Battery Materials Characterization

Focusing on micro and surface analysis techniques

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Battery materials characterization

Materials and structures

- Lithium ion battery structure
- Structural analysis
  - Anode
  - Cathode
  - Separator
- Electrode cross sections
- Advanced analysis techniques
  - Solid-Electrolyte Interface (SEI)
  - Lithium analysis
  - Combined AFM-in-SEM
- Technical Cleanliness & Contamination

Analytical Techniques

- Electron Microscopy
  - SEM (-STEM)
  - TEM (-STEM)
  - FIB (-SEM)
  - EDS, EBSD, WDS, EELS
- Surface Analysis
  - (TOF-)SIMS
  - LEIS
  - XPS
  - AFM-in-SEM
- Sample preparation
  - Ion milling
  - Laser micromachining

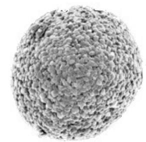
The Lithium Ion Battery

Spectral

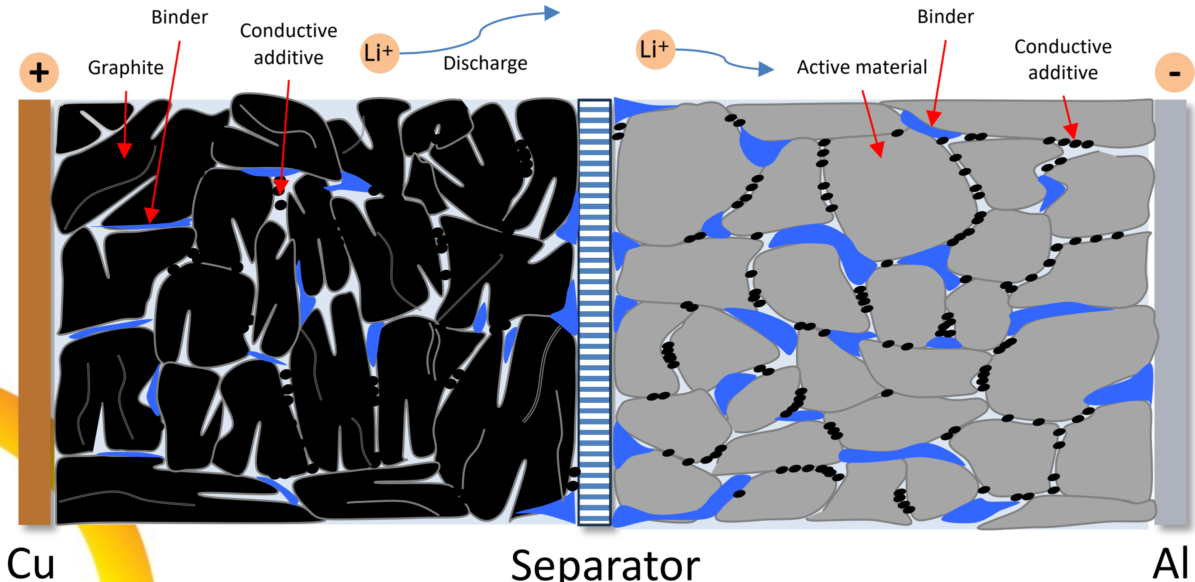
Anode

Graphite (C)
Lithium titanate (LTO)
Silicon (Si)

Cathode



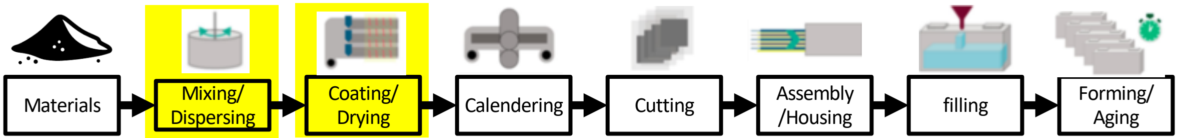
Lithium ferrous phosphate (LFP)
Lithium cobalt oxide (LCO)
Lithium manganese spinel (LMO)
Lithium nickel cobalt aluminium oxide (NCA)
Lithium nickel manganese cobalt oxides (NMCs)



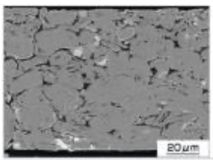
Structural analysis

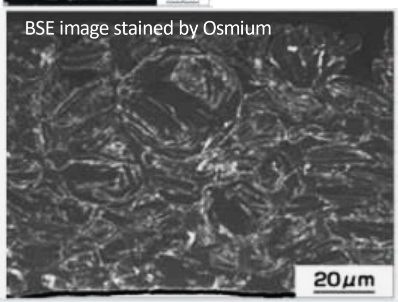
Spectra

Manufacturing Process

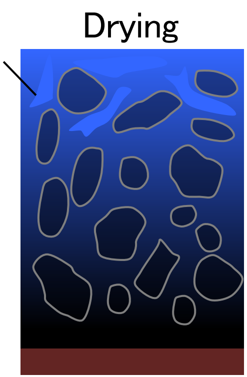


Analysis	Distribution of binder in anode

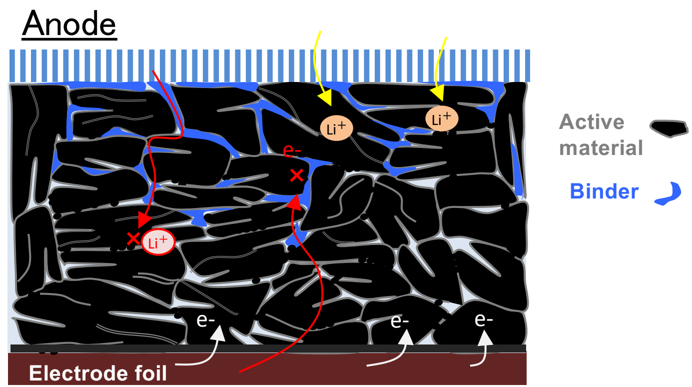




Unsuitable drying condition causes binder migration



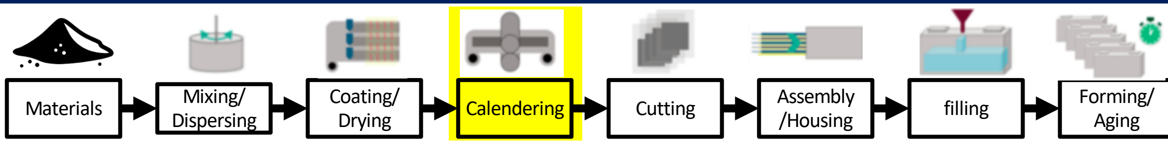
[Binder migration during drying of lithium-ion battery electrodes: Modelling and comparison to experiment - ScienceDirect]



Effect	High resistance

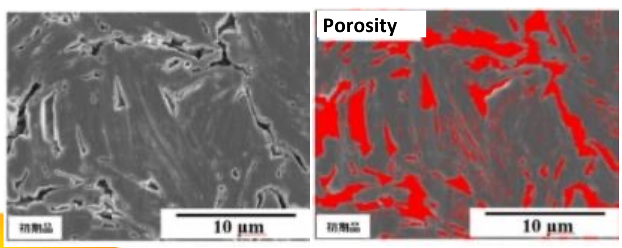
Structural analysis

Manufacturing Process

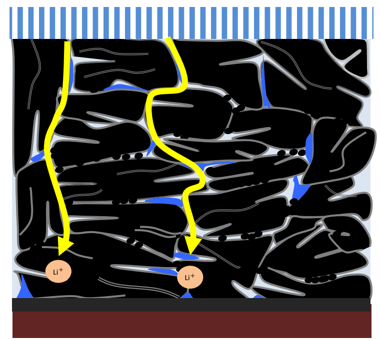


Analysis | Porosity and thickness of cathode/anode

Anode Active material

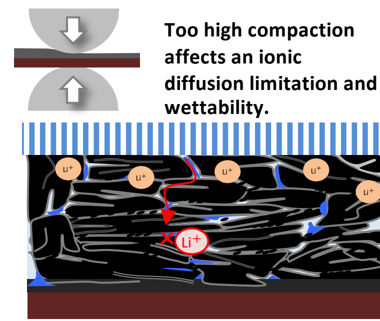


Porosity measurement



Moderate press

Too high compaction affects an ionic diffusion limitation and wettability.



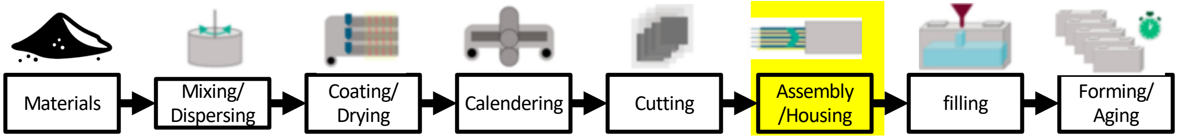
Too much press

Result | Ion conductivity

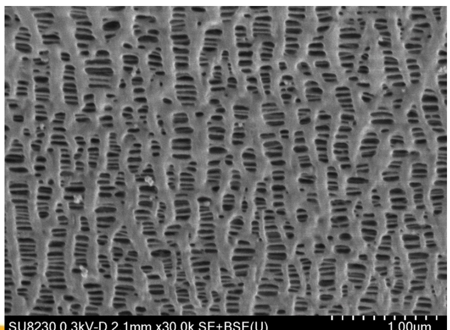
Structural analysis

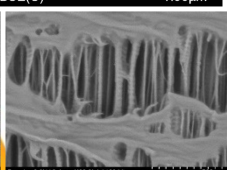
FE-SEM

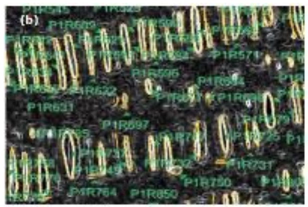
Manufacturing Process



Analysis Porosity of separator







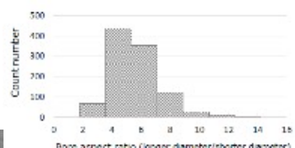


Figure 3. Distribution of the pore aspect ratio

《Porosity》

- A smaller value is preferable from the viewpoint of self-discharge, prevention of micro-short circuit, and mechanical strength
- A larger value is preferable from the viewpoint of charge-discharge cycle. Normally, it is set to about 40-50%.

《Hole diameter》

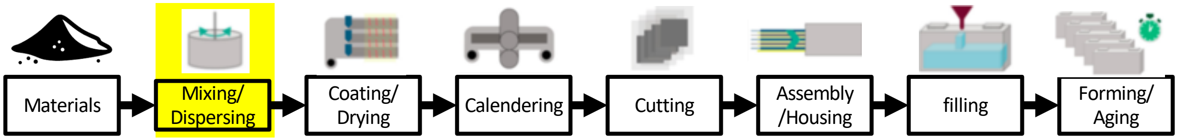
- The larger the maximum pore size leads to high ion conductivity.
- The smaller the maximum pore diameter leads the less self-discharge and micro-shorting occur.
- The larger the average pore diameter leads the faster the permeation rate of the electrolyte (better liquid absorption).
- If the pore size non-uniformity is large, the flow of ions becomes non-uniform, leading to deterioration in cycle characteristics.
- The average pore size is usually set at around 0.1 to 0.5 µm.

Result Self discharge, conductivity, etc

Structural analysis

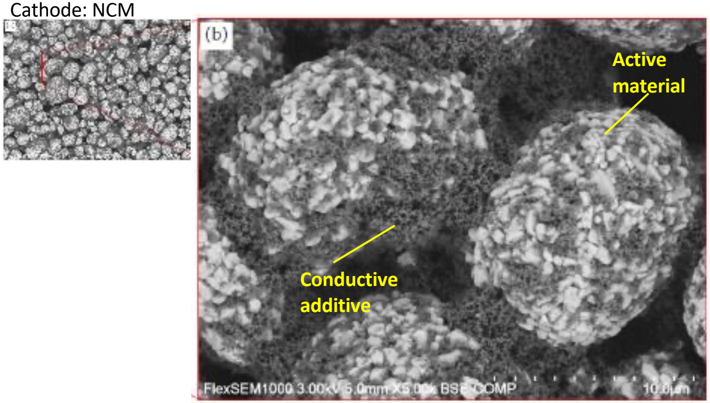

FlexSEM1000

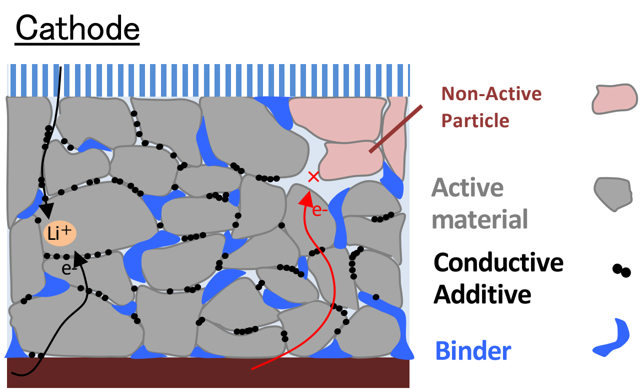
Manufacturing Process



Analysis Dispersion of active material and conductive additive in Mixing Process

Cathode: NCM



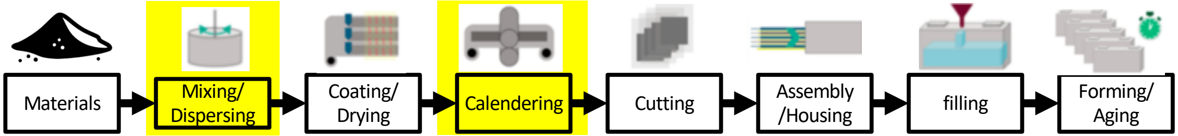


Samples provided by courtesy of Hajime Okui, DAINEN MATERIAL Co.,Ltd.

Result Low capacity

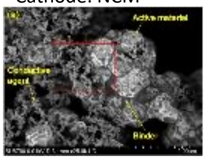
Structural analysis

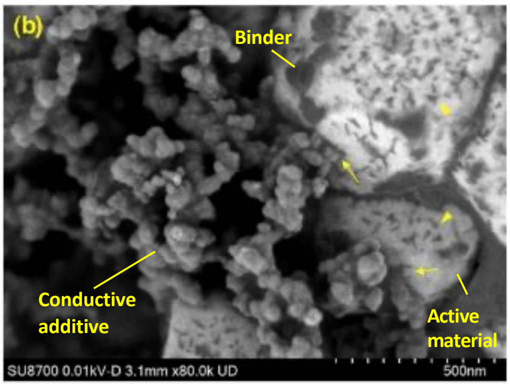
Manufacturing Process



Analysis Dispersion among active material, conductive additive and binder in Mixing Process

Cathode: NCM

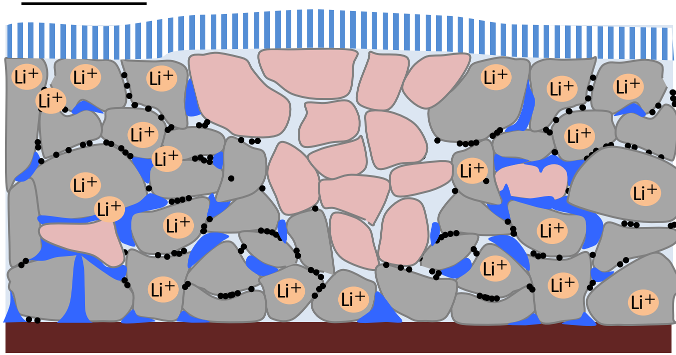




Distribution of conductive additive and binder around active material.

Samples provided by courtesy of Hajime Okui, DAINEN MATERIAL Co.,Ltd.

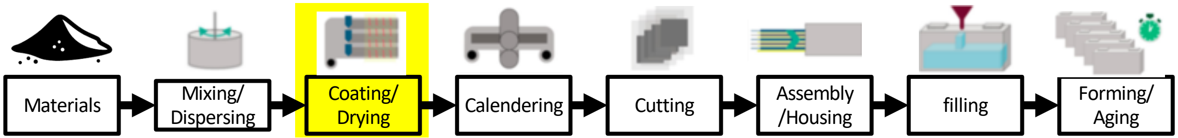
Cathode



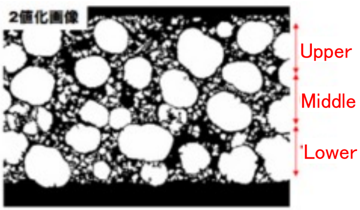
Result Low capacity

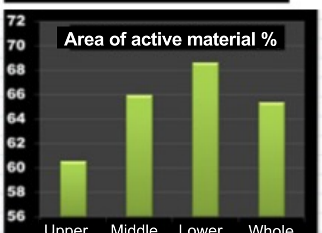
Structural analysis

Manufacturing Process

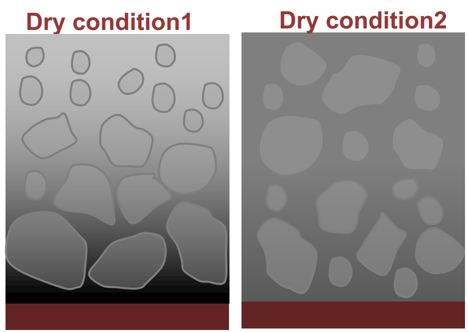


Analysis Dispersion of active material with various size after drying process





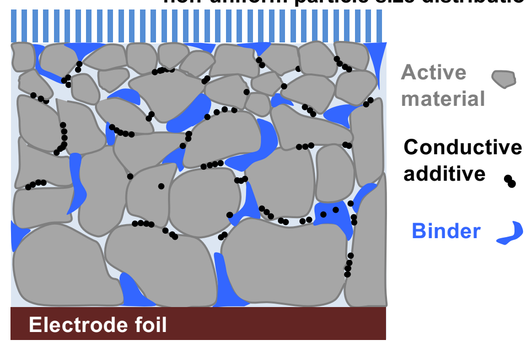
Coating/drying



Evaluation of positive electrode active material particle size and dispersion state by image analysis | Nissan Arc Co., Ltd. (nissan-arc.co.jp)

Cathode

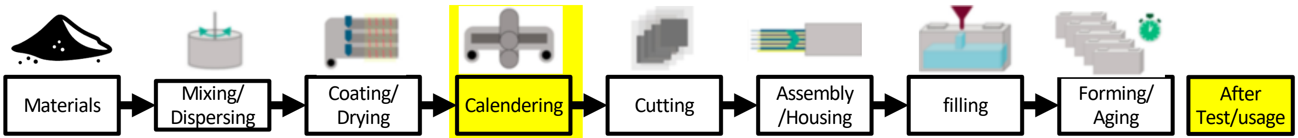
Unsuitable drying condition causes non-uniform particle size distribution.



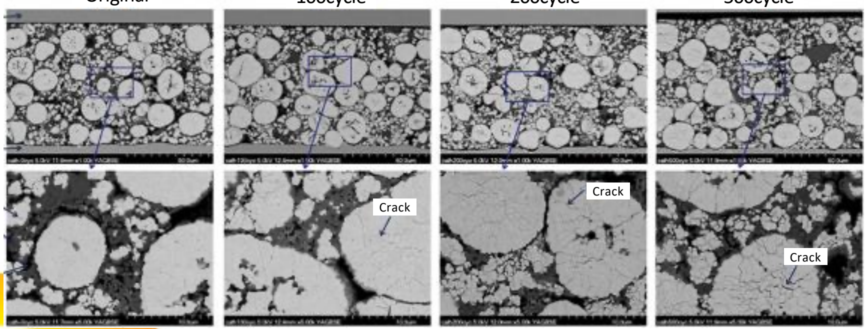
Result Lifetime

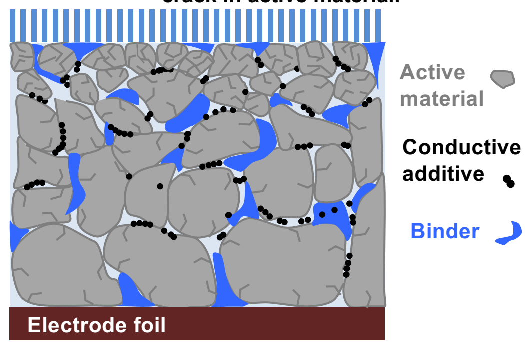
Structural analysis

Manufacturing Process



Analysis PSD & porosity after calendering





Morphological Observation of Cathode Materials
Nissan Arc Co., Ltd. (nissan-arc.co.jp)

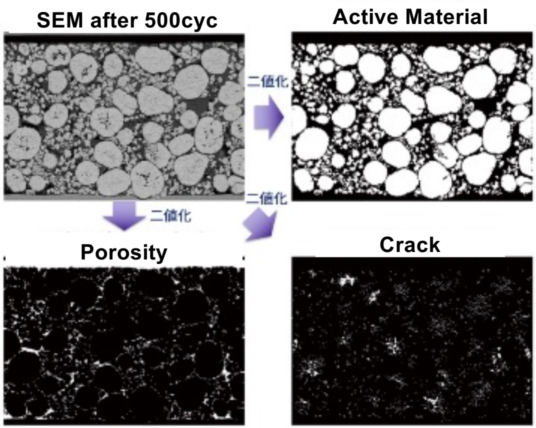
Result Lifetime

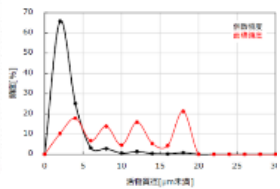
Structural analysis

Manufacturing Process

Materials → Mixing/ Dispersing → Coating/ Drying → **Calendering** → Cutting → Assembly /Housing → filling → Forming/ Aging

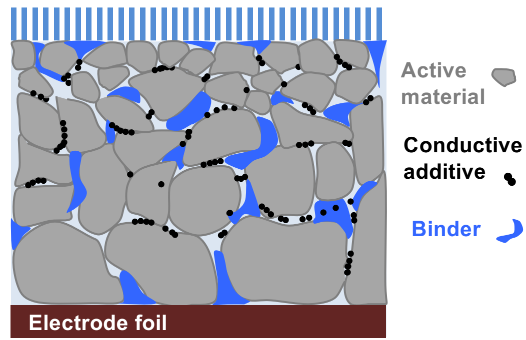
Analysis	PSD & porosity after calendering





Particle size distribution

Cathode

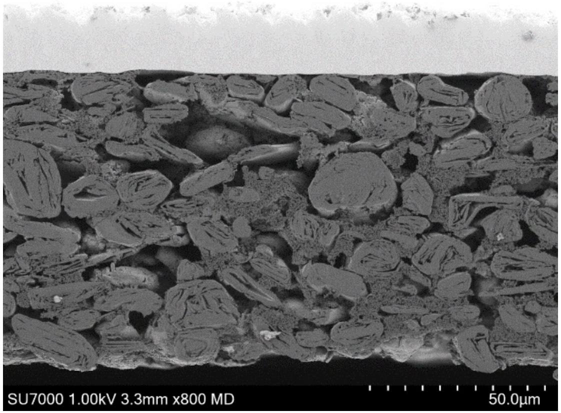


Result	Lifetime

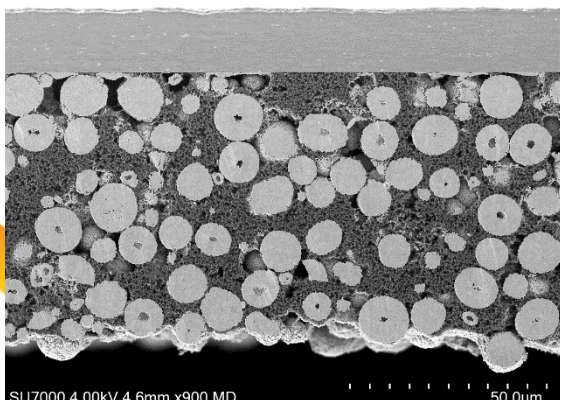
Morphological Observation of Cathode Materials
Nissan Arc Co., Ltd. (nissan-arc.co.jp)

Electrode cross sections

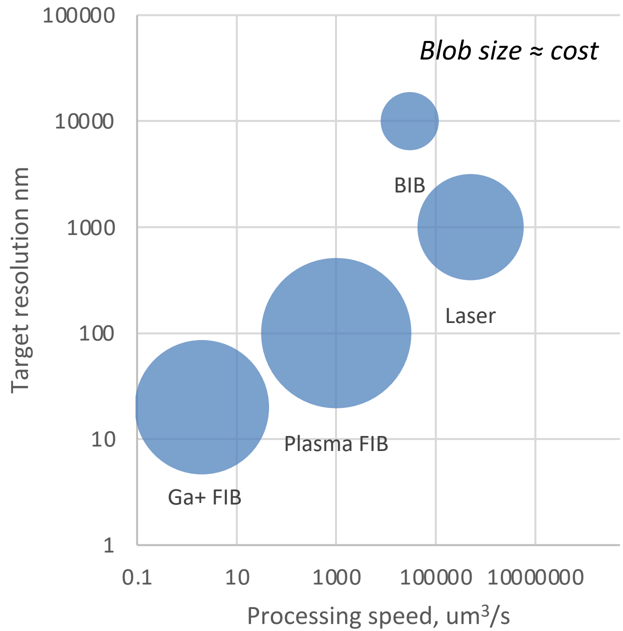
Anode



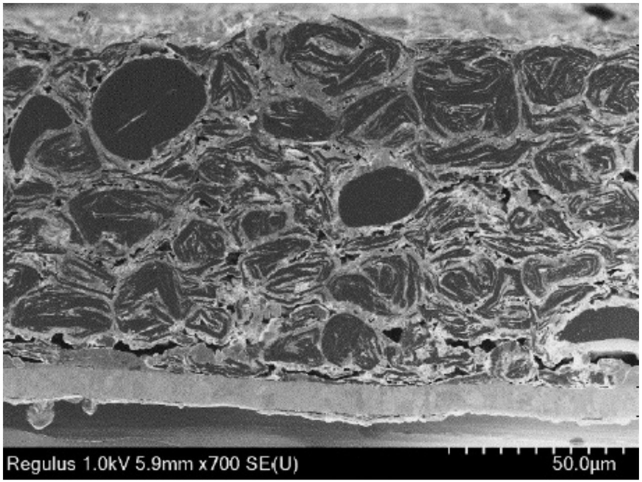
Cathode

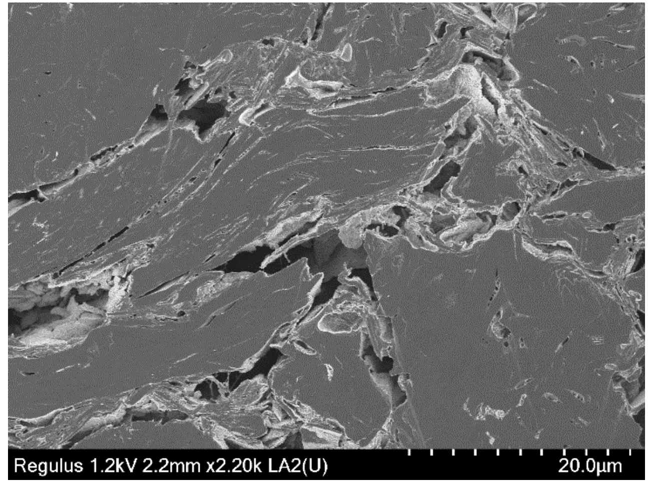


Cross section techniques

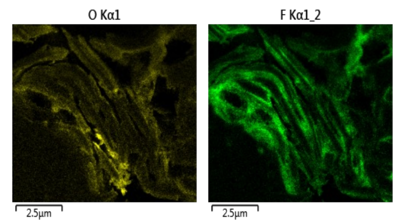


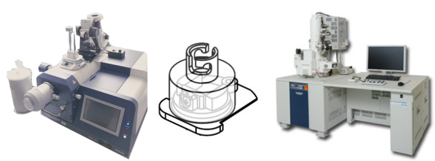
Inert sample transfer –
Analysis of SEI layer after cycling





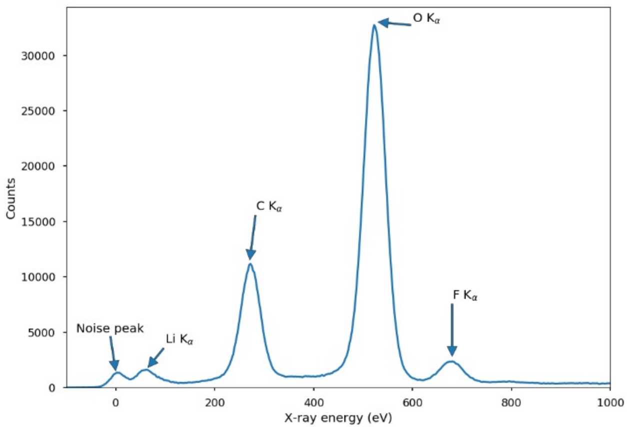
To study the Solid – Electrolyte Interface (SEI) formed during cycling it is often necessary to transfer the sample in vacuum or inert gas before analysis in the SEM.





Lithium Analysis

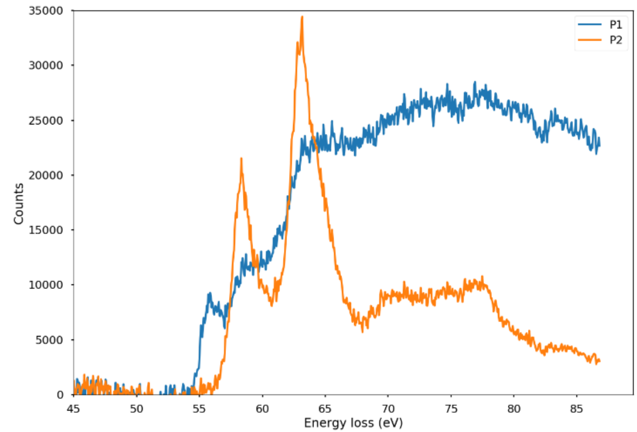
2 kV Windowless SDD



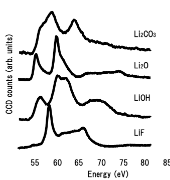
Spectrum with Oxford Extreme, windowless EDS detector.

Detector is capable in seeing the Li Kα signal, but Li has only few electrons and bonded in an oxide state the probability to emit an X-ray photon is very small.

30 kV EELS

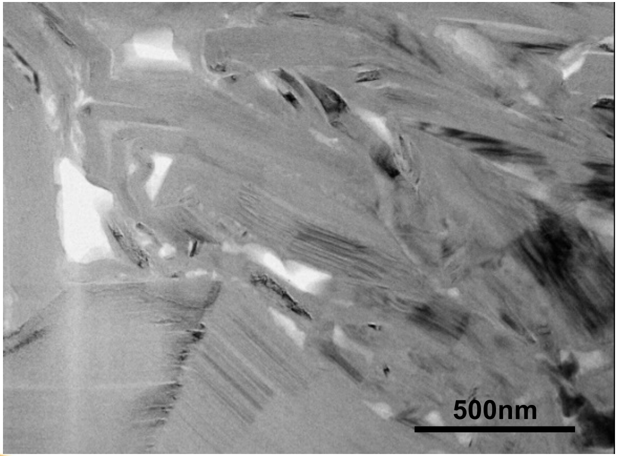


It is now possible to mount EELS (Electron Energy Loss Spectrometer) also in a 30kV SEM/STEM. With EELS it is possible to detect Li and also see its chemical bonding state.

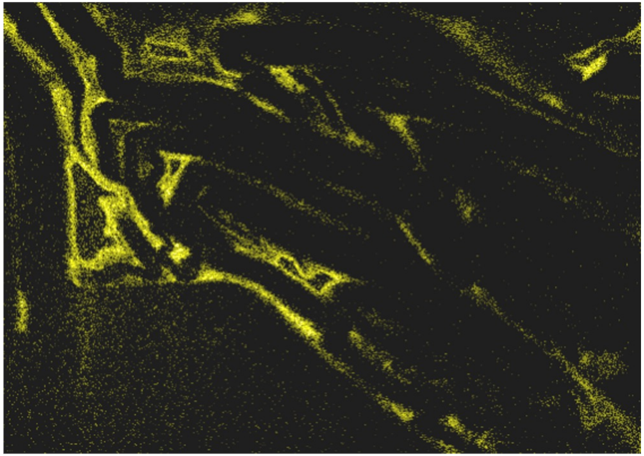


EELS mapping of Li distribution

BF-STEM image



EELS mapping（Li-K）



Instrument：HD2700 STEM、Analysis tool：EV3000、Accel voltage：200 kV、magnification 60kx、
Probe size：0.5 nm Ip：400 pA、mapping time：10 sec.

Active Cathode Material Coating

Spectral

To study the amount of active cathode material coating that remains after cycling the LiCarbEx method was developed by Tascon.
Low Energy Ion Scattering (LEIS) is a chemical analysis technique with an information depth of 1 atomic layer (~0.3 nm).
Unfortunately, in practice, these cathode materials are covered with a layer of Li_2CO_3 and LiOH that have to be removed before analysis of the coating coverage.

LiCarbEx Method

tascon
Analytical Services & Consulting

O atoms remove hydrocarbons

↓

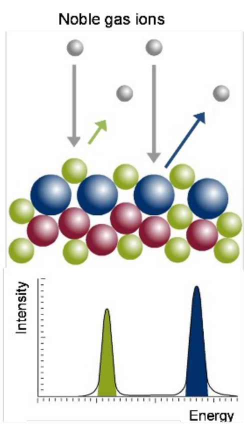
LiCarbEx removes LiOH and Li_2CO_3

↓

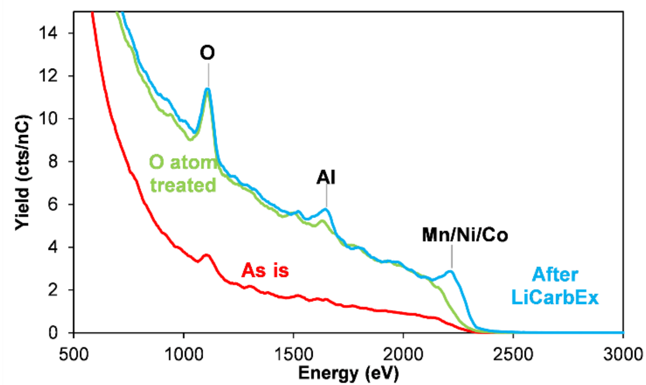
Analysis of (coated) cathode material

↓

Result is coating closure in %



LEIS principle

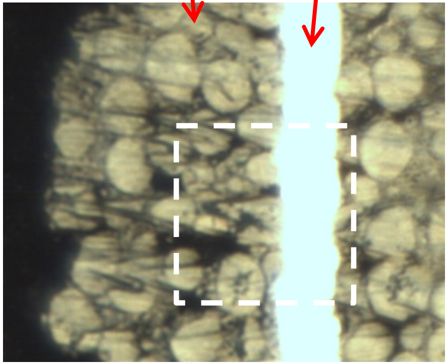


Combined AFM and SEM imaging

Optical microscope image

Cathode active material layer

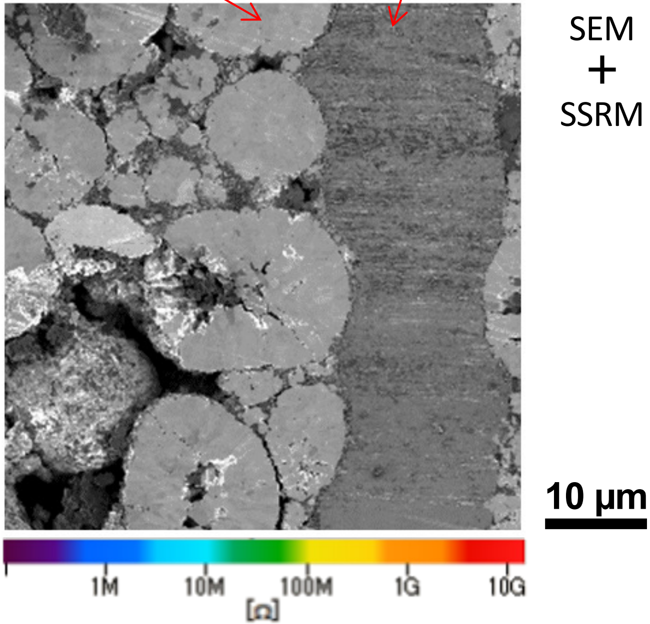
Al foil current collector



Cathode active material

Al foil

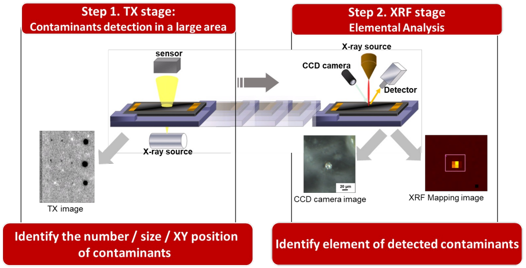
SEM + SSRM



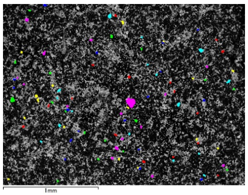
Atomic Force Microscopy (AFM) can add functional imaging options to the topography and chemistry contrasts provided by SEM.

Technical cleanliness TecSa

- EA8000 Combined transmission X-ray with uXRF elemental analysis, Fast screening for particles down to 20 um size Millions of particles/hour

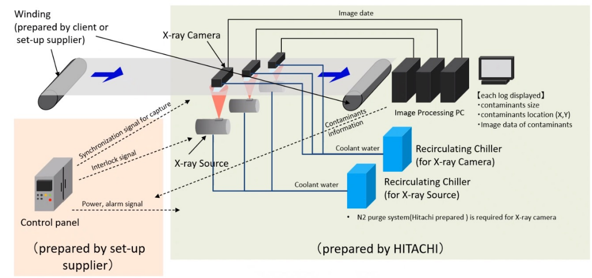


- SEM with automated EDS for particle analysis
  Up to 30.000 particles/hour
  particles size down to <1um
  (but only surface inspection)



- Inline X-ray detection of particles
  Count and size only, no chemistry
  <100 m/min, particles >30-50 um
  (looks through the material)

Example of **3 units** system



Our technique portfolio

Spectral

- Electron Microscopy
  - SEM (-STEM)
  - TEM (-STEM)
  - FIB (-SEM)
  - EDS, EBSD, WDS, EELS
- Surface Analysis
  - (TOF-)SIMS
  - LEIS
  - XPS
  - AFM-in-SEM
- In-situ tools
  - Mechanical testing
  - Nanoindentation
  - Micromanipulation
  - Electrical probing
  - Heating, cooling, …
- Sample Preparation
  - Grinding, polishing
  - Cleaning
  - Ion milling
  - Laser micromachining

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