BATTERY MATERIAL QUALITY: THE IMPORTANCE OF PHYSICAL PROPERTIES

Anthony Chalou
Head of Market Development,
Anton Paar

June 20, 2024 at 8 AM Pacific Time

COVALENT METROLOGY

Anton Paar

COVALENT ACADEMY

Industrial Applications of Advanced Metrology

Episode 37

COVALENT METROLOGY

Modern, digitally-empowered analytical services platform delivering quality data and expert analysis to accelerate advanced materials and device innovation.

Comprehensive Solutions Stack

50+ Cutting-edge instruments in-house, 150+ Techniques

Analytical Services

Advanced Modeling

Method Development

Custom Consulting Solutions

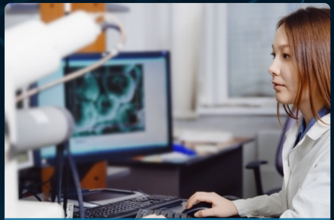
High-touch, High-Quality Services

Ionic Membership Program

Enterprise Metrology Solutions

Instant, Secure Access to Data and Reports

Expanding Toolkit in Custom Digital Platform



Flexible Business Models

LiveView™ (real-time collaboration)

Co-op and Tool-share Opportunities

Training and Certification on Instrumentation

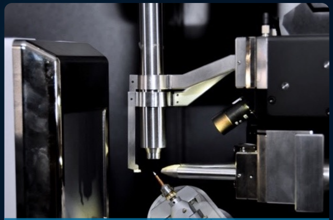
Laboratory Audits

Rich Network of Partnerships

Partner to World's Leading Instrument Manufacturers and Labs

Expanding access to Advanced Instruments and Analysis Tools

Lab Connections and Applications Learning



Who We Are, Who We Serve

50+ People, 14 PhDs

Comprehensive, Modern Analytical Capabilities

$20M +State-of-art Lab in Sunnyvale, CA

600+ Clients, 15-30 new clients / week

Covalent's Analytical Services & Technical Groups

COVALENT METROLOGY

Enterprise Metrology Solutions: Failure Analysis & EM

Electron Microscopy

- S/TEM
  with EDS; EELS; Electron Diffraction; SAED
- FIB-SEM & HR-SEM
  with EDS; EBSD; 3D Tomography
- Lamella Preparation
  incl. specialized lift-outs

Failure Analysis

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

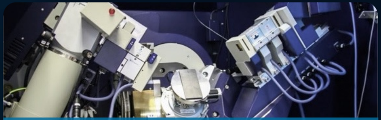
Materials, Chemicals, and Surfaces

Microscopy & Profilometry

- Chromatic Aberration
- Digital Optical Microscopy
- Laser Scanning Confocal Microscopy
- White Light Interferometry
- Scanning Acoustic Microscopy (SAM)

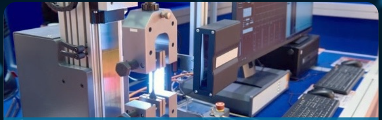
Analytical Chemistry

- Mass Spectroscopy:
  ICP-MS and LA-ICP-MS; GCMS
- ICP-OES / GDOES
- Raman
- NMR (solid / liquid + 1,2,3 nuclei)
- XPS, UPS, ISS
- SIMS, TOF-SIMS



X-ray Characterization

- X-Ray Diffraction (XRD)
- X-Ray Reflectometry (XRR)
- Micro-computed X-ray Tomography (Micro-CT)
- 2D / 2.5D / 3D X-ray Inspection & X-ray Radiography
- ED-XRF / WD-XRF



Mechanical Testing

- AFM & Advanced AFM Modes (EFM, KPFM, MFM, PFM, PiFM)
- Nano-indent / Nano-scratch
- Rheometry / Viscosity
- DMA / TMA (bend/stretch/compression)
- Tensile testing

Misc. Material Properties

- Thermal Analysis: DSC, TGA
- Surface Zeta Potential
- Porometry / Pycnometry
- Gas Adsorption / Chemisorption
- Foam Density / Skeletal Density / Tap Density
- Particle Analysis: DLS / ELS / size distribution / zeta potential

Optical Characterization

- Fourier Transformed Infrared Spectroscopy (FTIR and ATR-FTIR)
- Spectral Ellipsometry & Advanced Optical Modeling
- UV-Vis-NIR Spectroscopy

Covalent Partners

COVALENT METROLOGY

Today's webinar is in partnership with

Anton Paar

- **Partnership with Anton Paar announced in May, 2020**
  - Established the **Anton Paar Demonstration Facility in Covalent's Silicon Valley Laboratory** with goals of
    - Expanding industry access
    - Developing new analytical applications
  - Later expanded partnership to deliver industry-leading porous materials and powders analysis
  - Partners **continue to collaborate in advanced applications development**

- **Anton Paar Instruments** at Covalent Metrology include:
  - **SurPASS 3**
  - **Litesizer 500**
  - MCR 702 Rheometer / DMA
  - STeP 6 Nanoindentation platform
  - Ultrapyc 5000 Micro
  - Autosorb iQ C-XR-XR with CryoSync accessory
  - Porometer 3G and DualAutoTap
  - NEW Upgraded Nova 800 BET (Gas Adsorption) Analyzer

Other Covalent Partners

Rigaku

JEOL Solutions for Innovation

HORIBA Scientific

ThermoFisher SCIENTIFIC

TELEDYNE CETAC TECHNOLOGIES Everywhereyoulook™

KEYENCE

Digital Surf

PVA TePla

J.A. Woollam

Asylum Research an Oxford Instruments company

TA Instruments

Toray Research Center, Inc.

COVALENT METROLOGY

Anthony Chalou

Head of Market Development, Anton Paar

Anton Paar

- Anthony Chalou is the **Head of Market Development** at Anton Paar
- He holds **two Masters degrees in Applied Analytical Chemistry** and has **more than 20 years of experience with analytical instrumentation**, both in scientific applications as well as in sales and marketing
- His **current focus is on the characterization of physical properties of materials used in the R&D and QC of lithium-ion batteries**

ANTON PAAR SOLUTIONS FOR

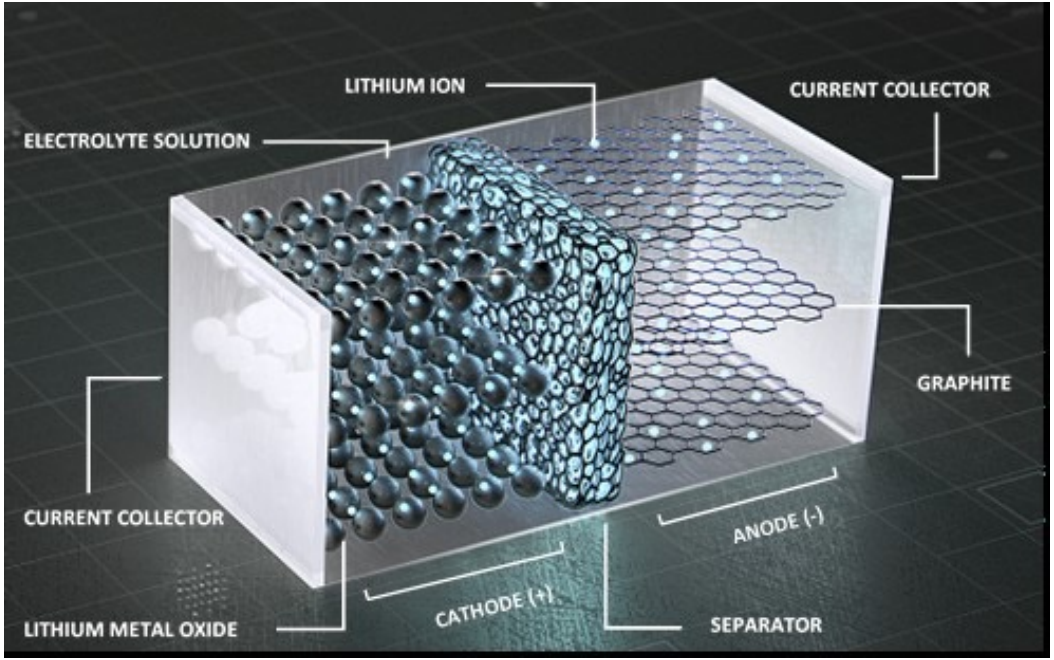
BATTERY MATERIAL CHARACTERIZATION

Anthony Chalou
Head of Market Development
Anton Paar GmbH

OUTLINE

- Main components
- LIB Types
- LIB Chemistries
- Cell formats
- Pros & cons of common formats
- Battery trilemma
- Emerging trends
- Physical parameters of raw materials
- Physical parameters of slurries
- Questions

MAIN COMPONENTS OF A LITHIUM ION BATTERY



TYPES OF LITHIUM ION BATTERIES

Ternary lithium ion (LIB)

- Most researched & used type of Li ion batteries
- Nickel-rich cathodes provide higher energy densities, especially when combined with Silicon based anodes
- Need reduction in production costs

Lithium Sulfur (Li-S)

- Sulfur is the main low-cost material used
- During discharge, lithium sulphides are formed at the cathode
- Low cycle life and safety concerns need to be further evaluated prior to full adoption

Estimated energy density range (Wh/kg)

100	**200**	**300**	**400**	**500**	**600**	**700**	**800**

Lithium Iron Phosphate (LFP)

- Mainly produced in China; few western manufacturers
- Cost advantage: No Co or Ni, and low cost of Iron and Phosphate
- Excellent cycle life, and improved safety
- Suffers from low energy density

Solid state lithium (SSB)

- The electrolyte is in solid form
- Very high energy density as well as safety, which make this type adoptable by the automotive industry
- Challenges in material compatibility and manufacturability in series are still issues that stand in the way of full market maturity

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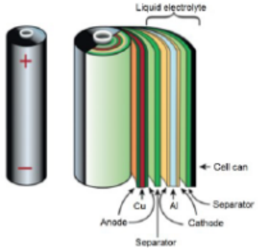
LITHIUM-BASED RECHARGEABLE SYSTEMS

Technology	Anode	Cathode
Lithium Cobalt Oxide 3.6V	Graphite –Gr/Si	LCO
Lithium Manganese Oxide Spinel 3.8V	Graphite –Gr/Si	LMO
Lithium Nickel Manganese Cobalt 3.7-3.8V	Graphite –Gr/Si	LNMC (111,532, 622, 811)
Lithium Nickel Cobalt Aluminum 3.65V	Graphite –Gr/Si	LNCA
Lithium Iron Phosphate 3.2V	Graphite –Gr/Si	LFP*
Lithium Manganese Iron Phosphate 3.7V	Graphite –Gr/Si	LMFP*
Lithium Titanite Oxide 2.3/2.4V	LTO	NMC, LMO, LFP
Lithium Nickel-Rich Oxide 3.8V	Graphite –Gr/Si	eLNO*
Lithium Metal 3.7V	Lithium Metal	NMC
*Lithium Nickel Manganese Oxide Spinel 3.8V (Mn Rich)***	Graphite –Gr/Si	LNMO*
*Lithium Sulfur 2.4V***	Lithium Metal	Sulfur*

** Cobalt free*
*** R&D stage*

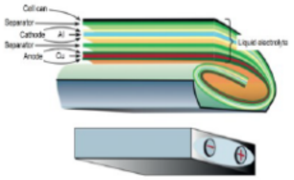
MOST COMMON FORMATS OF BATTERY CELLS

Cylindrical



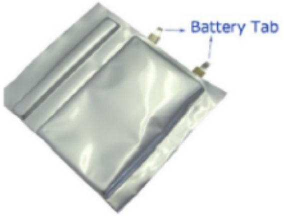
A spirally wound design (jelly-roll). Designated by size, e.g. 18650 cylindrical battery (Diameter: 18.6 mm, length: 65.2 mm; code for cylindrical shape: 0)

Prismatic



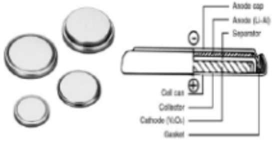
A prismatic design indicate a flat battery design. The stacks can be wound (as shown in the photo) or stacked (with alternating cathode/separator/anode structure). The stacks are usually inserted into rigid casing to form prismatic containers

Pouch



Rather than rigid metallic casing, conductive foil-tabs are welded to the electrodes and seal the battery fully. The stacks inside can be wound or stacked. Swelling and gassing could be a concern for pouch cells.

Coin cell



Also known as button cell. The cells are stacked into a tube. Most coin cells are single-use.

Source: J.M. Tarascon, Nature 2001, Sanyo and Panasonic

PROS AND CONS OF THE DIFFERENT FORMATS OF BATTERY CELLS

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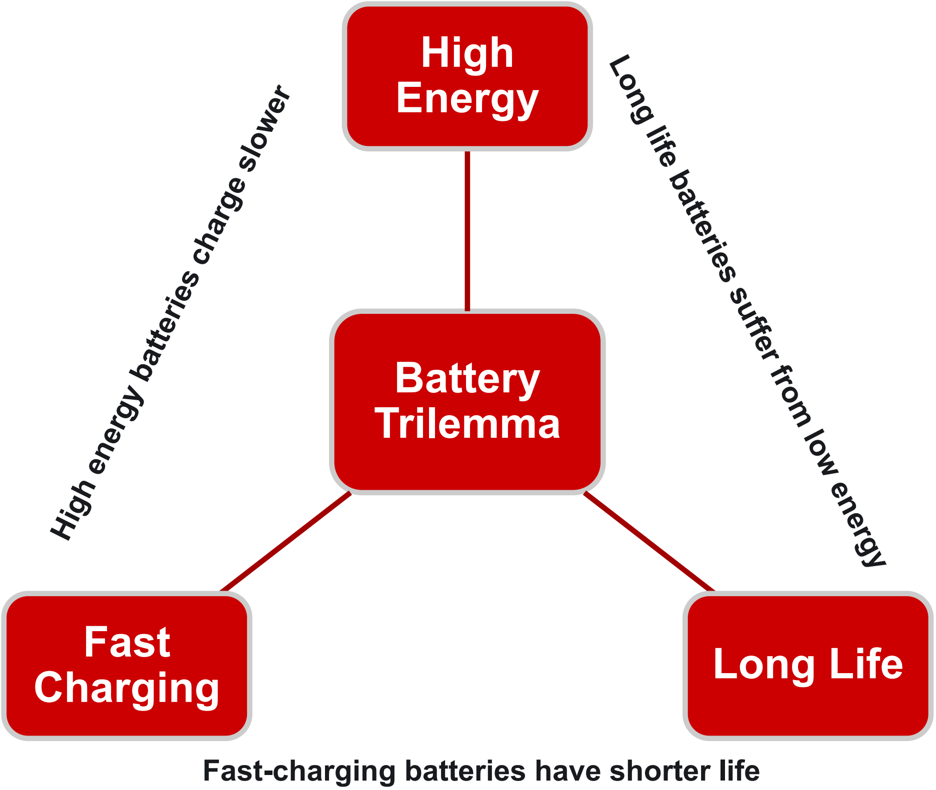
Cylindrical		Prismatic		Pouch	
+	-	+	-	+	-
High energy density	Space inefficiency	High energy density	Mainly large and high-capacity cells	High volumetric energy density	Mechanical limitations
Wide operating voltage range	Low volumetric energy density (at pack level)	Wide operating voltage range	Requires special orders	Wide operating voltage range	Requires special orders
Wide power density range	Thick	Wide power density range	Thicker than pouch cells	Wide power density range	Swelling
Good cycle life (500-1000 cycles)	No custom sizes	Good cycle life (500-1000 cycles)	No standard sizing	Good cycle life (500-4000 cycles)	No internal safety devices
Low self-discharge (~1% / month)	Difficult thermal management	Low self-discharge (~1% / month)	Difficult thermal management	Low self-discharge (~1% / month)	Vulnerable to shock and vibration
Quick charge possible		Quick charge possible		Quick charge possible	
Internal safety devices		Internal safety devices		Better thermal management	
Standard sizes (no custom orders)		Customization possible for mass production		Easy to custom make	
Robust		Robust		Mass production for large cells	
Mass production		Thin (Better pack volume)		Thin (Better pack volume)	

THE “IDEAL” BATTERY



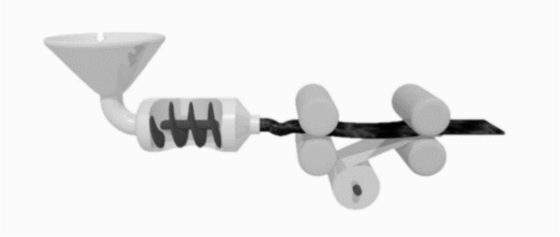
EMERGING TRENDS

RECYCLING

- Black mass
- Hydrometallurgy
- Pyrometallurgy
- New regulations

SOLID STATE BATTERIES

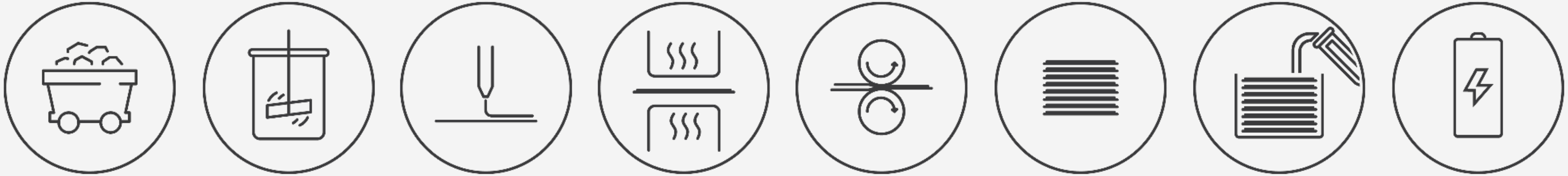
- Enhanced safety
- Extended lifespan
- Increased energy density
- More expensive
- Challenges in scaling up



DRY COATING

- No solvent use
- Lower production cost
- Better performing batteries
- Challenges in production speed needs

BATTERY MATERIAL CHARACTERIZATION



Raw Material
- BET Surface area
- Pore size
- Pore volume
- Particle size
- Particle shape
- Skeletal density
- Tapped density
- Powder Rheology
- Defect ratio
- Crystallinity

Slurries
- Flow behavior
- Slurry viscosity
- Zeta potential
- Density
- Percent solids
- Solvent concentration
- Particle size
- Particle shape

Coating
- Flow behavior
- Slurry viscosity
- Sedimentation stability
- Mechanical properties

Drying
- Adhesion
- Mechanical properties

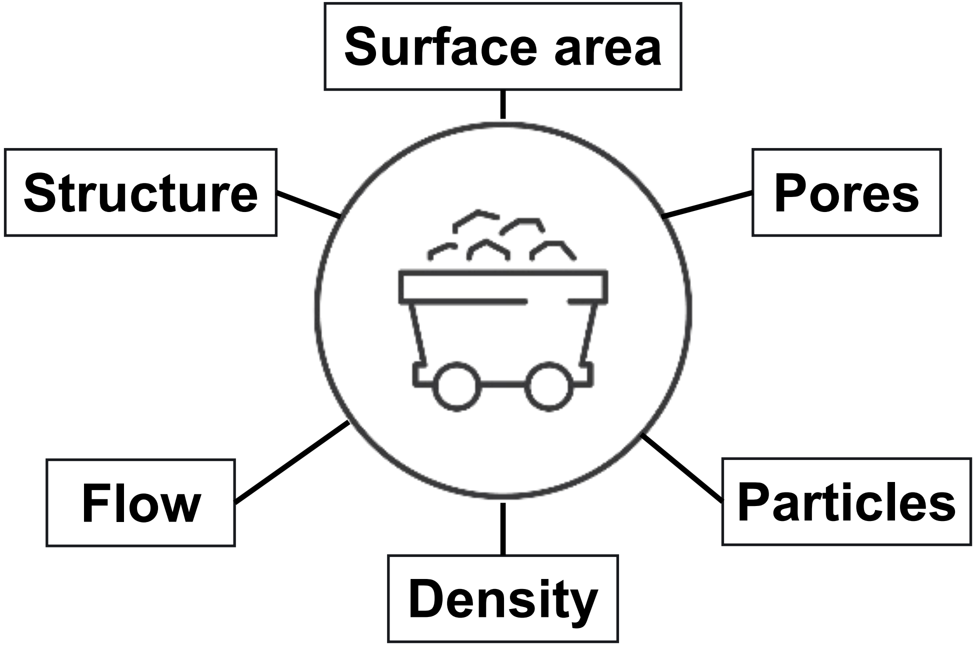
Calendering
- Hardness & elastic modulus
- Adhesion
- Mechanical properties

Stacking
- Separator pore size
- Separator pore volume
- Mechanical properties

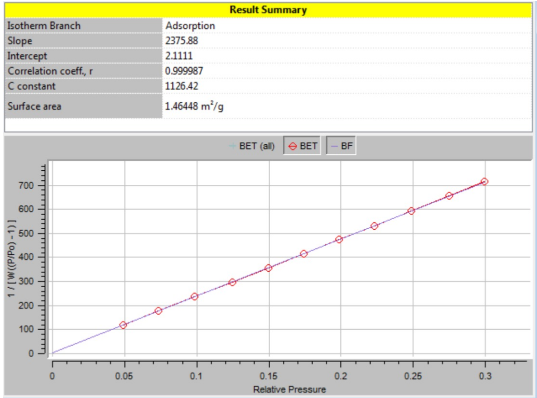
Electrolytes
- Separator pore size
- Separator pore volume
- Electrolyte viscosity
- Electrolyte density
- Electrolyte flash point

Battery Cell
- In operando characterization
- In situ characterization

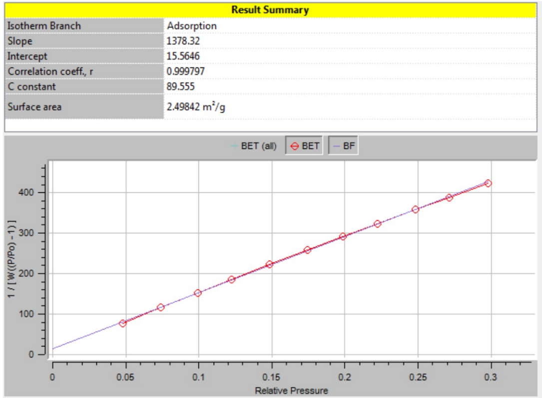
IMPORTANT PHYSICAL PARAMETERS OF BATTERY RAW MATERIALS



BET SURFACE AREA



Eleven-point BET plot for NMC

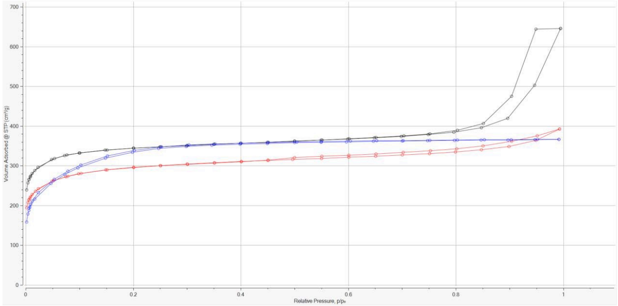


Eleven-point BET plot for graphite

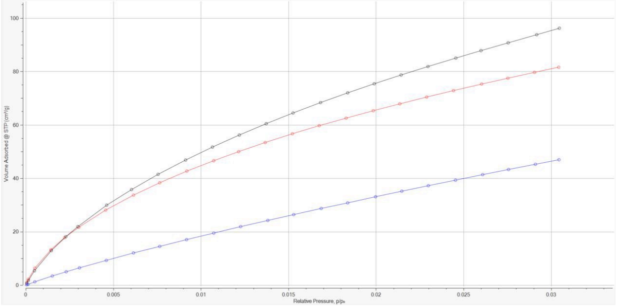
NOVA Series

- Surface area of electrode material directly influences charge transfer between active materials and electrolyte
- Surface area is optimized for electrical performance and to minimize adverse chemical reactions
- Specific surface area of electrode materials is determined by the cryogenic adsorption of a gas (such as N2)
- Method uses gas sorption data to quantify the number of molecules of adsorbate in a monolayer on the surface of the material

PORE SIZE AND PORE VOLUME



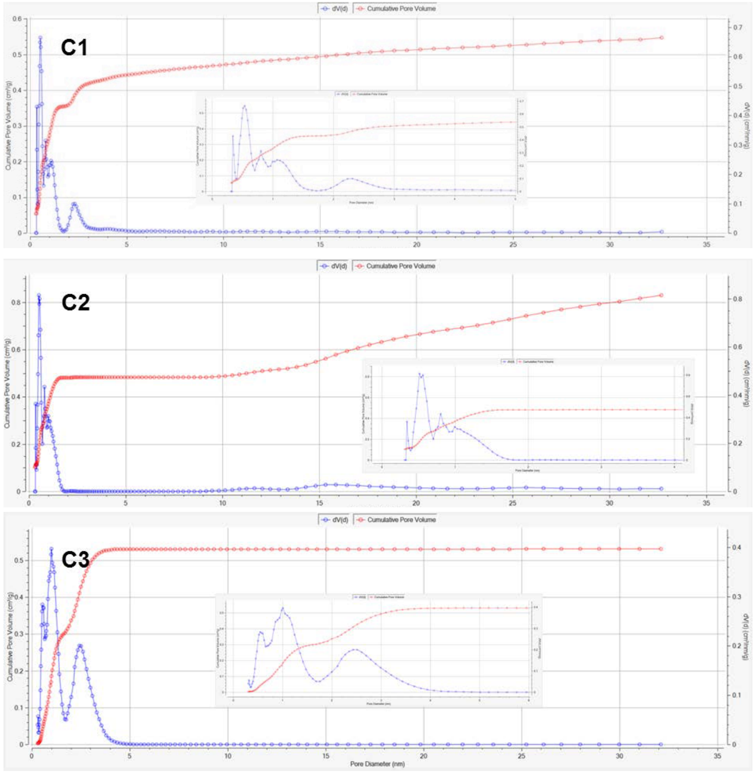
N_2 isotherm on 3 types of hierarchical carbon samples (mesopores)



CO$_2$ isotherm on 3 types of hierarchical carbon samples (micropores)

NOVA Series

Kaomi Software



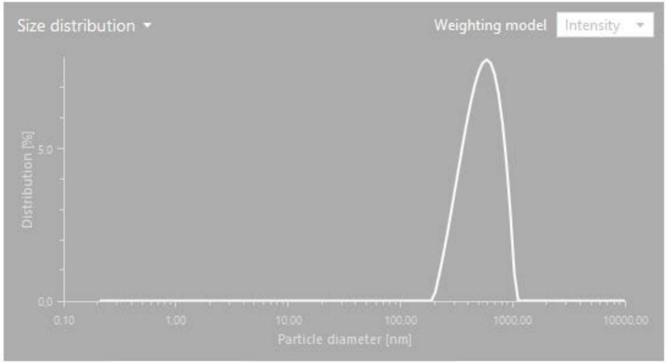
Merged CO_2 (273 K) and N_2 (77 K) DFT pore size distributions (blue) and cumulative pore volumes (red) for three carbons

PARTICLE PARAMETERS*

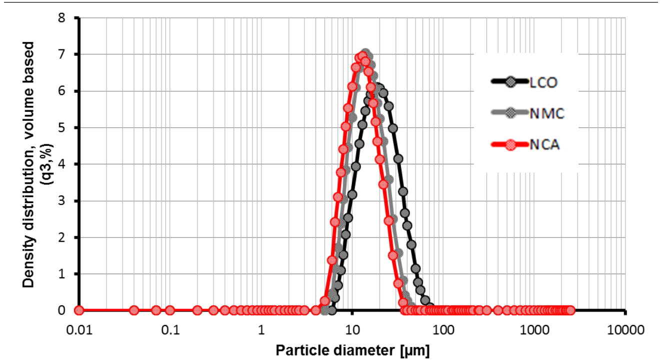
Size		Size distribution		Shape	
Small size		**Uniform**	**Broad**	**Single crystal structure**	
Shorter Li-ion transport distance	Larger SSA	Better cycle performance	Higher energy density	Higher electrode packed density	Difficult to manufacture
Better rate performance	More side reactions	Higher production difficulty	Poor cell homogeneity	Better cycle performance	Higher cost

**Adapted from J. Zhang et al. "Balancing particle properties for practical lithium-ion batteries", Particuology, Vol. 61, (2022), P. 18-29*

PARTICLE SIZE



Intensity-weighted particle size distribution of carbon black



Particle size distribution of three different cathode materials

Litesizer

Dynamic light scattering (DLS)
Electrophoretic light scattering (ELS)

0.3 nm — 10 µm

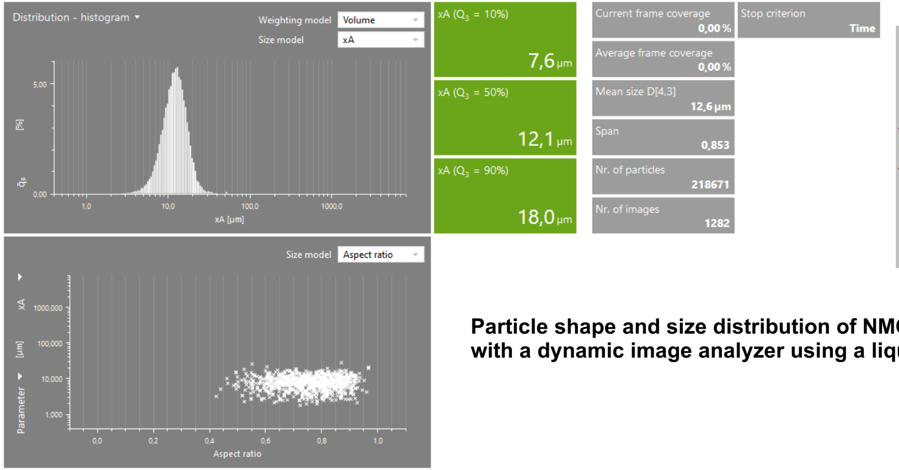
40 nm — 2.5 mm

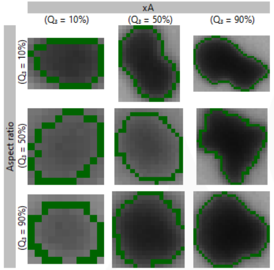
Particle Size Analyzer (PSA)

Laser diffraction (LD)

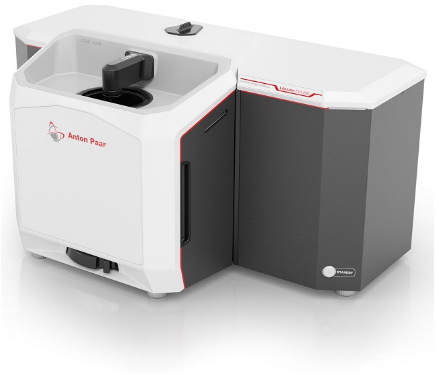
PARTICLE SHAPE

Measurement results





Particle shape and size distribution of NMC cathode material measured with a dynamic image analyzer using a liquid flow dispersion unit



Litesizer DIA

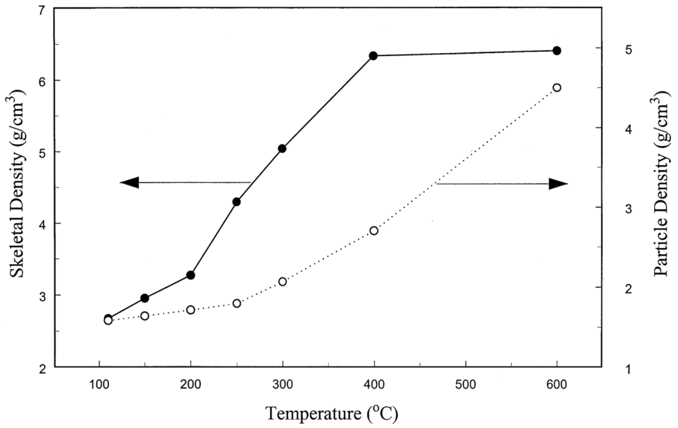
Particle shape affects parameters such as:

- Homogeneity of the slurry
- Uniformity of the coating on current collectors

For electrode material, near-spherical shape is preferred

SKELETAL DENSITY

- Skeletal density, or true density, is measured by gas pycnometry
- Greater skeletal density of electrode material → higher energy density of batteries



Increase of skeletal density with increasing thermal treatment of nickel oxide electrode material

Principle of gas pycnometry:

Instead of weighing the displaced liquid, gas volumes are assessed via pressure measurements before and after expansion into an empty volume

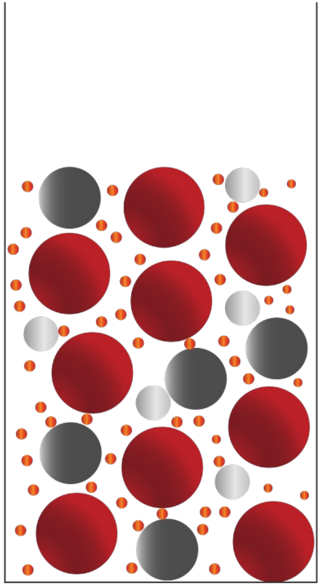
Ultrapyc Series

TAPPED DENSITY

- Tapped density, also known as bulk or packing density, is an important parameter in battery material characterization, and incorporates:
  - Volume of the solid phase
  - Volume of pores within particles
  - Volume of the spaces between particles

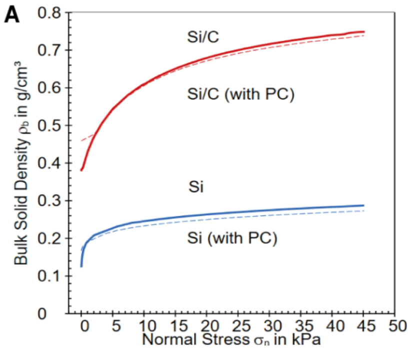
- For solid battery material, a greater tapped density produces more efficient energy management

Example: $LiNiCoMnO_2$ cathode material,
mixed particle sizes results in greater tapped density and better electrochemical performance than with single particle size systems

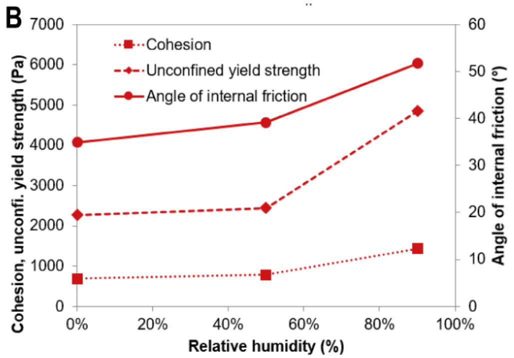


Autotap

POWDER RHEOLOGY



PC = Pre Compaction



Compressibility of Si and Si/C samples as a function of normal stress

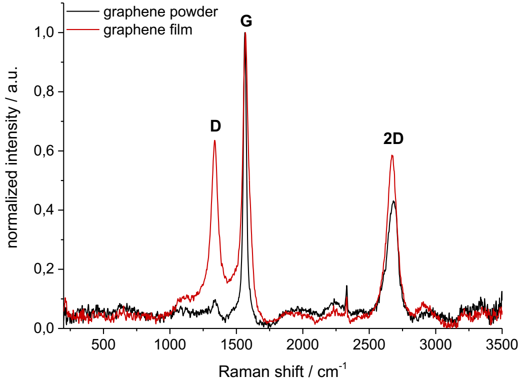
- Si/C is denser than Si (also confirmed by gas pycnometry)
- Si almost completely lacks compressibility (densification)
- Si powder readily densifies under its weight; it is very flowable => it acts as a flow-aid

MCR 302e / Powder shear cell

Powder flow parameters of Si/C samples as a function of moisture

- Small effect of moisture levels between 0 % - 50 %
- For moisture levels >50 % reduction in flowability, due to formation of menisci between particles
- Important information for storage and transportation conditions

DEFECT RATIO

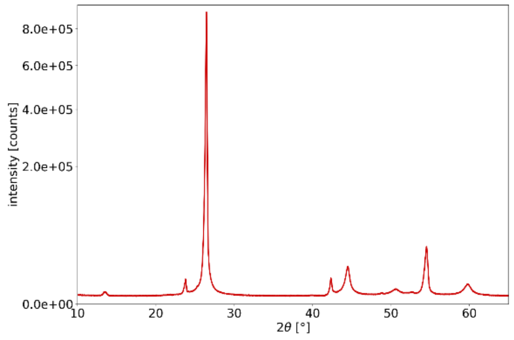


Raman spectra of graphene powder (black) and a graphene film (red).

Cora 5001

- “Graphitic” or “G” band at 1580 cm^{-1}: sharp signal in ordered graphite compared to amorphous carbon
- “Defect” or “D” band around 1350 cm^{-1}: signal associated with the breathing vibrations of the carbon atoms, becomes visible around defects
- The overtone of the D band, commonly referred to as the “2D” band, around 2680 cm^{-1}: for symmetry reasons, the 2D band in pure single-layer graphene is a perfect single-component peak
- “Defect ratio” is the ratio of the D and G band intensities (I_D / I_G) that changes with the introduction of defects. Another ratio is the one between the G and the 2D band intensities (I_{2D} / I_G) which changes with the number of layers

DEGREE OF CRYSTALLINITY



Diffractogram of a graphite anode material

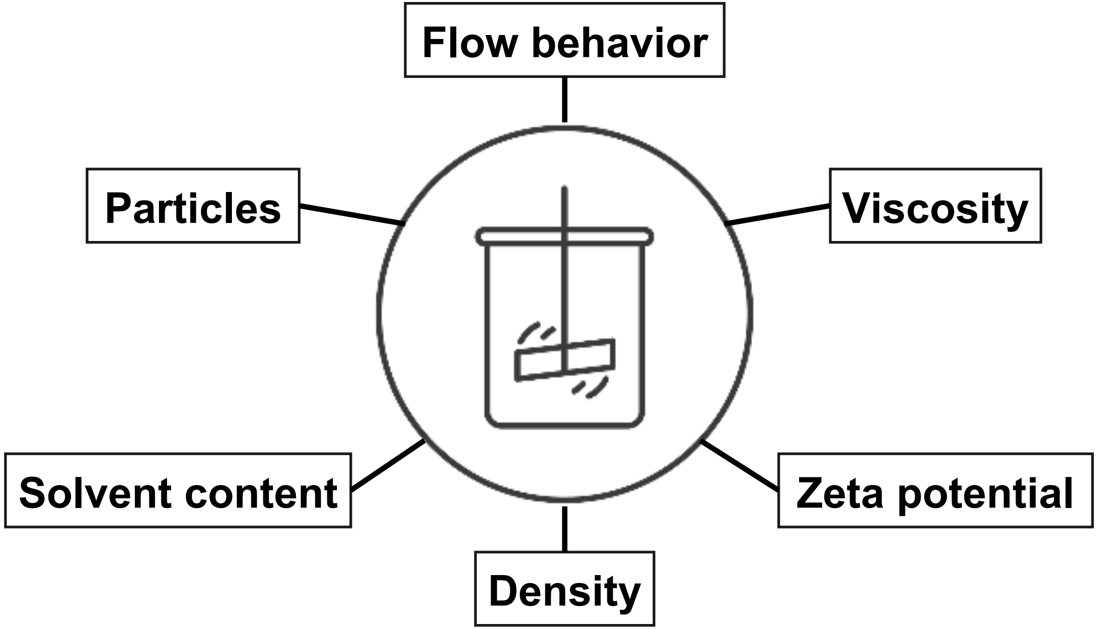
Crystallite size (nm)	Degree of graphitization (%)
41.2	92.7

- Powders with high degree of crystallinity facilitate electron mobility in the battery cell
- XRD gives information on the crystal structure, crystallite size, and phase purity of battery raw materials
- XRD is capable of detecting minor impurities when comparing the diffractogram of a known material with that of a contaminated one
- Specialized gas-tight sample holders also make it possible to measure air-sensitive materials without sample degradation

Sample holders for air-sensitive battery materials

XRDynamic 500

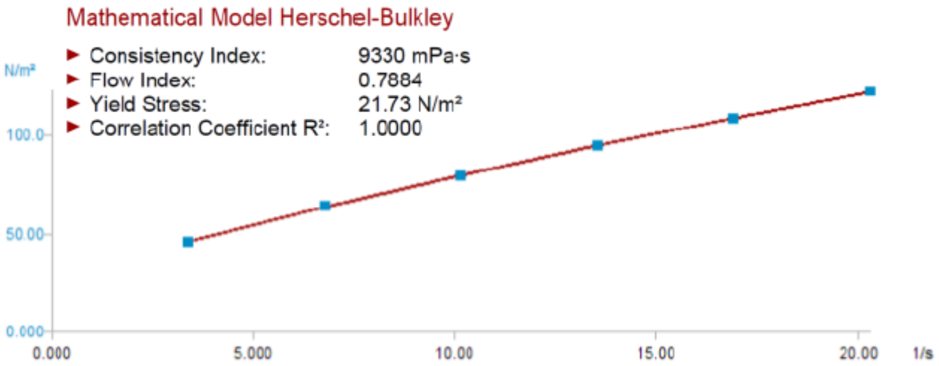
IMPORTANT PHYSICAL PARAMETERS OF BATTERY SLURRIES



FLOW BEHAVIOR

Speed [rpm]	Torque [%]	Temperature [°C]	Viscosity [mPa·s]
60	82.4	40	5945

Dynamic viscosity of slurry with single point measurement

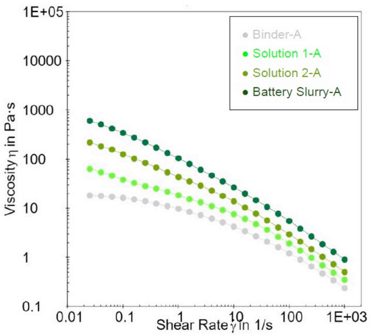


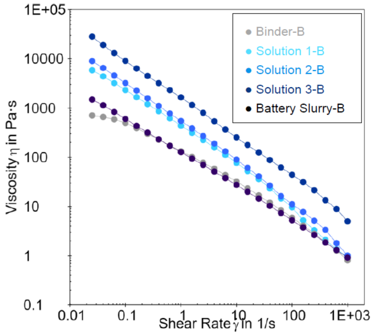
Calculated Herschel-Bulkley parameters to determine the flow behavior of slurry

The flow index is a description of the Newtonian or non-Newtonian behavior of the sample. A flow index that is smaller than 1 indicates that this slurry is shear-thinning – as is the case here for this slurry.

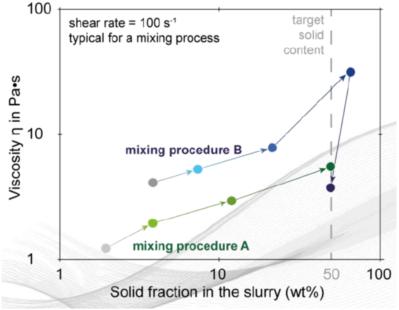
ViscoQC 300

SLURRY VISCOSITY





Viscosity curves measured after stepwise addition of components, representing the processing steps for mixing procedures A and B

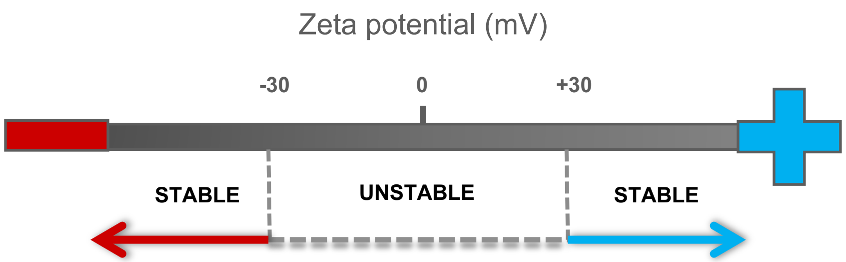


Comparison of mixing procedures A and B in terms of total solid fraction and viscosity, at constant shear rate

MCR 302e

ZETA POTENTIAL (ζ)

- The zeta potential describes the stability of colloidal dispersions.
- Zeta potential is an important parameter for the characterization of particles in infusions and emulsions.
- The higher the magnitude of the zeta potential (highly + OR highly -), the more stable the colloid.
- Zeta potential is measured by electrophoretic light scattering (ELS)
- During an ELS measurement an electric field is applied, which induces a collective motion of particles: particles with a higher zeta potential will move faster than less-charged particles.



Omega cuvette

Litesizer 500
Dynamic light scattering (DLS)
Electrophoretic light scattering (ELS)

DENSITY AND PERCENT SOLIDS

› Gas pycnometry can be used to determine the density and percent solids of electrode slurries
› This is relevant for optimizing the surface area of the solid electrode

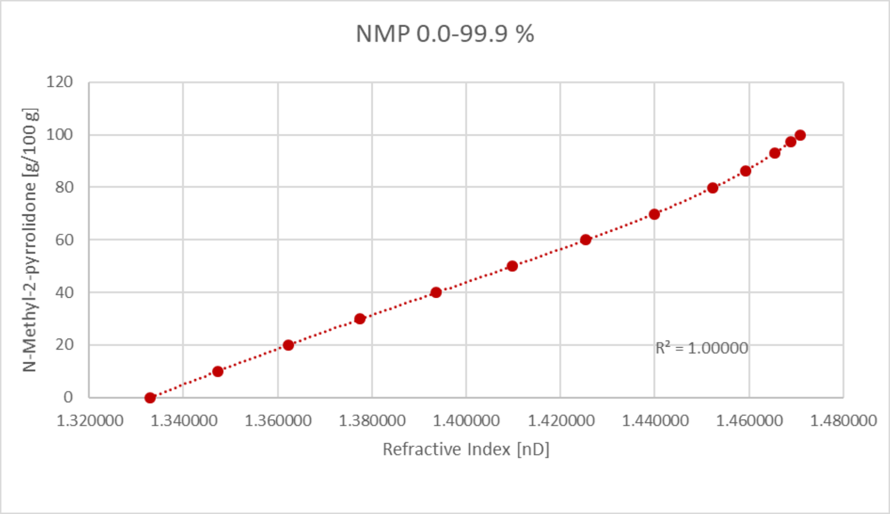
Ultrapyc Series

% solids formulated	Measured density (g/cm^3)	% solids calculated
41.45	1.3459	41.52
33.9	1.2682	34.27
26.30	1.1977	26.86
17.75	1.1226	17.96
15.22	1.1001	15.05
10.57	1.0688	10.81
6.41	1.0388	6.50
2.52	1.0121	2.45

Formulated and calculated % solids in slurries with measured densities

SOLVENT CONCENTRATION

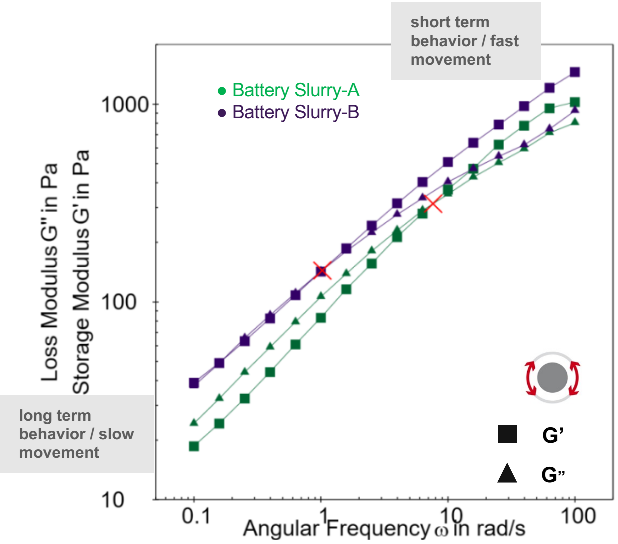
- N-Methyl-2-pyrrolidone (NMP) is a strongly polar aprotic solvent commonly used in battery slurry preparation to dissolve binders like PVDF
- NMP is also used as a solvent for lithium salts in electrolytes
- Because of its relative high price as well as its negative environmental impact, NMP is often recovered after use in the manufacturing process of lithium batteries
- Refractive index correlates with the concentration of NMP, so it is a quick and inexpensive way to measure it from 0.0% to 99.9%



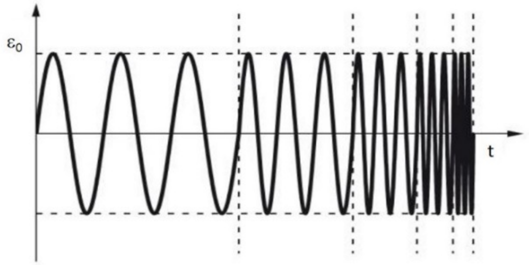
Refractive Index of different NMP concentrations measured at 20 °C and 589 nm

Abbemat 550

SEDIMENTATION STABILITY



Frequency sweeps of sample battery slurry A and battery slurry B.



Schematic profile of the applied deformation during a frequency sweep test

- A slurry is considered stable when the storage modulus G' is higher than the loss modulus G"
- High frequencies enable evaluation of the samples' short-term behavior, while low frequencies simulate the behavior of the sample over a long time
- G">G' would be considered the cross-over point where the slurry sediments
- In this example, slurry B exhibits better stability (cross-over at ~ 1 rad/s) compared to slurry A (cross-over at ~ 10 rad/s)

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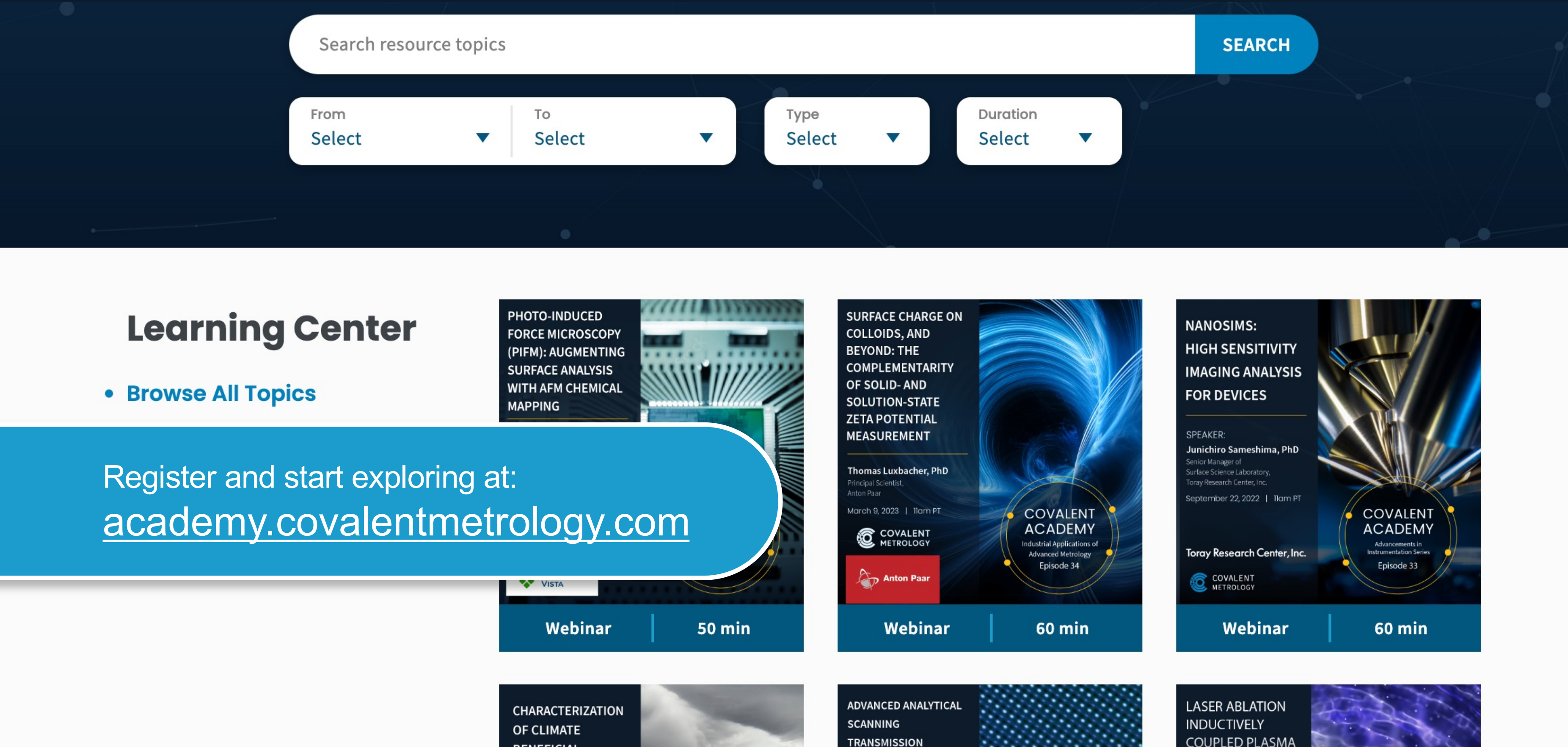
QUESTIONS?

Anton Paar

www.anton-paar.com/us-en/products/industries/application/lithium-ion-batteries/

View On-Demand Recordings in the Covalent Academy

COVALENT METROLOGY



Register and start exploring at:
academy.covalentmetrology.com

Q & A
Session

COVALENT METROLOGY

Thank you.