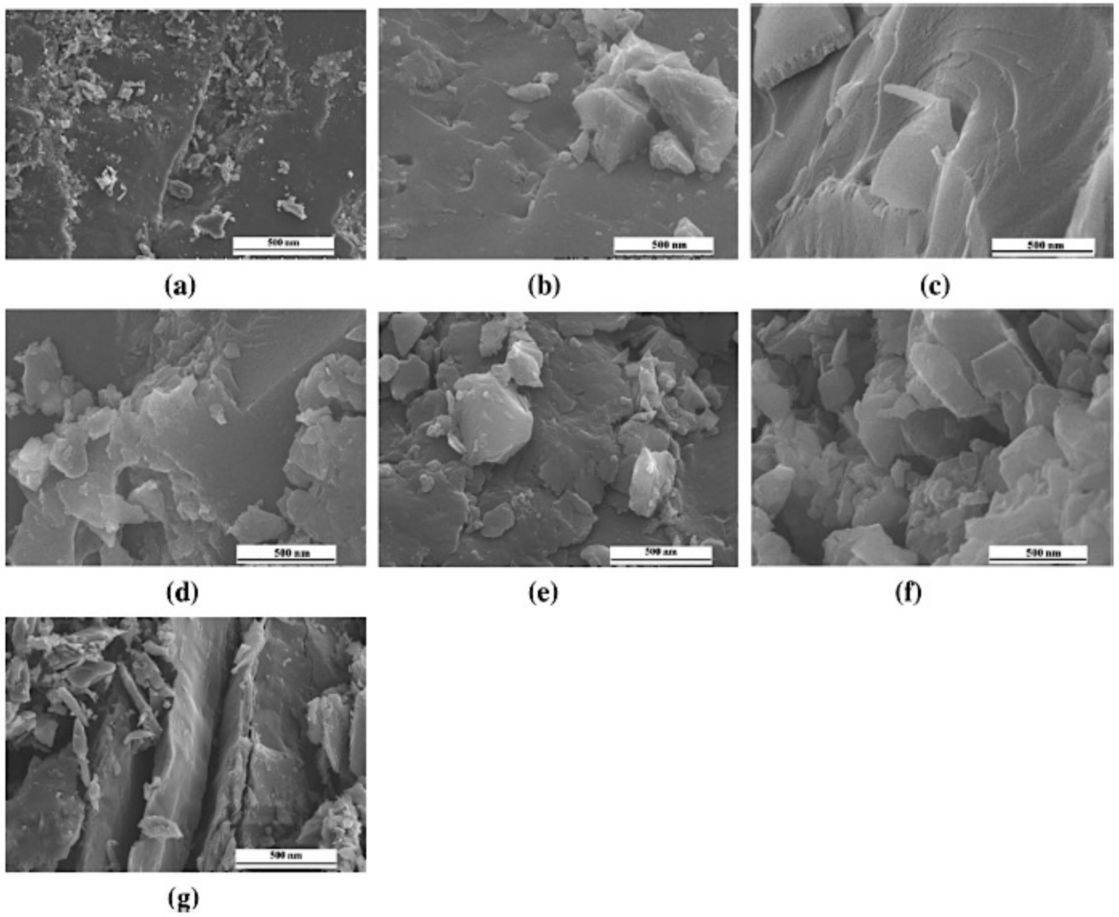


Fig. 3 SEM results of selected samples. **a** WJD, **b** PY, **c** DX, **d** YW, **e** GQ, **f** ZC, **g** ZZ

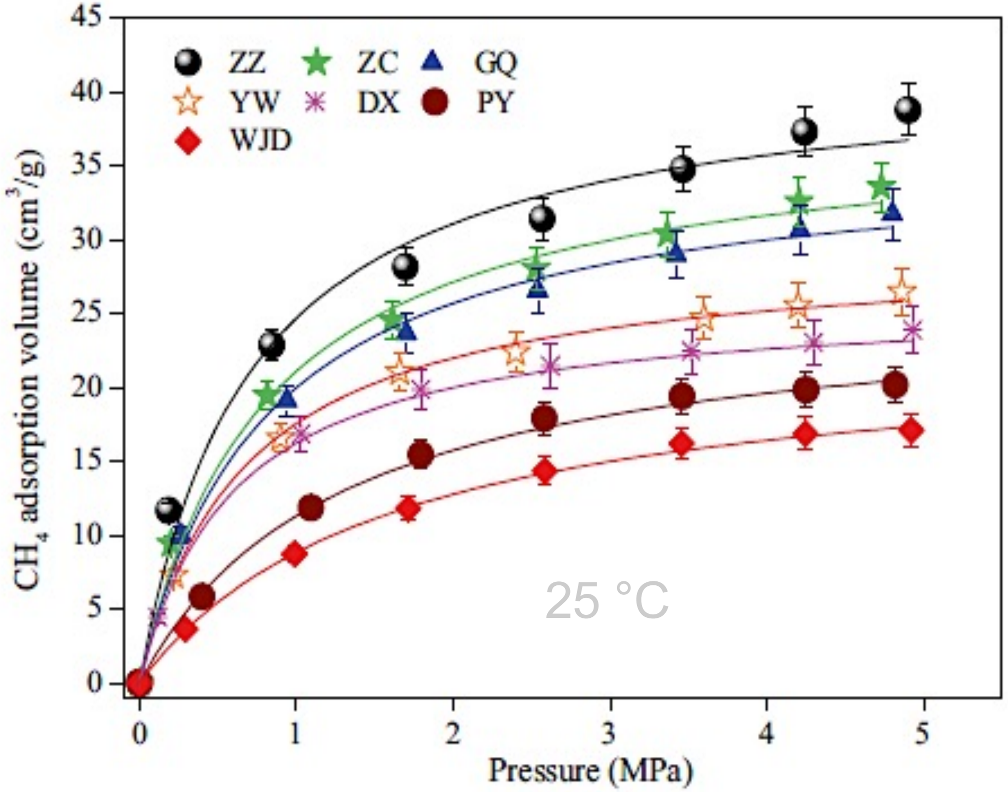


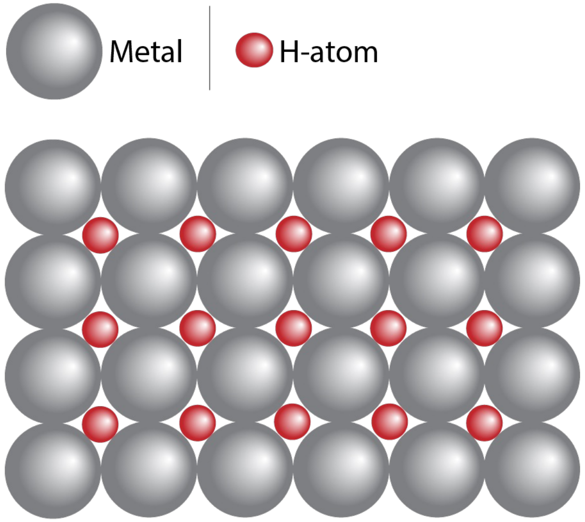
Fig. 5 Adsorption isotherms of methane on samples

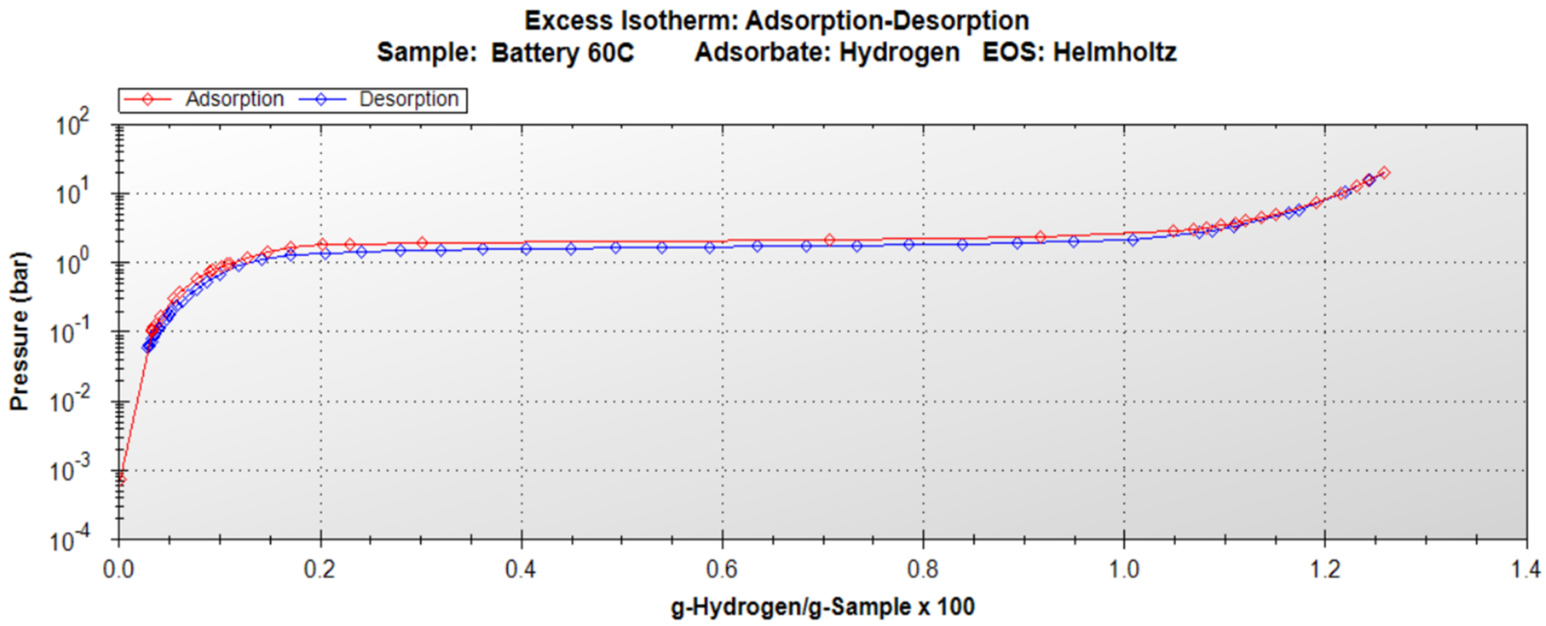
Fu, Y; Liu, X; Ge, B; Liu, Z. Role of chemical structures in coalbed methane adsorption for anthracites and bituminous coals. *Adsorption* **2017**, 23:711–721

OPTIMIZING HYDROGEN STORAGE FOR CARBON FOOTPRINT REDUCTION

METAL HYDRIDES

PRESSURE-COMPOSITION-TEMPERATURE (PCT PLOT)

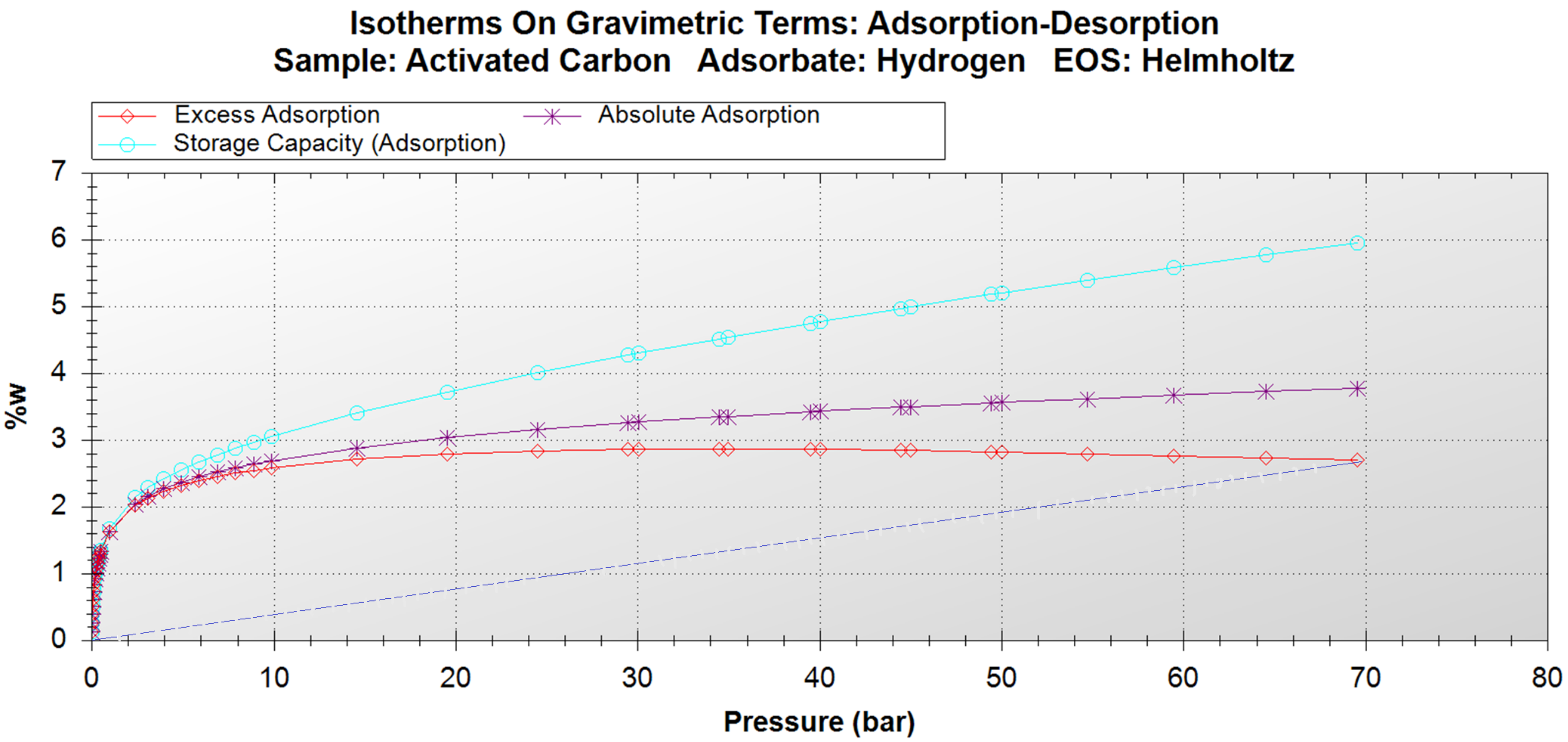




The hydrogen moves in and out of the lattice structure, which is completely reversible.

ADSORBENT PERFORMANCE PROPERTIES

HIGH PRESSURE ISOTHERMS & STORAGE CAPACITY



BENEFICIAL ADVANCEMENTS

Traditional	Advance	Benefit
Helium void volume	Analysis without helium	Conserve non-renewable resource (helium)
Samples treated as unknown	Intelligent gas dosing based on historical data	High throughput mesopore analysis
Nitrogen/77K micropore analysis	Argon /87K	Time saving ~50%
Liquid argon	87K using LN_2	Instant availability
25K	Stability at ~20K	Maximizing hydrogen density
Macroscopic models for pore size	Molecular modelling of adsorption behavior in pores of different shapes	Increased pore size accuracy
n/a	Hysteresis scanning	Network information

REVIEW & SUMMARY

- Surface area: extent of where solids interact with their surroundings
- Pore size and volume: define how fluids move in, out and through a porous solid
- Battery electrodes
- Environmental catalysts
- Greenhouse gas adsorbents
- Hydrogen storage
- All characterized by the various forms of gas sorption measurements

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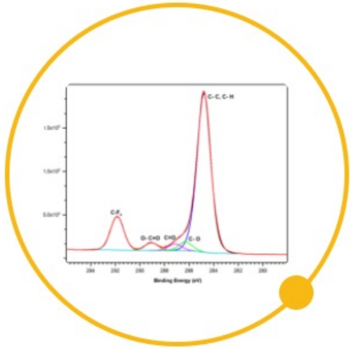

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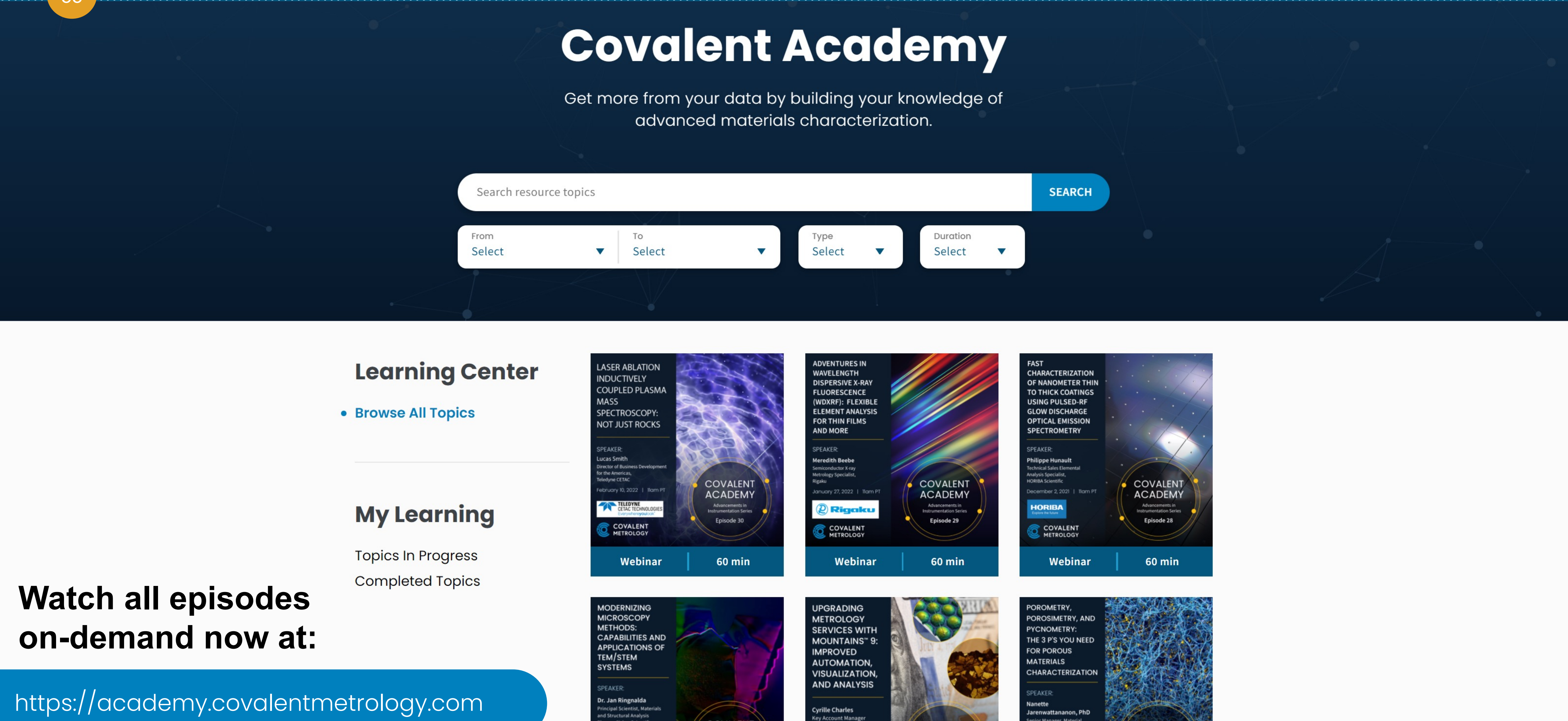

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Q & A
Session

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Thank You