# SEM: an essential tool for making better batteries

***Les journées pédagogiques du GN-MEBA***
***2 et 3 décembre 2024 à Jussieu, Paris***



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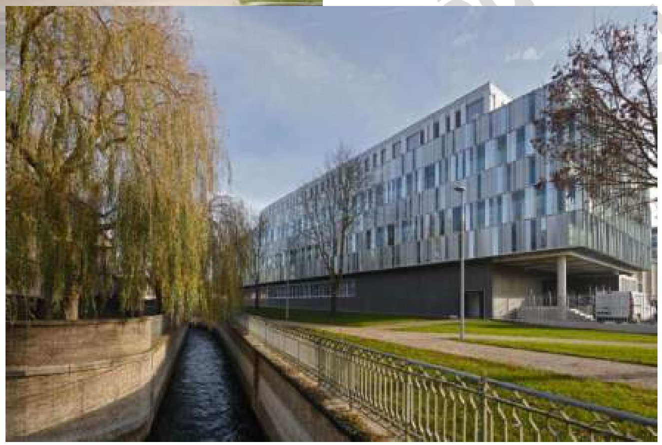
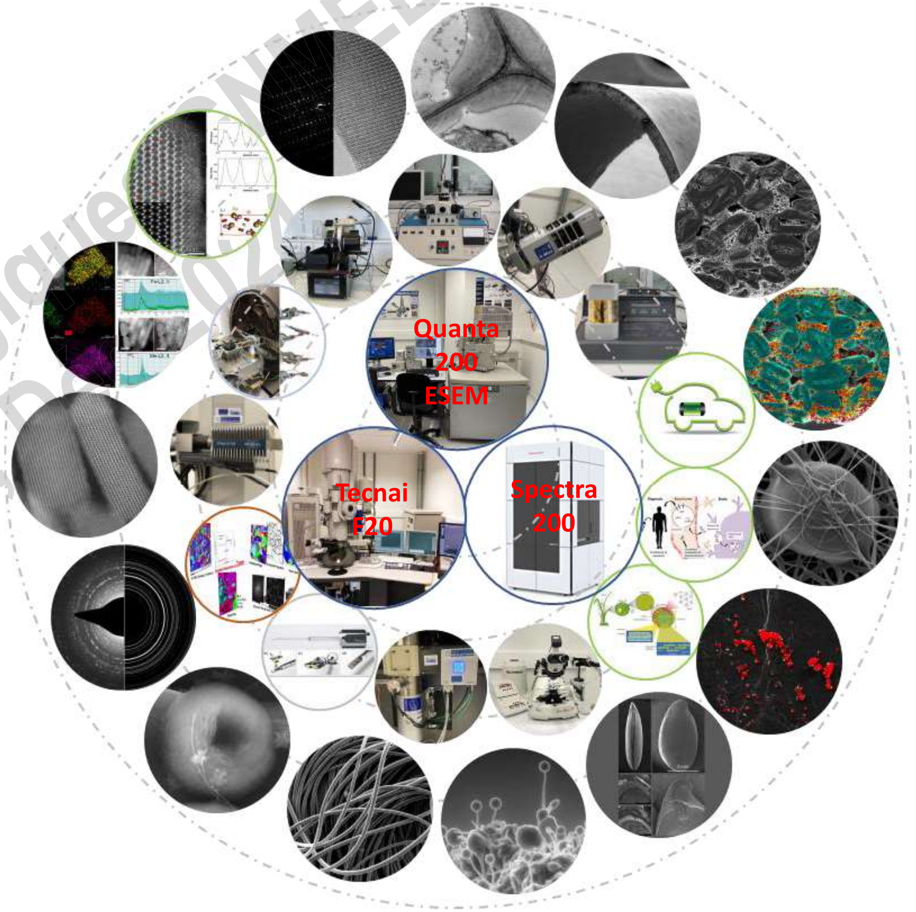
# Plateforme de Microscopie Electronique
# Université de Picardie Jules Verne (UPJV), Amiens



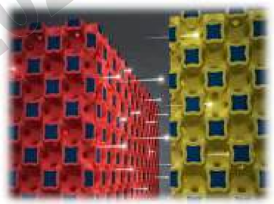


# LRCS/RS2E

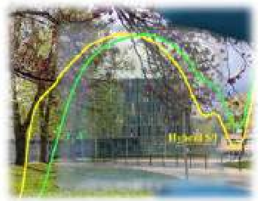
## Laboratoire de Réactivité et Chimie des Solides
## Réseau sur le stockage électrochimique de l'énergie


**Synthèse de matériaux organiques et inorganiques**

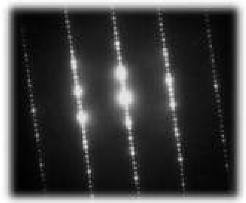
**Electrochimie des matériaux et systèmes**



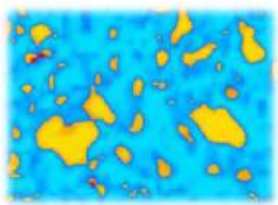
**Systèmes (3-D Printing, Prototypage, Cellules solaires)**



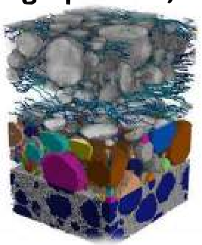
**Diffraction, Operando, Cristallochimie**



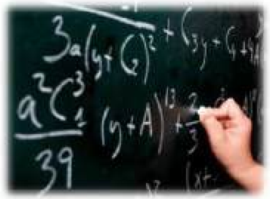
**Spectroscopies & Spectrométries**



**Microscopie Electronique, Tomographie RX, AI,….**



**Physics-Based Modeling**



**Data-Driven Modeling**

LRCS utilise et développe des outils et méthodes de pointe autour du stockage et de la conversion de l'énergie

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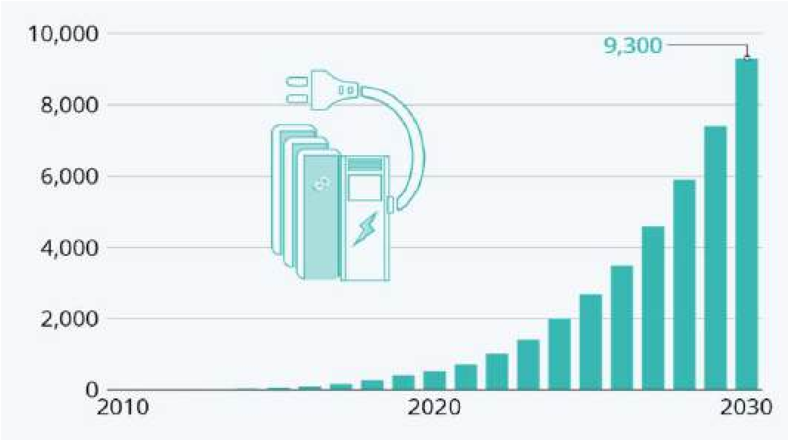
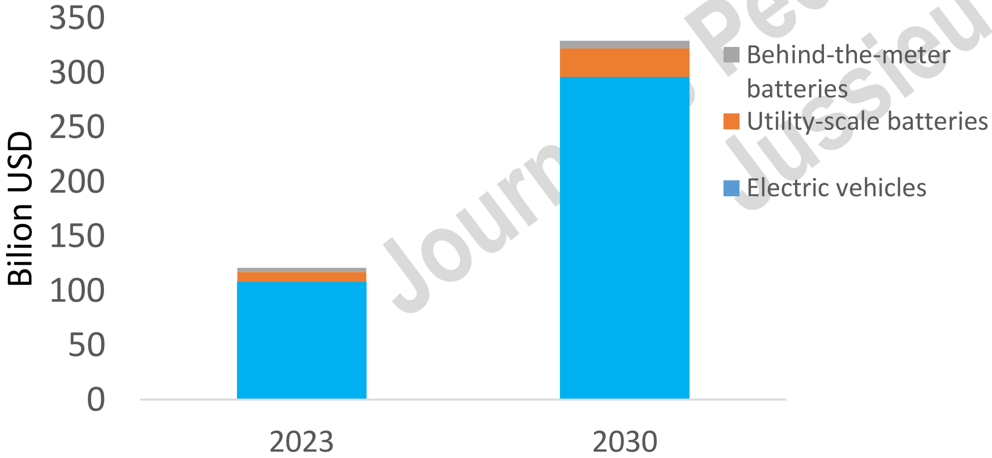
# Batteries today

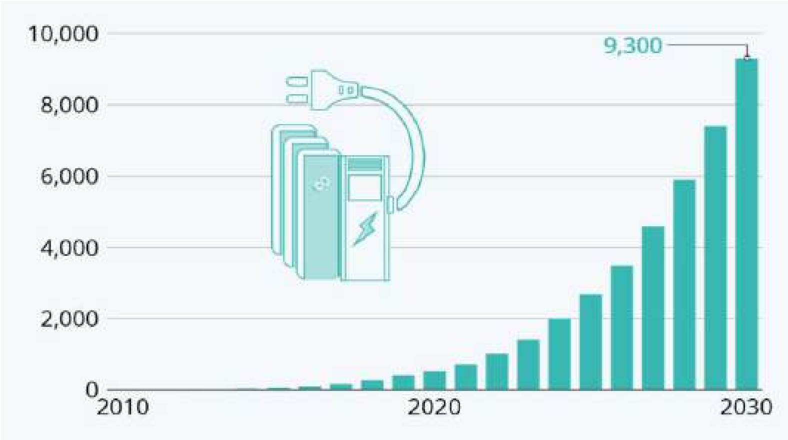



Cumulative Li-ion battery demand for Electric Vehicles/Energy storage application (in GW hours). *Source: Statista*




Battery pack market size by application and Stated Policies Scenario. *source: www.iea.org*


# Batteries today

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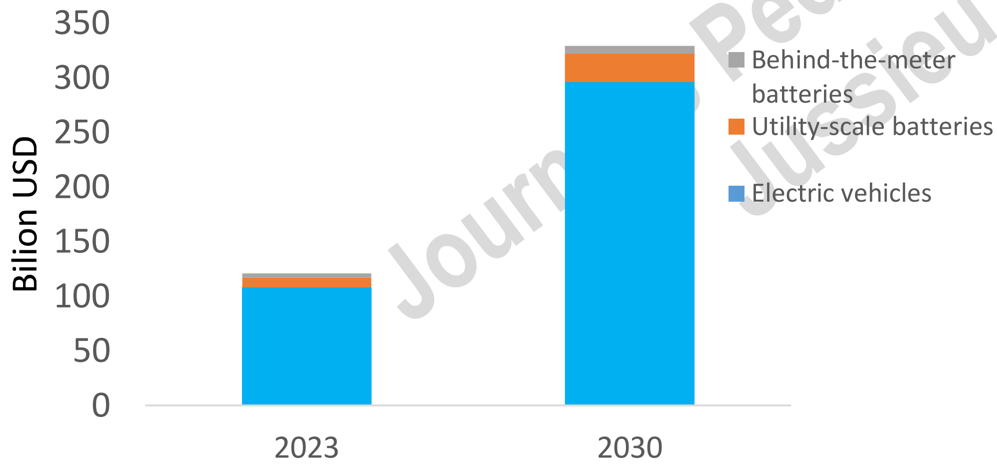


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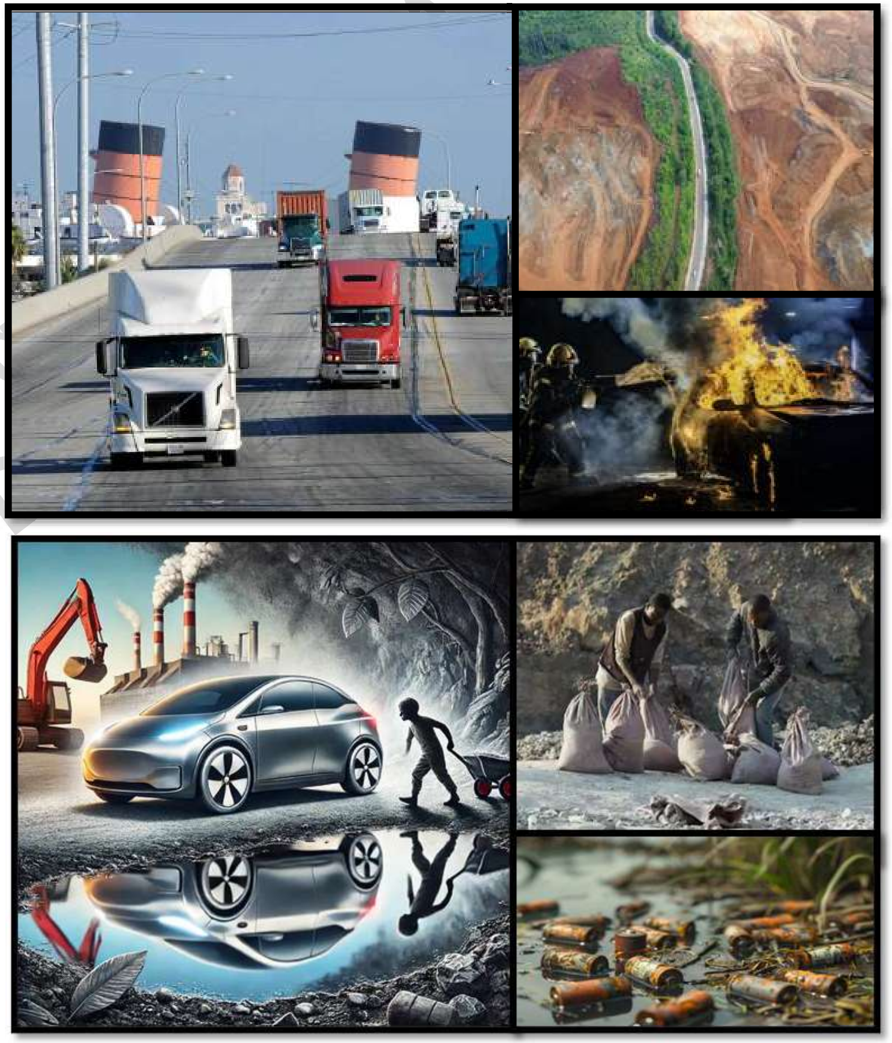


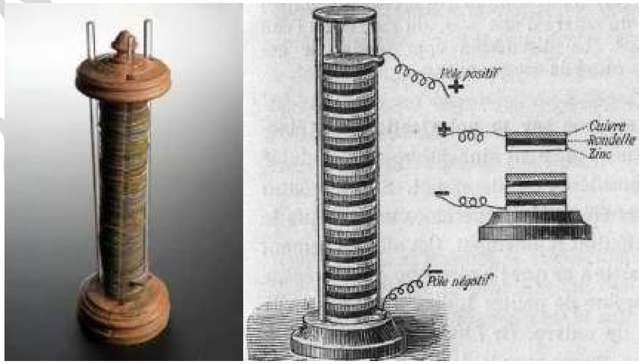
# Batteries for tomorrow

# Battery’s origin and evolution

Field Artillery Battery

Electrical battery

Electrochemical battery




# Battery diversity

Li-Ion battery

Coin battery


Zinc Carbon battery


Lead-acid battery


Sealed lead-acid

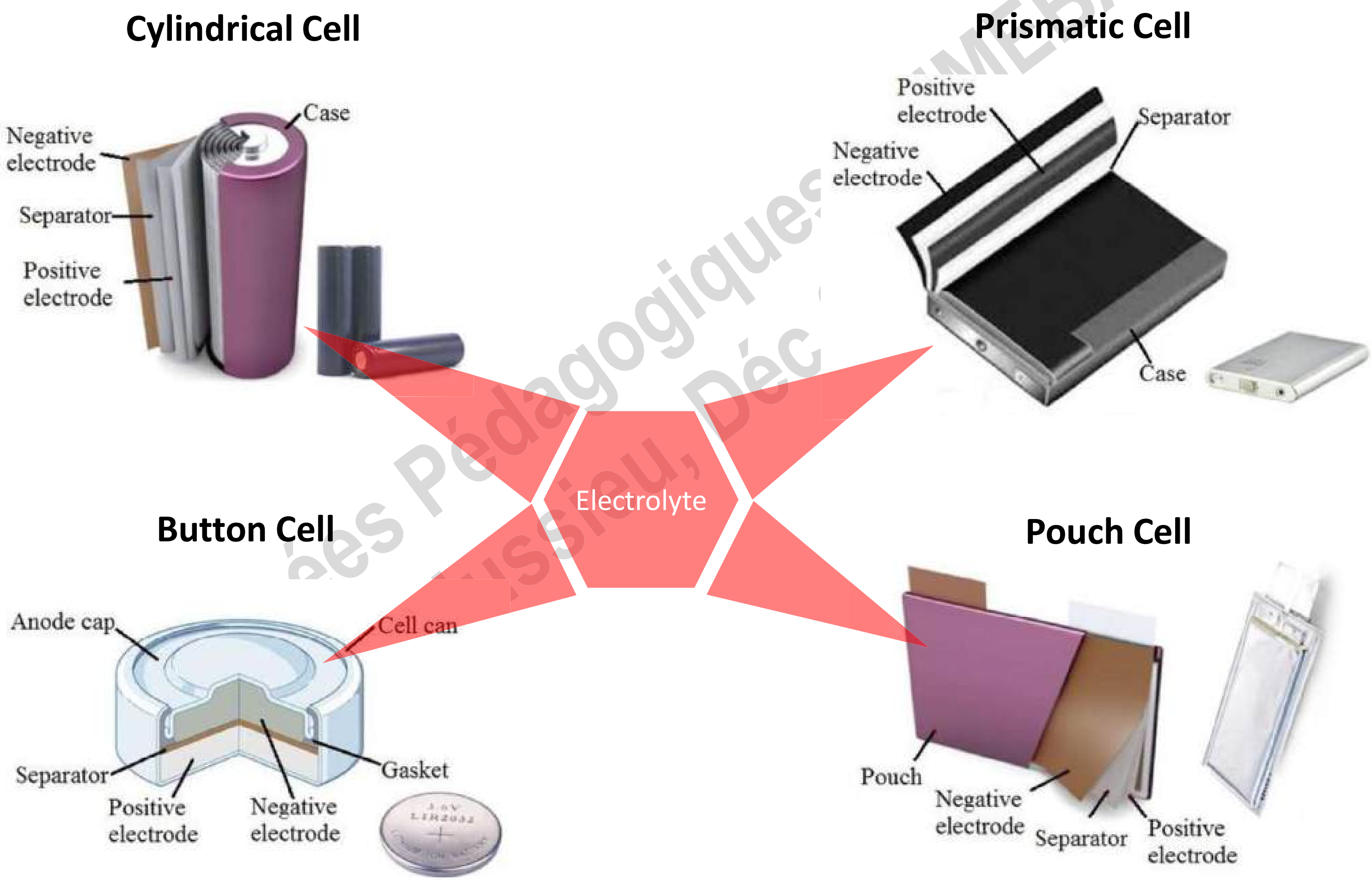

Ni-MH battery

Ni-Cd battery

Alkaline Battery


Zinc-Air battery

# Batteries main components



# Batteries main components



### Anode

- **Carbon-based materials** (e.g. graphite)
- **Metals** (e.g., lithium, silicon)
- **Metal oxides** (e.g. lithium titanium oxide)

### Electrolyte

- **Liquid organic solvents** with dissolved salts (e.g. $LiPF_6$ Li-ion batt.)
- **Solid ceramics** (e.g. LLZO)
- **Polymers** (e.g. PEO-based)

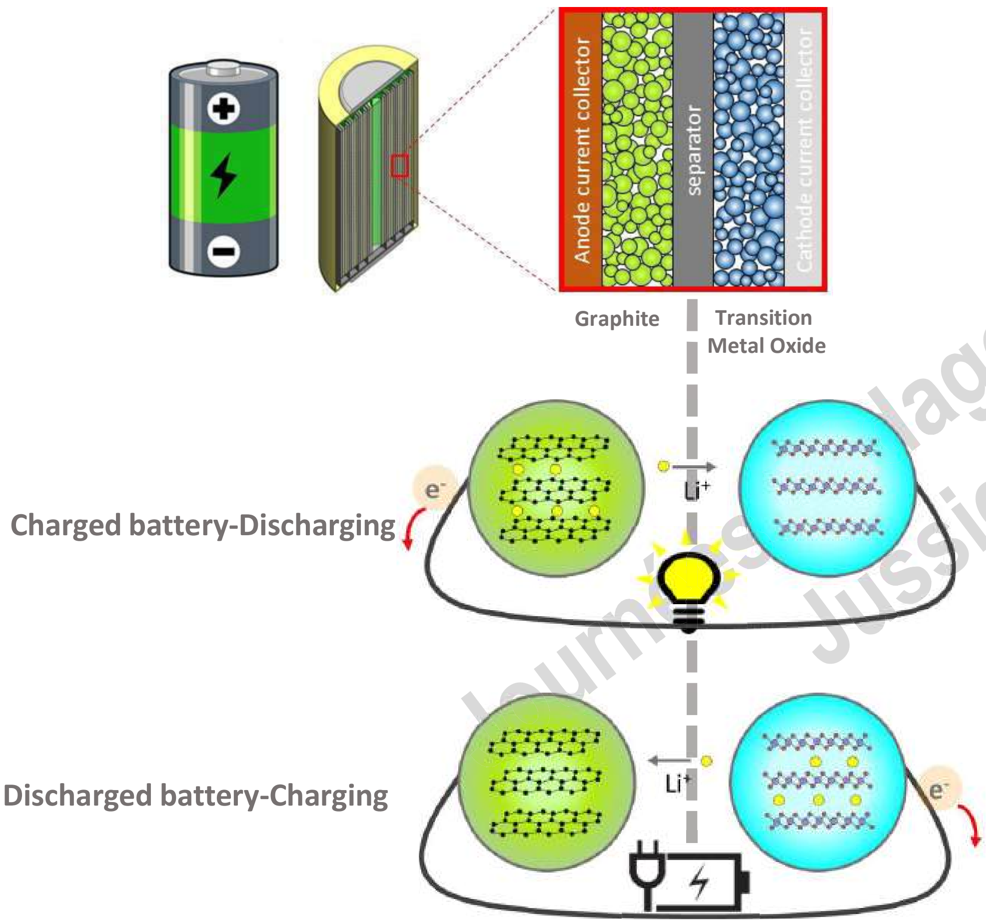
### Separator

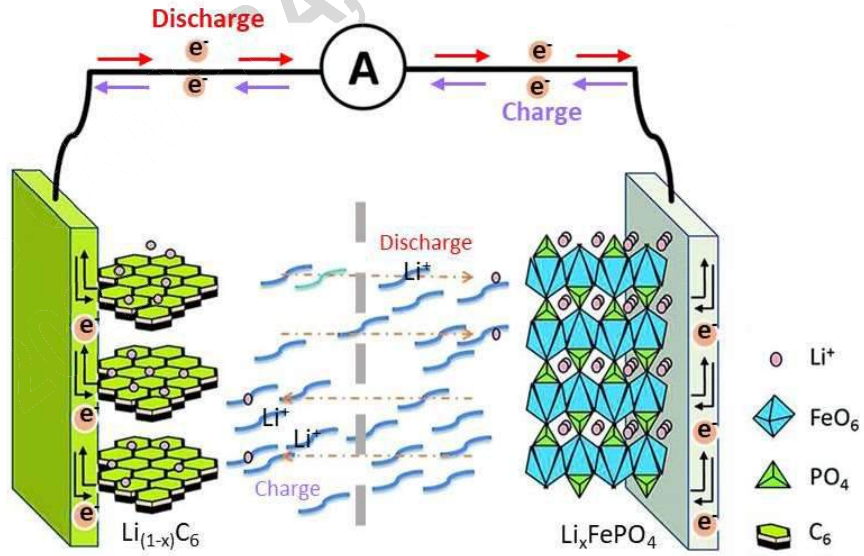
- **Microporous polymers** (e.g. polyethylene, polypropylene)
- **Ceramic-coated polymers**
- **Nonwoven fibers**

### Cathode

- **Metal oxides** (e.g. lithium cobalt oxide, nickel cobalt manganese)
- **Metal sulphides**
- **Polyanionic compounds**

# Inside the battery (electrochemical cell)

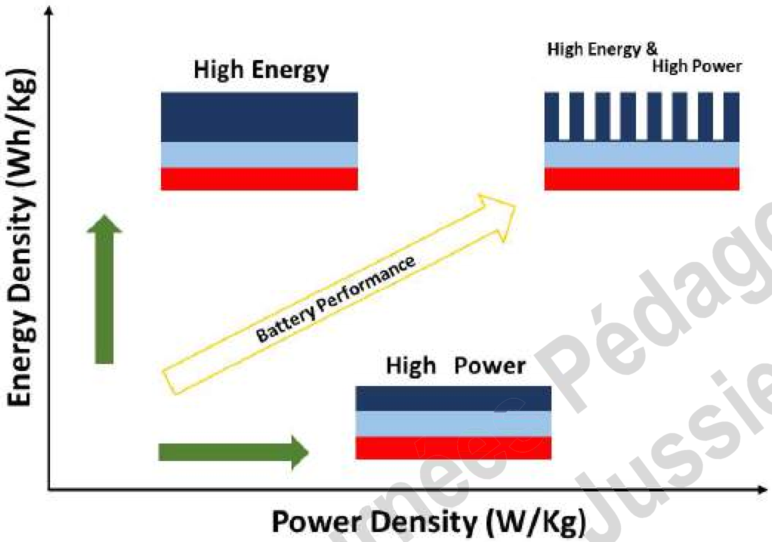


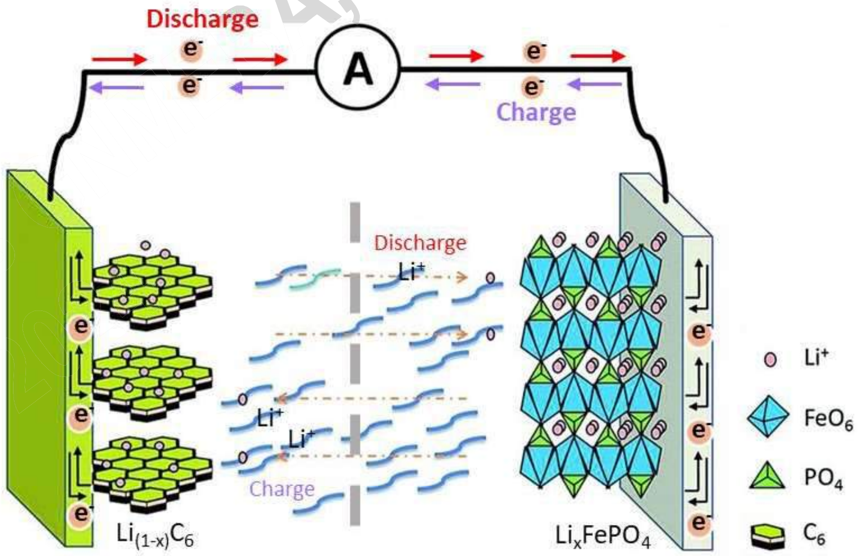




| Anode | Electrolyte | Separator | Cathode |
|---|---|---|---|
| Graphite/ Carbon | EC:EMC | Monolayer (PP) | Lithium Cobalt Oxide (LCO) |
| Lithium Titanium Oxide (LTO) | EC:DEC | Trilayer (PP/PE/PP) | Lithium Manganese Oxide (LMO) |
| Silicon | EC:PC:DMC | Ceramic | Lithium Iron Phosphate (LFP) |
| Silicon Carbon | | | Lithium NCA Oxide (NCA) |
| | | | Lithium NMC Oxide (NMC) |
| | | | Other variation |

*Image modified after: Billy Wu*
*https://www.billywu.xyz*
*https://etn.news/energy-storage*

# Inside the battery (electrochemical cell)

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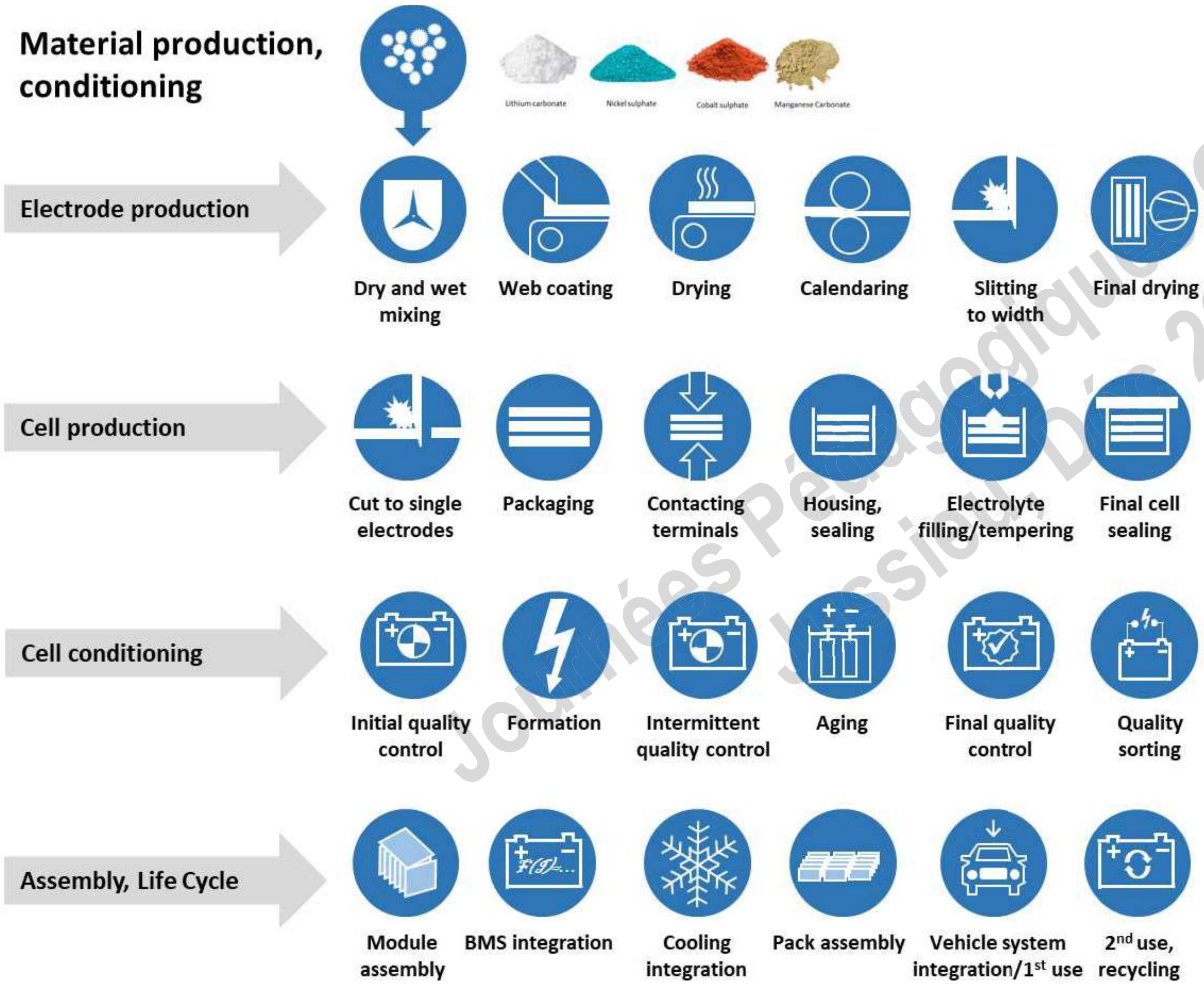
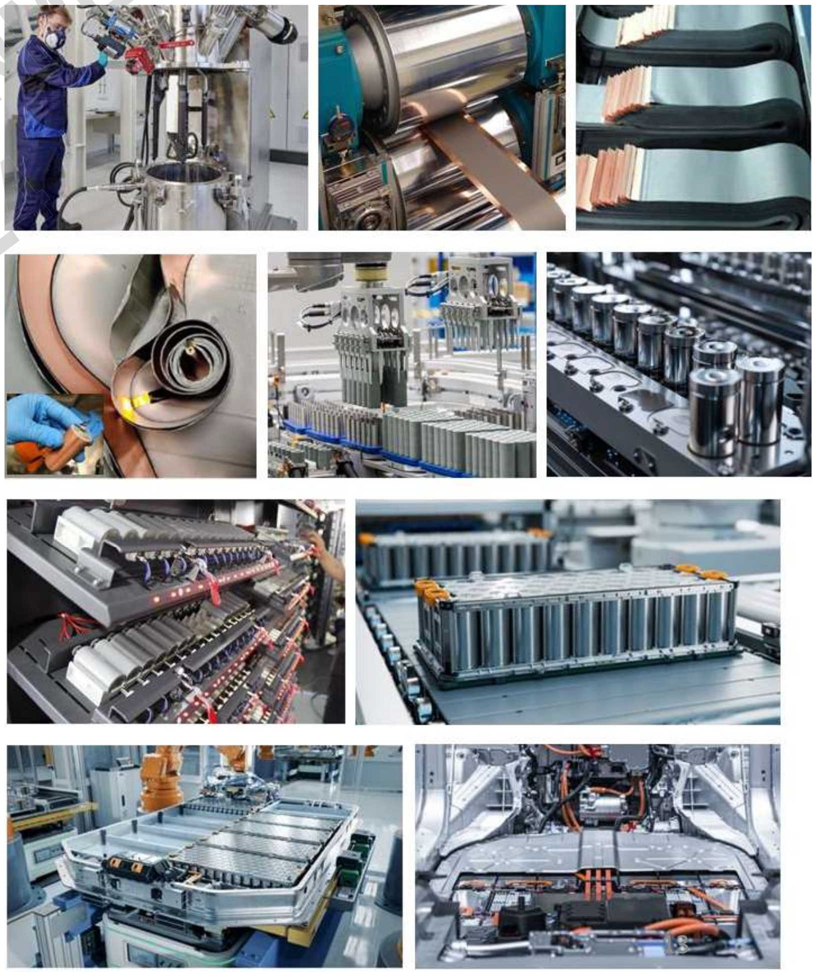
| | | | Other variation |



*https://energyeducation.ca*

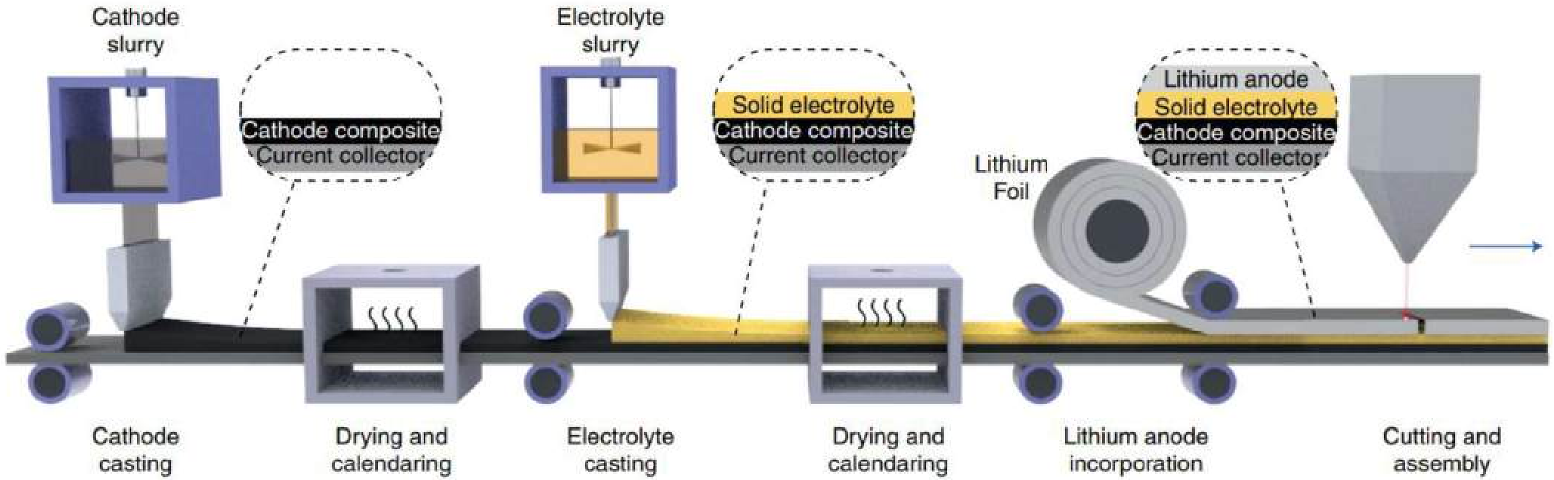
# Li-ion battery manufacturing

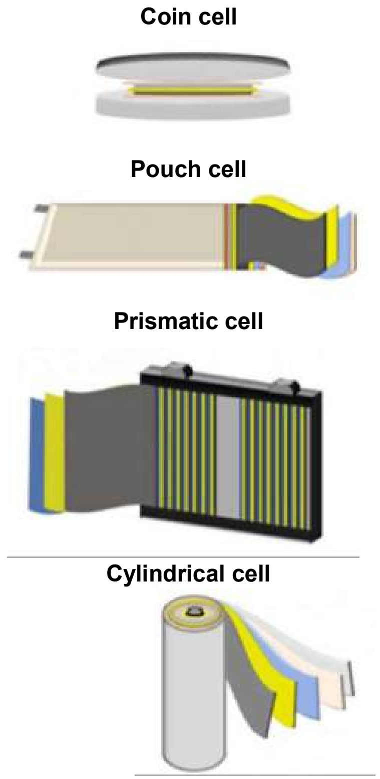


# All solid-state battery (ASSB) manufacturing

Next generation of energy storage: promising greater safety, energy density and performance



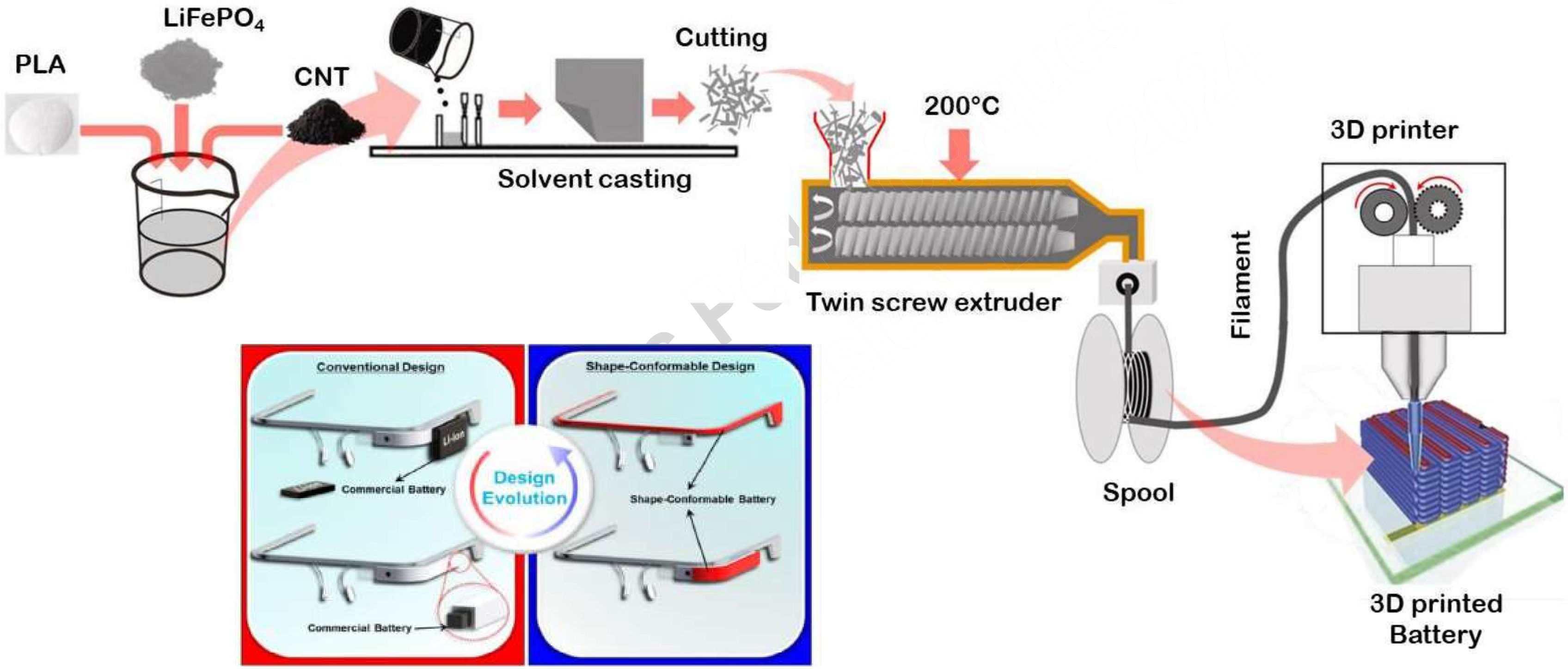



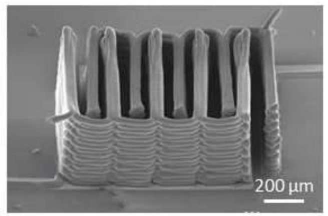

*Images: modified after tan et al. 2020, Zeman et al. 2022*

# 3D-Battery Manufacturing

Customized designs, improved performance, and streamlined manufacturing

## Filament Fabrication and 3D printing



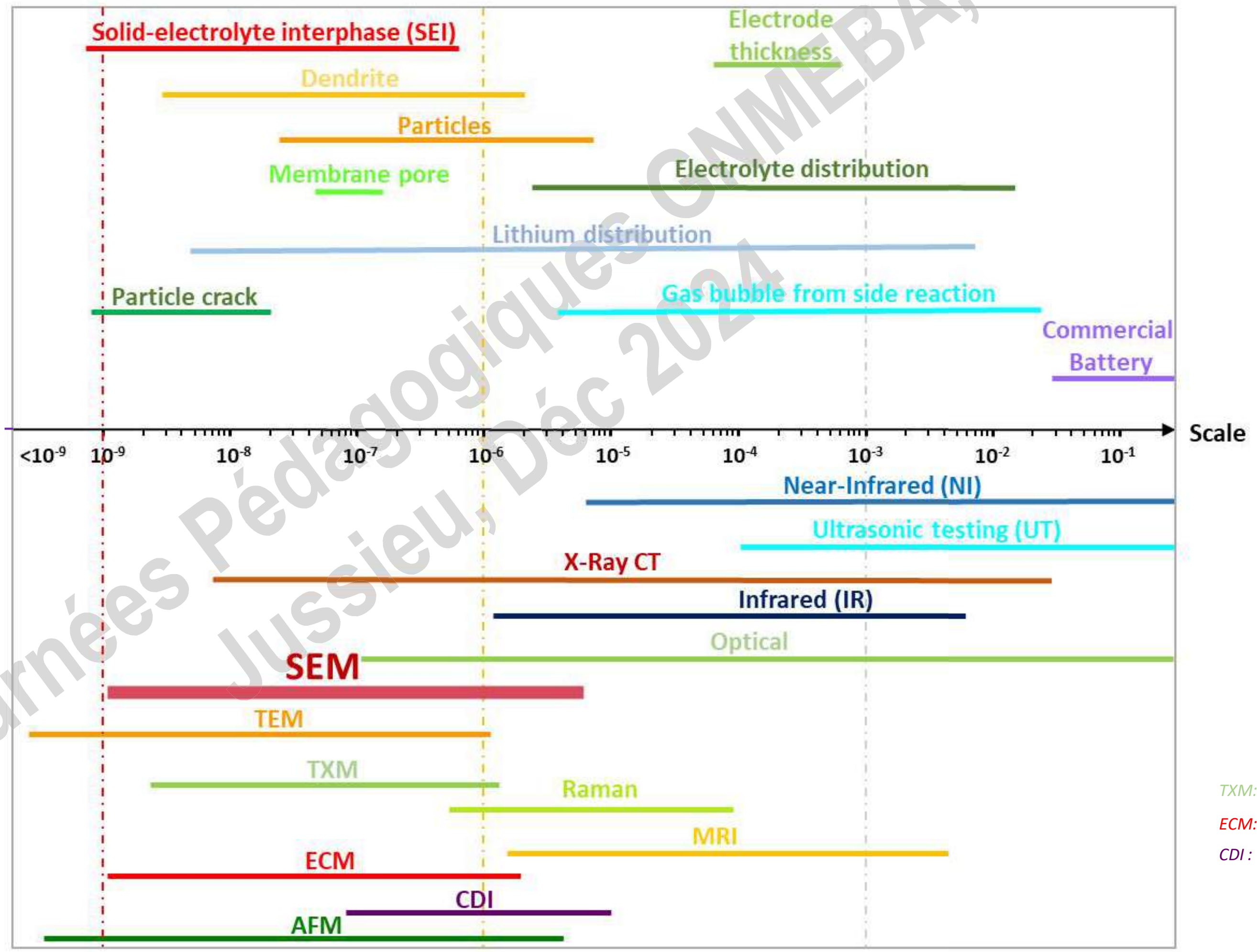

*Schematic: modified after www.unitalities-me.com and Seas.Harvard.edu,*
*Image: Kime et al. Nano Lett. 2015, 15, 8, 5168–5177*

# Visualization of battery materials

# Visualization of battery materials

**Features of battery materials**

**Imaging Techniques**




*TXM: Transmission X-ray Microscopy*

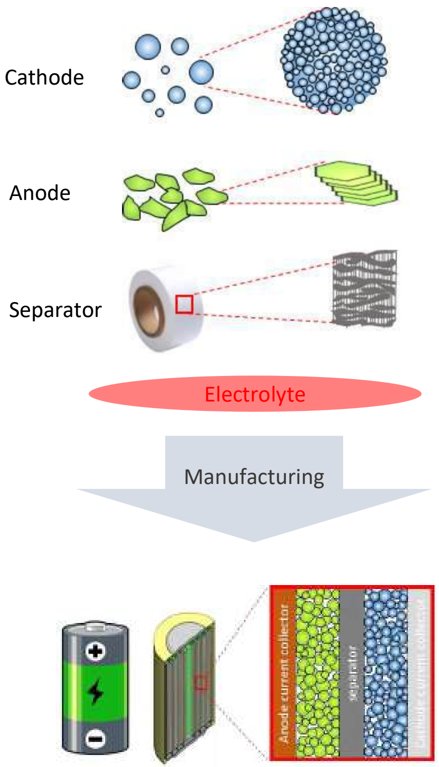
*ECM: Equivalent Circuit Model*

*CDI : Coherent Diffraction Imaging (CDI)*

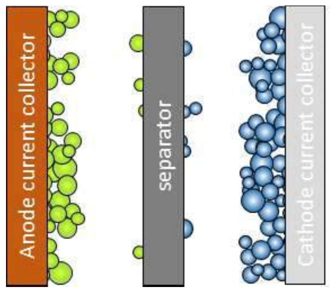
*Modified after: Villarraga-Gómez et al. 2022.*

# SEM observation of battery materials

## Primary materials

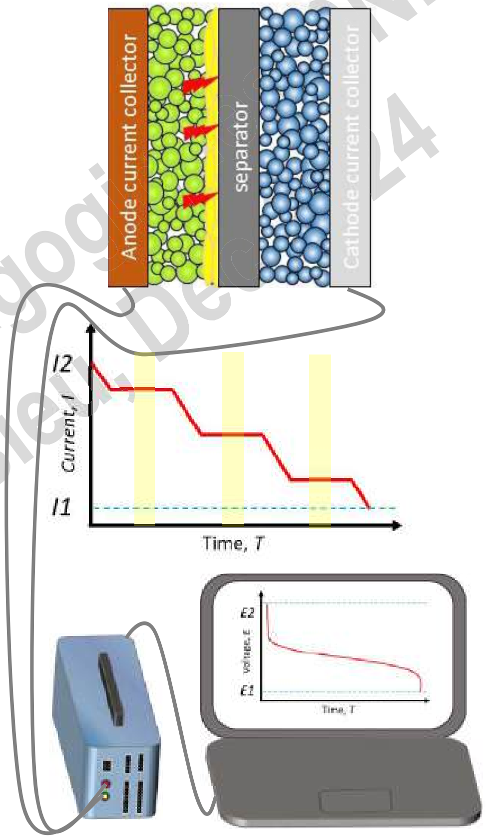



## *Ex situ*



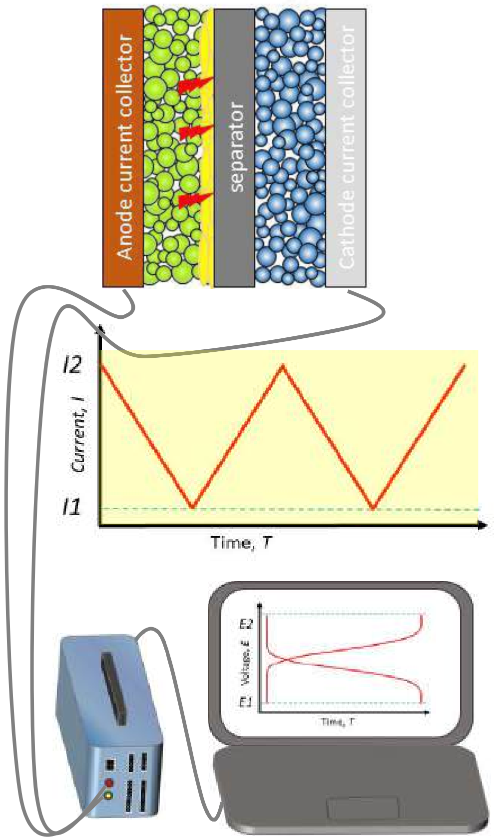

## *In situ*

Focusing on controlled experiments to understand dynamic variations

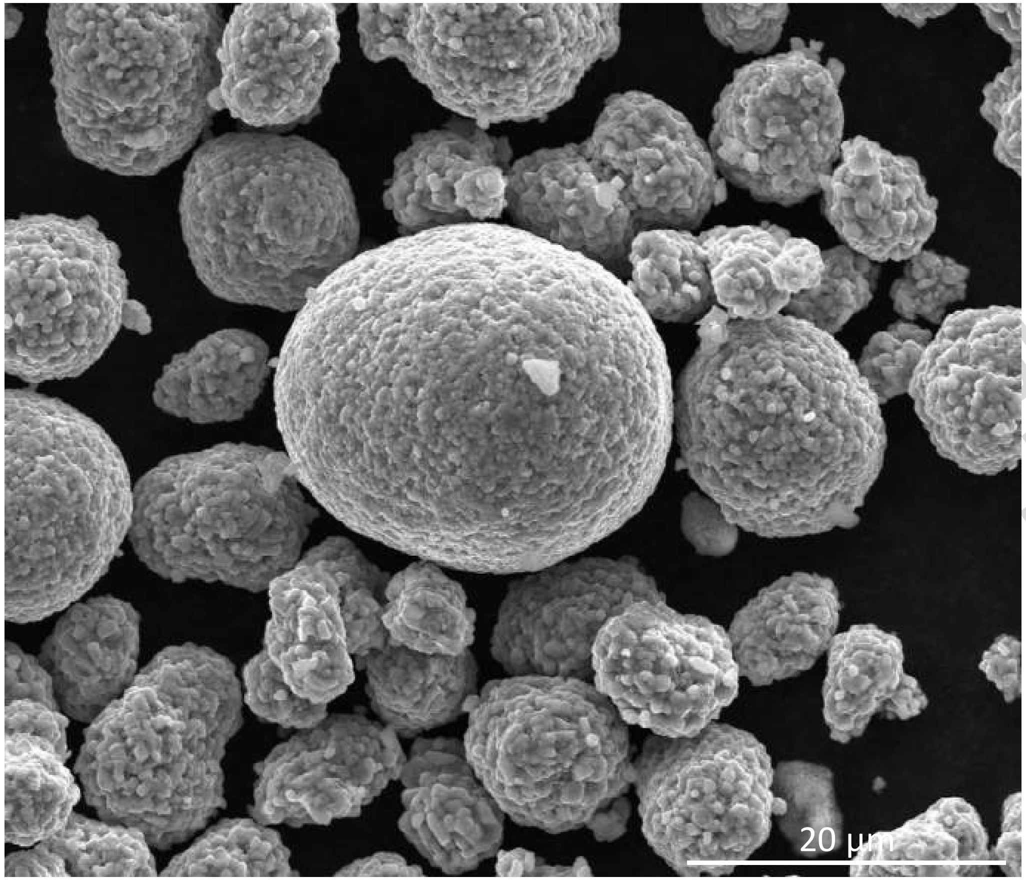



## Operando

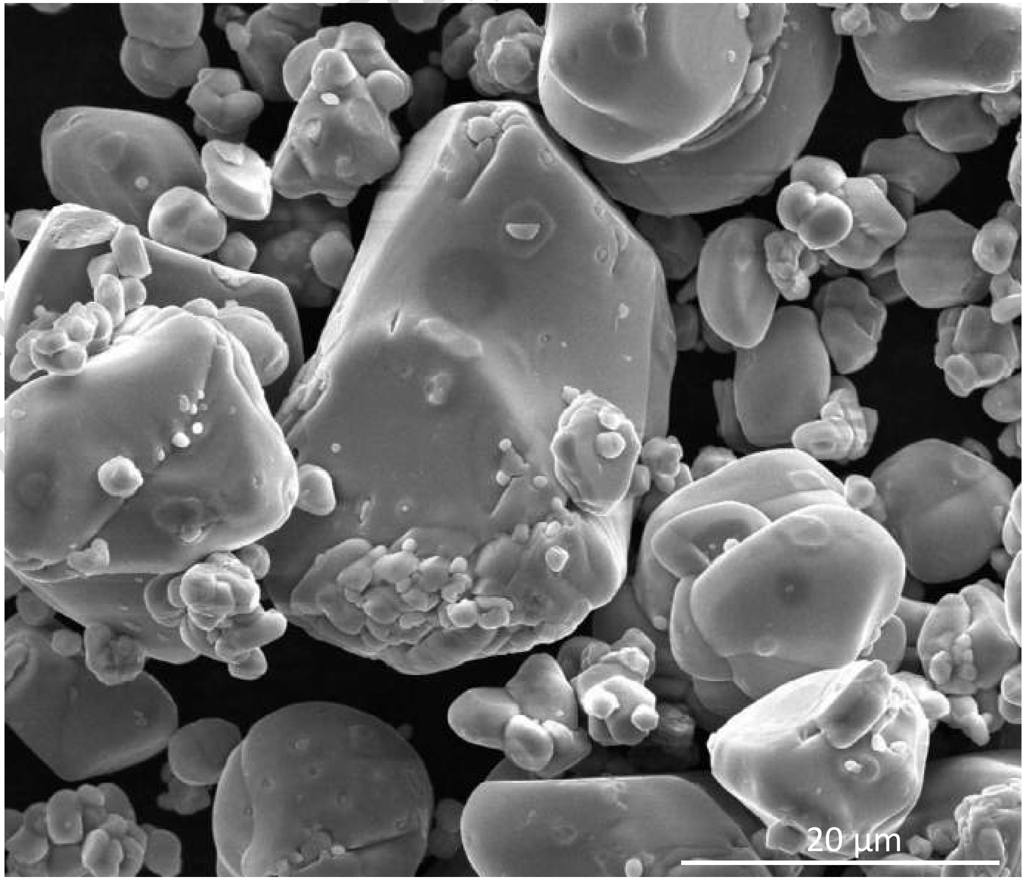
Analyzing reactions during active operation, particularly the matched charge/discharge profiles



# SEM for analysis of primary battery materials

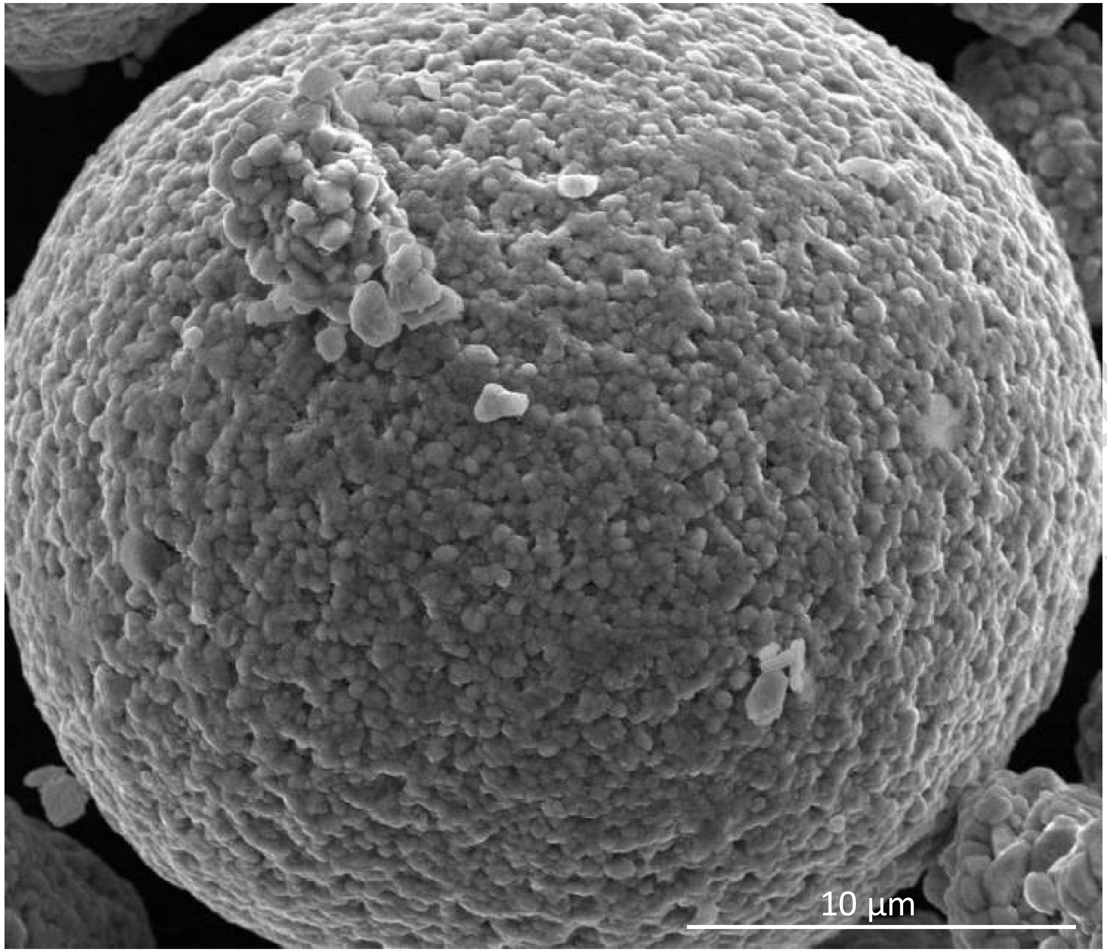


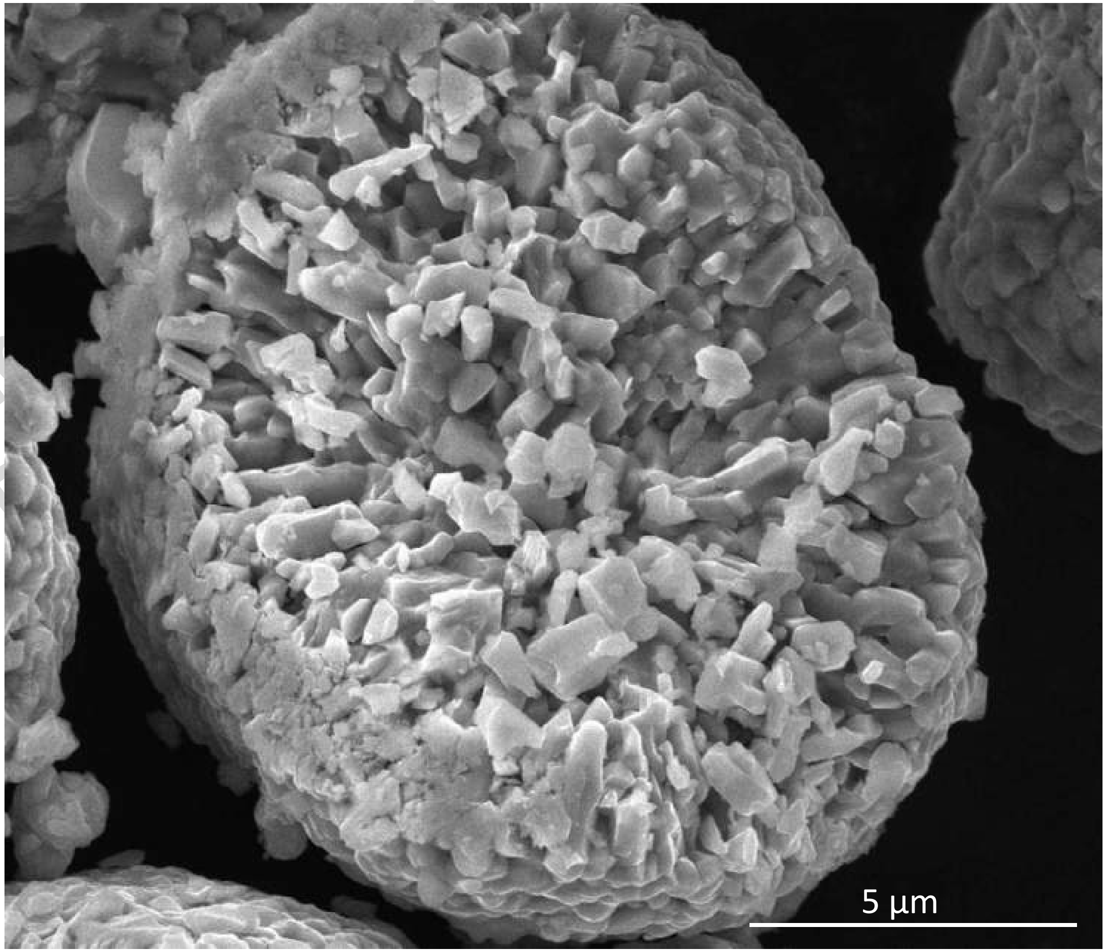

NMC (Nickel Manganese Cobalt Oxide)




LCO (Lithium Cobalt Oxide)

# SEM for analysis of primary battery materials

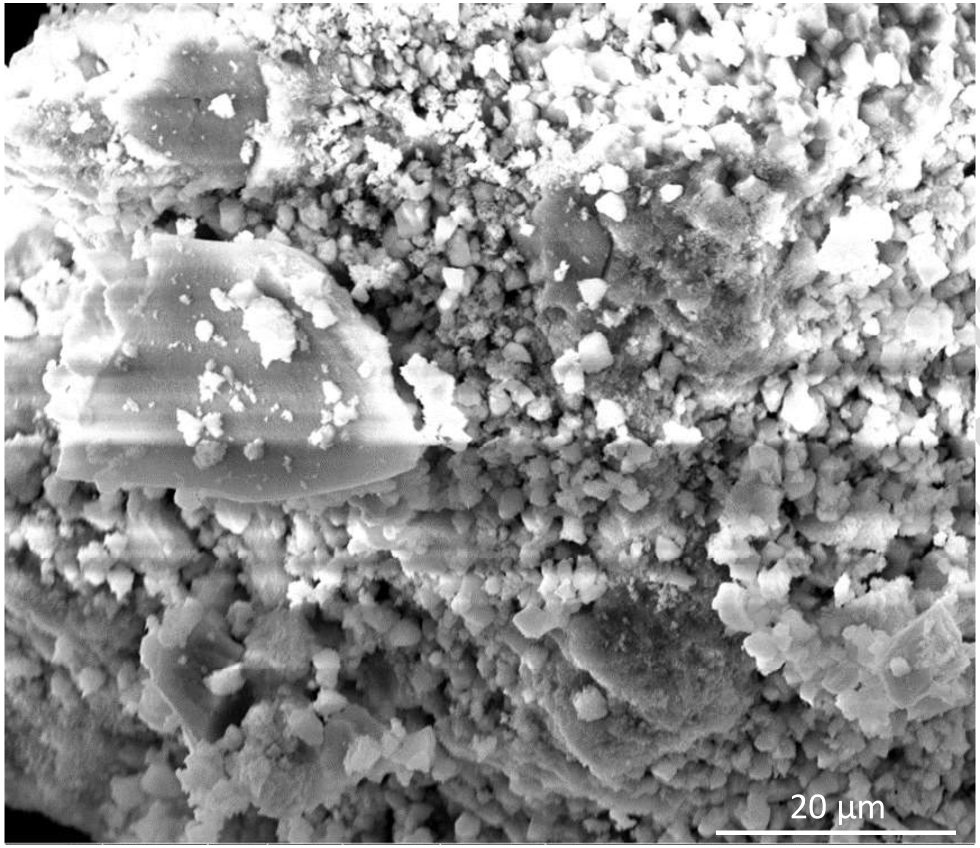


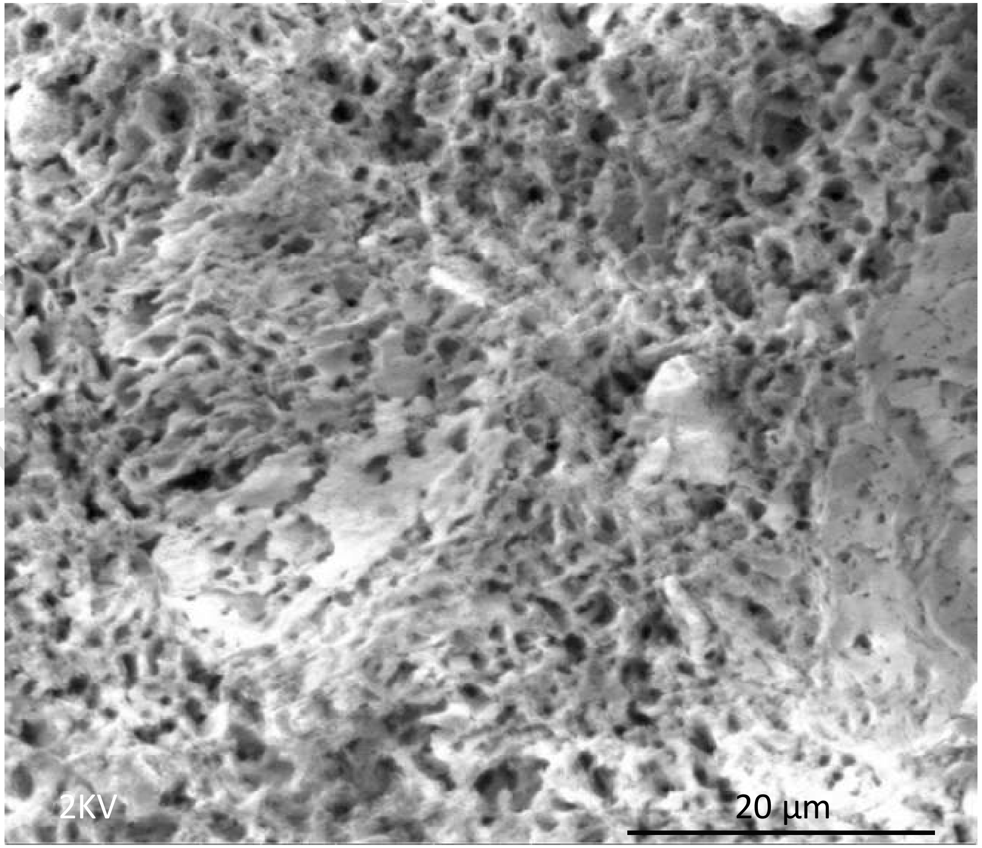




$Li_3PO_4$ used in synthesis of cathode or conductive thin-film electrolyte on battery materials

# SEM for analysis of primary battery materials

Non-conductive samples

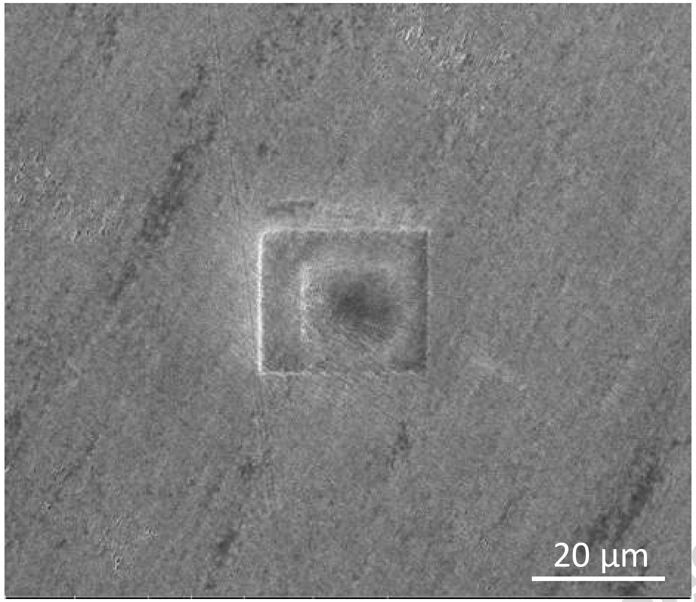


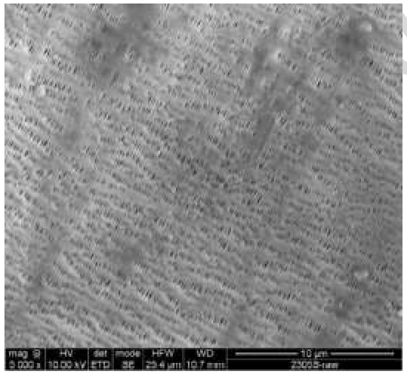

$NaTi_2(PO_4)_3$ (NTP) and NTP+PVDF used as anode material in aqueous Na-ion batteries (ASIBs) considered as one of the next-generation large-scale rechargeable batteries

# SEM for analysis of primary battery materials

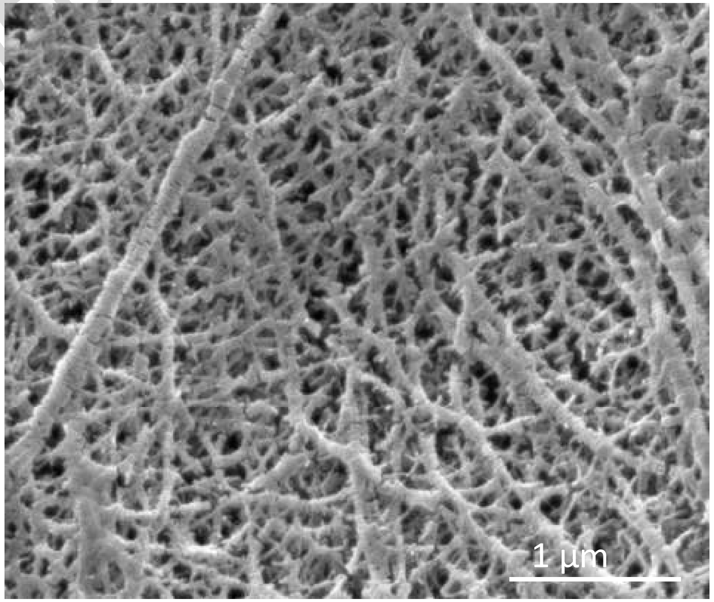
## Non-conductive samples



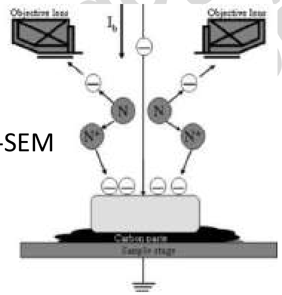

Battery separator



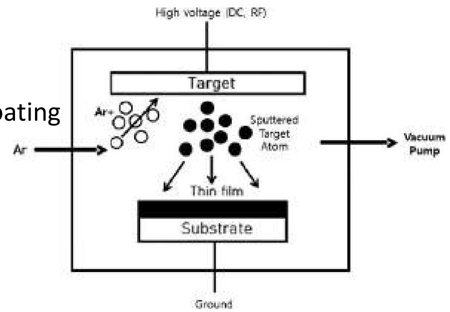
**Low voltage, Low vacuum, sputter coating, etc**

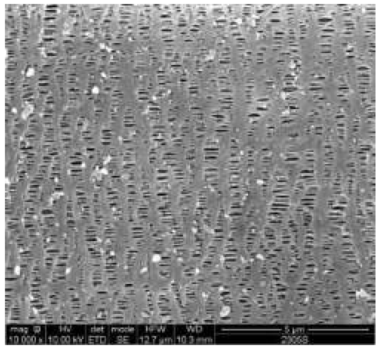



LV-SEM

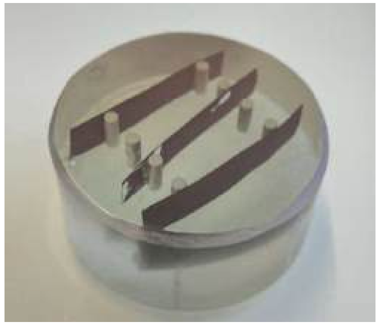



Sputter coating

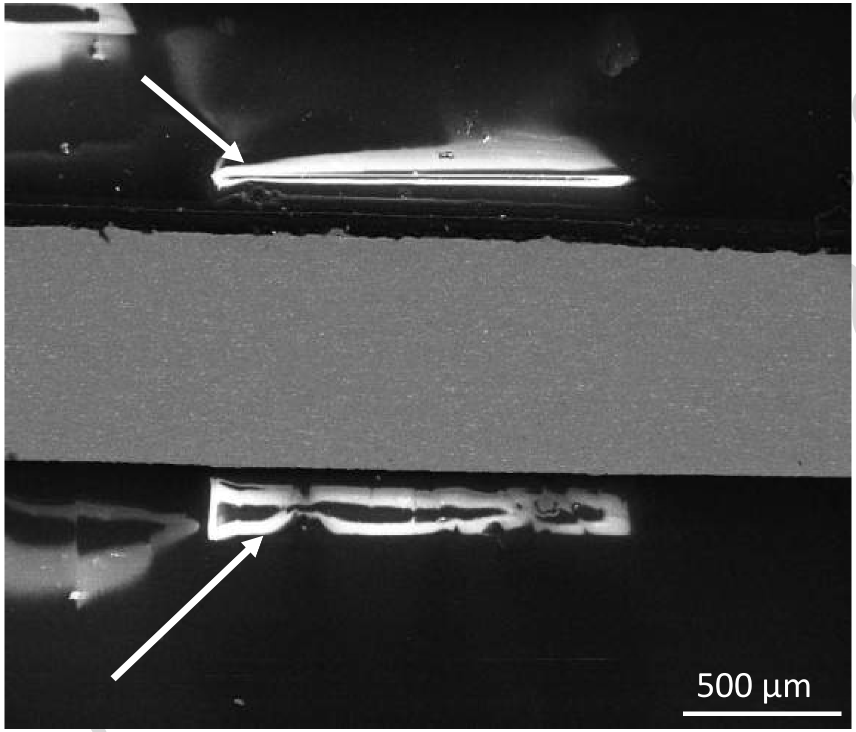


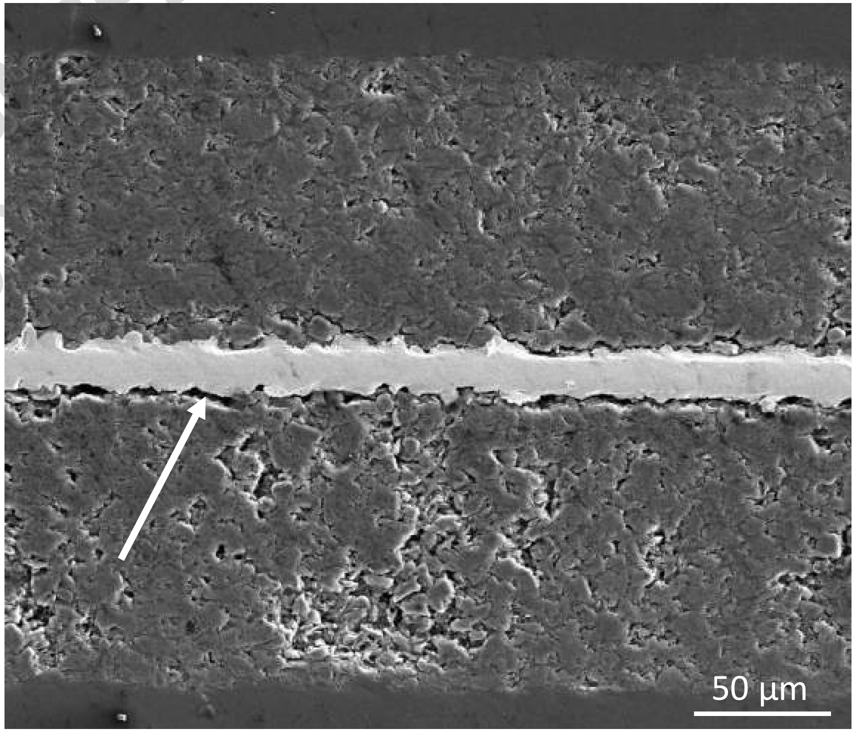



# SEM observation of battery components



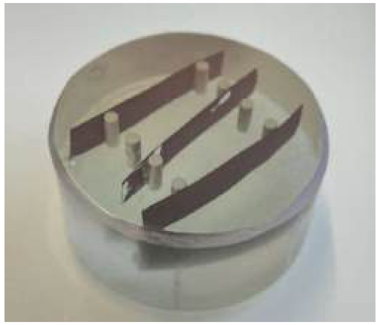
Conductive resin



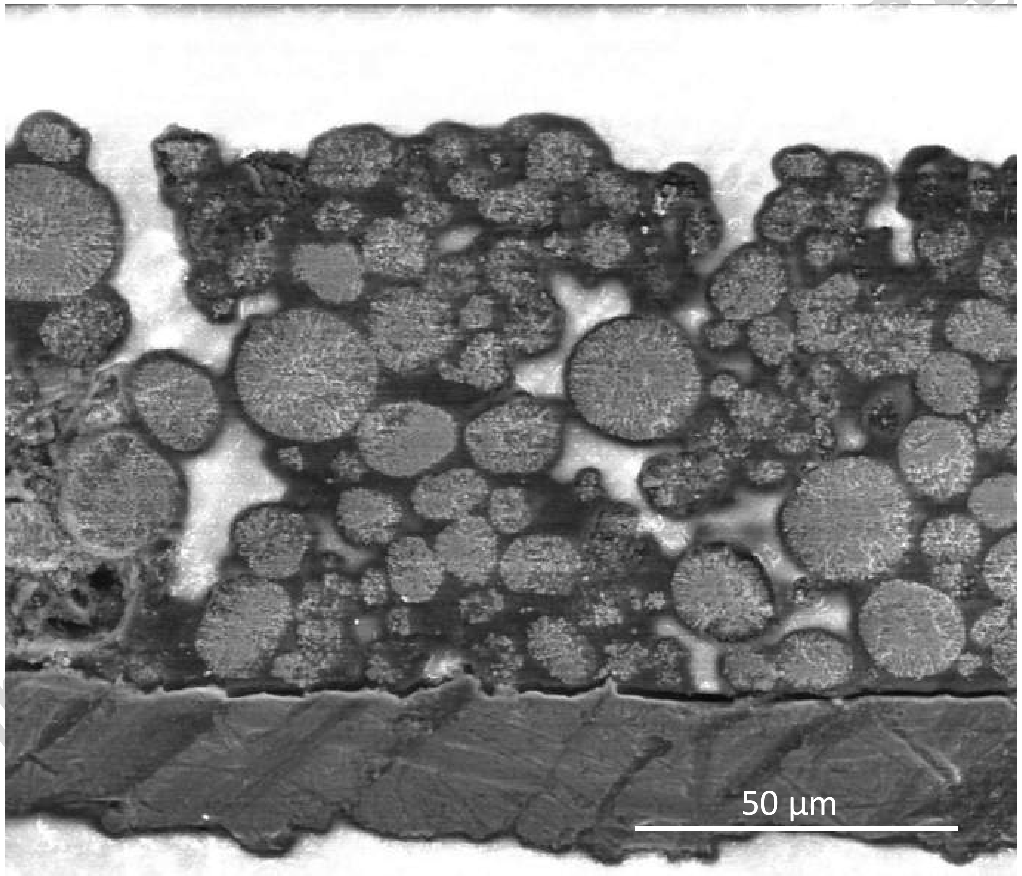




Resin embedding of battery electrodes for polishing the cross section

# SEM observation of battery components

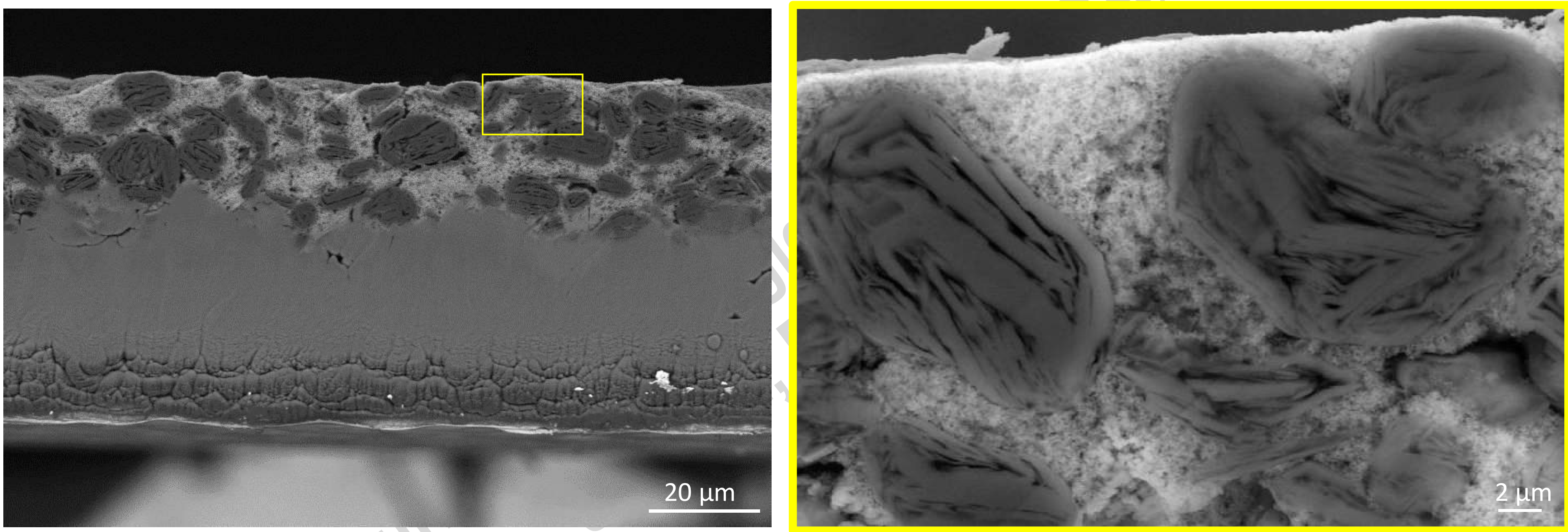


Conductive resin




Resin embedded NMC electrode for cross section observation

# SEM observation of battery components

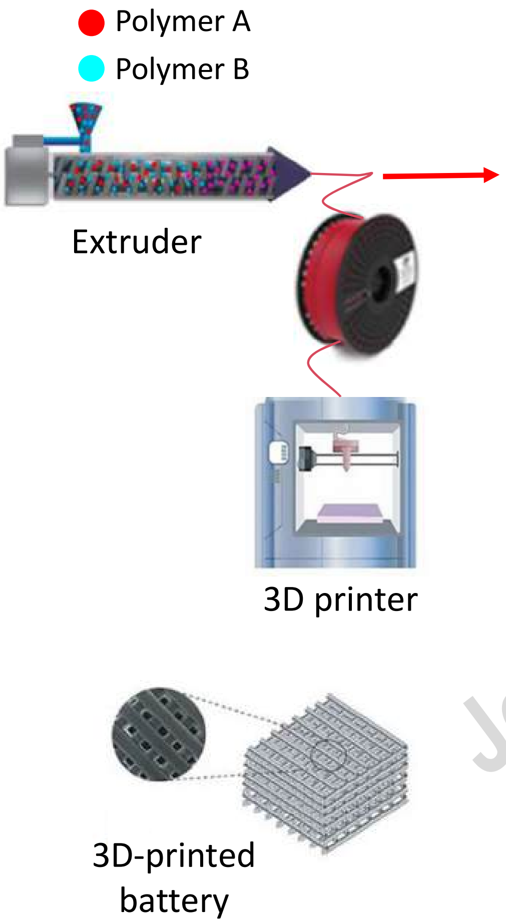


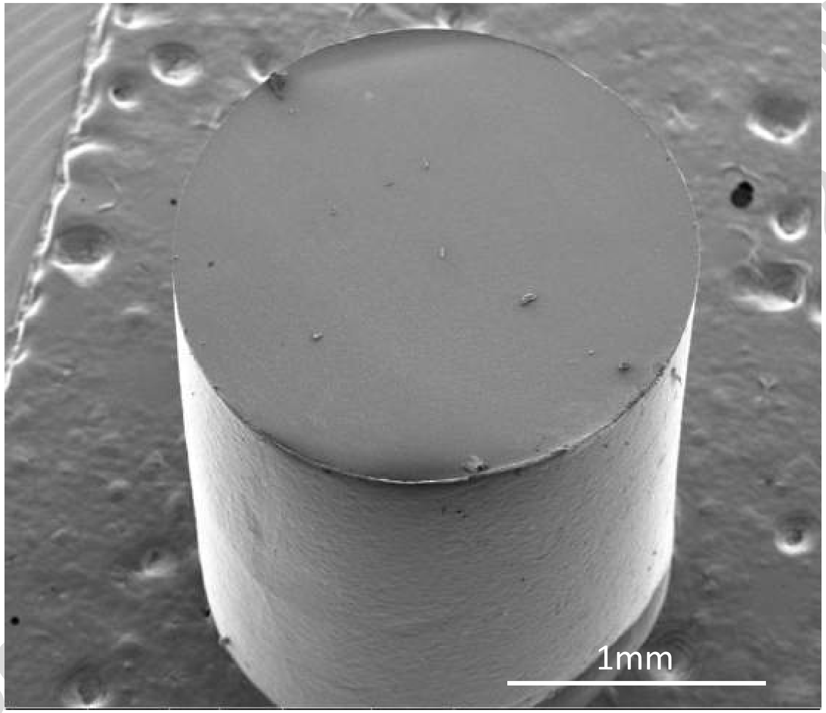

A Graphite/silicon anode cross section with a Cu current collector, prepared by ion milling

*Sample preparation: Imene Esteve, impmc*

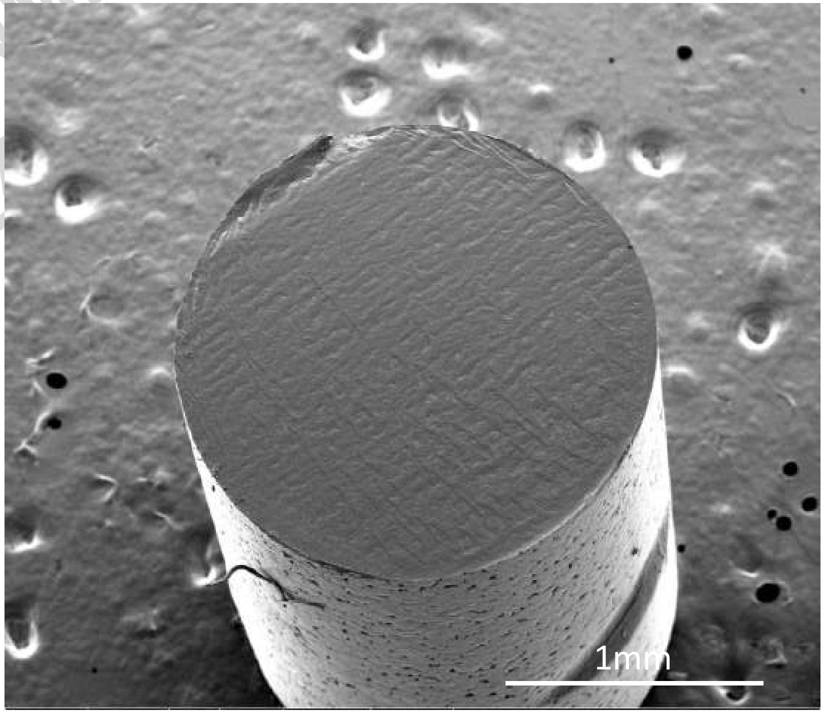
# SEM observation of 3D-printed battery components

## Extruded filaments for 3D-printing




PP/PBE 50/50

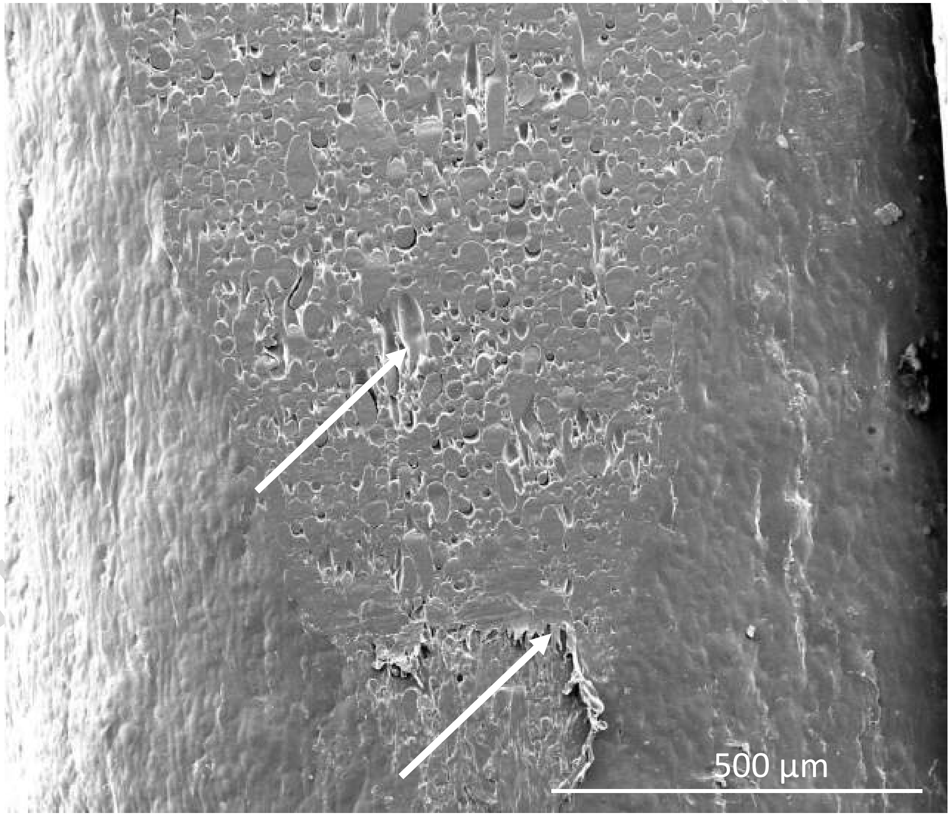



PP/PBE 75/25

Cylindrical filaments from the co-rotative twin-screw extruder

# SEM observation of 3D-printed battery components

Study of polymer blend for 3D-printing of batteries

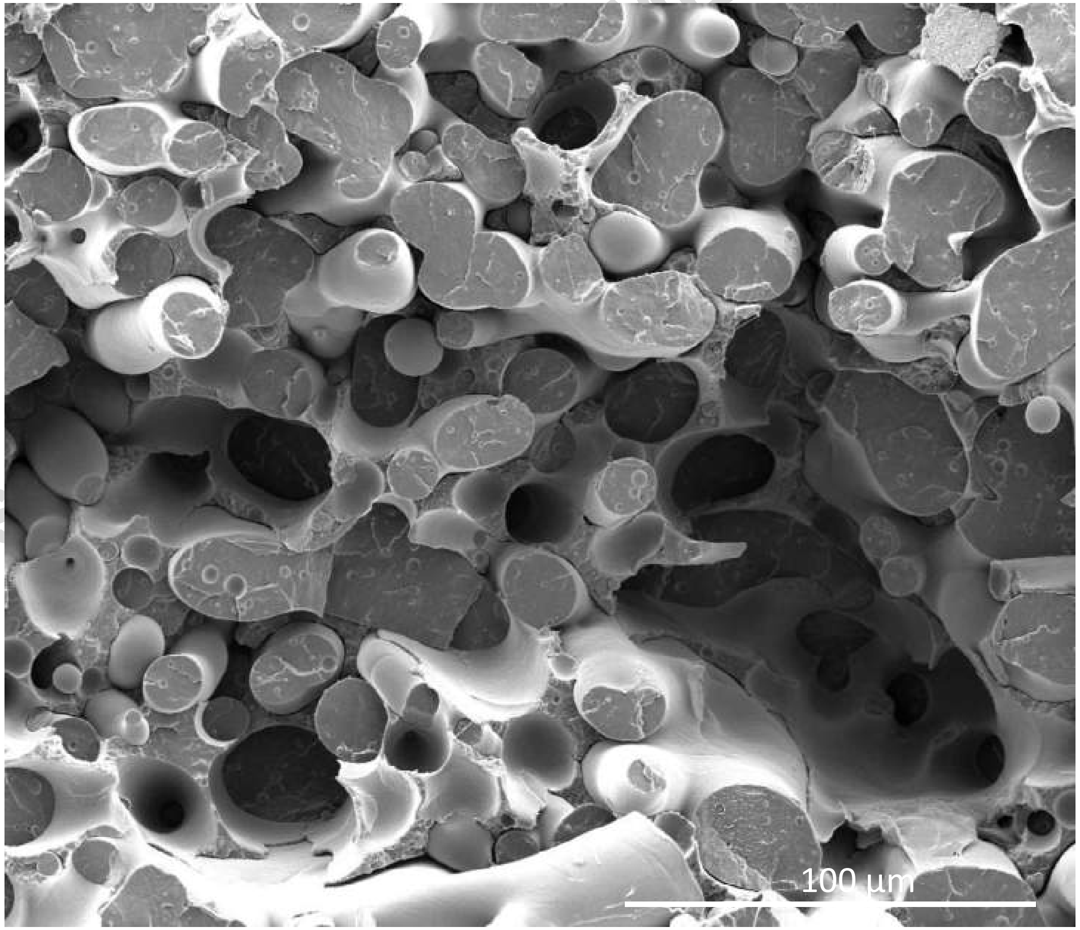



PP/PCL 60/40

# SEM observation of 3D-printed battery components

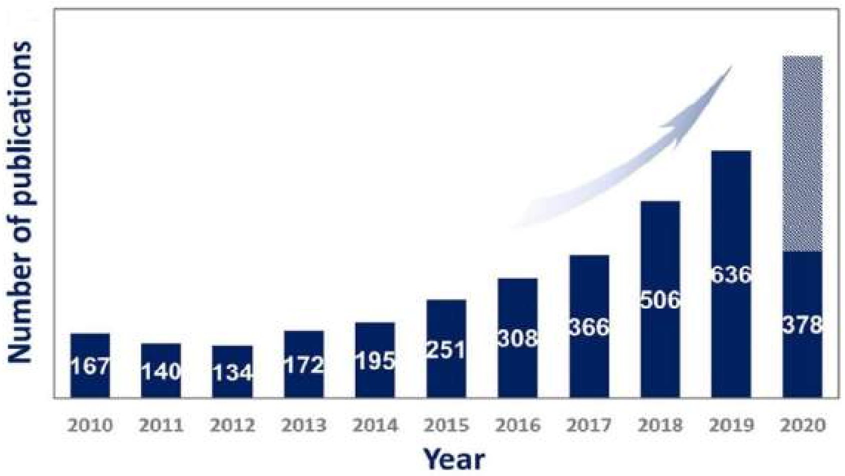
## Study of polymer blend for 3D-printing of battery

Cryogenic fracturing using liquid nitrogen



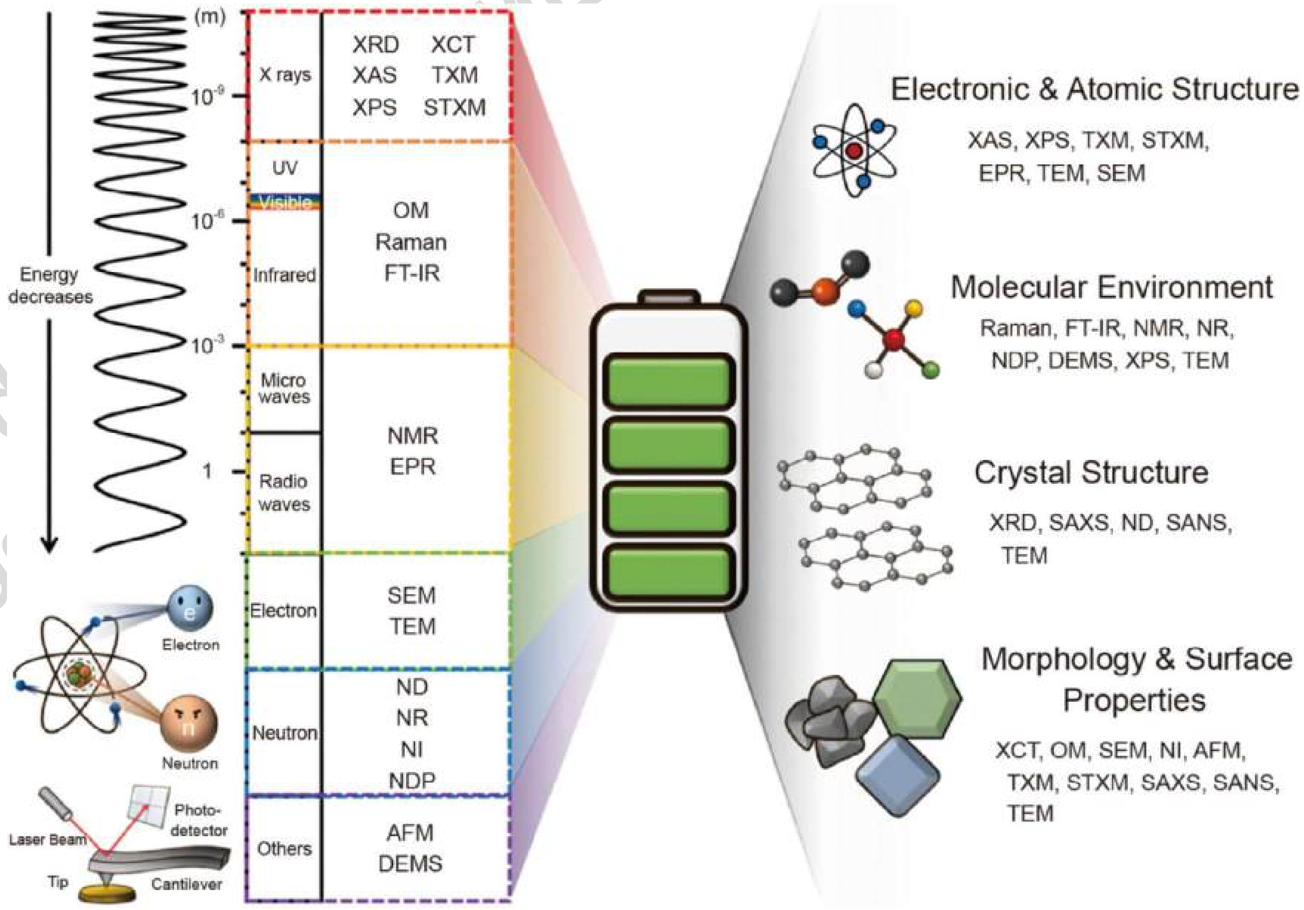

Phase continuity: PP/PCL 70/30 v%

# *in situ*/Operando studies of battery materials



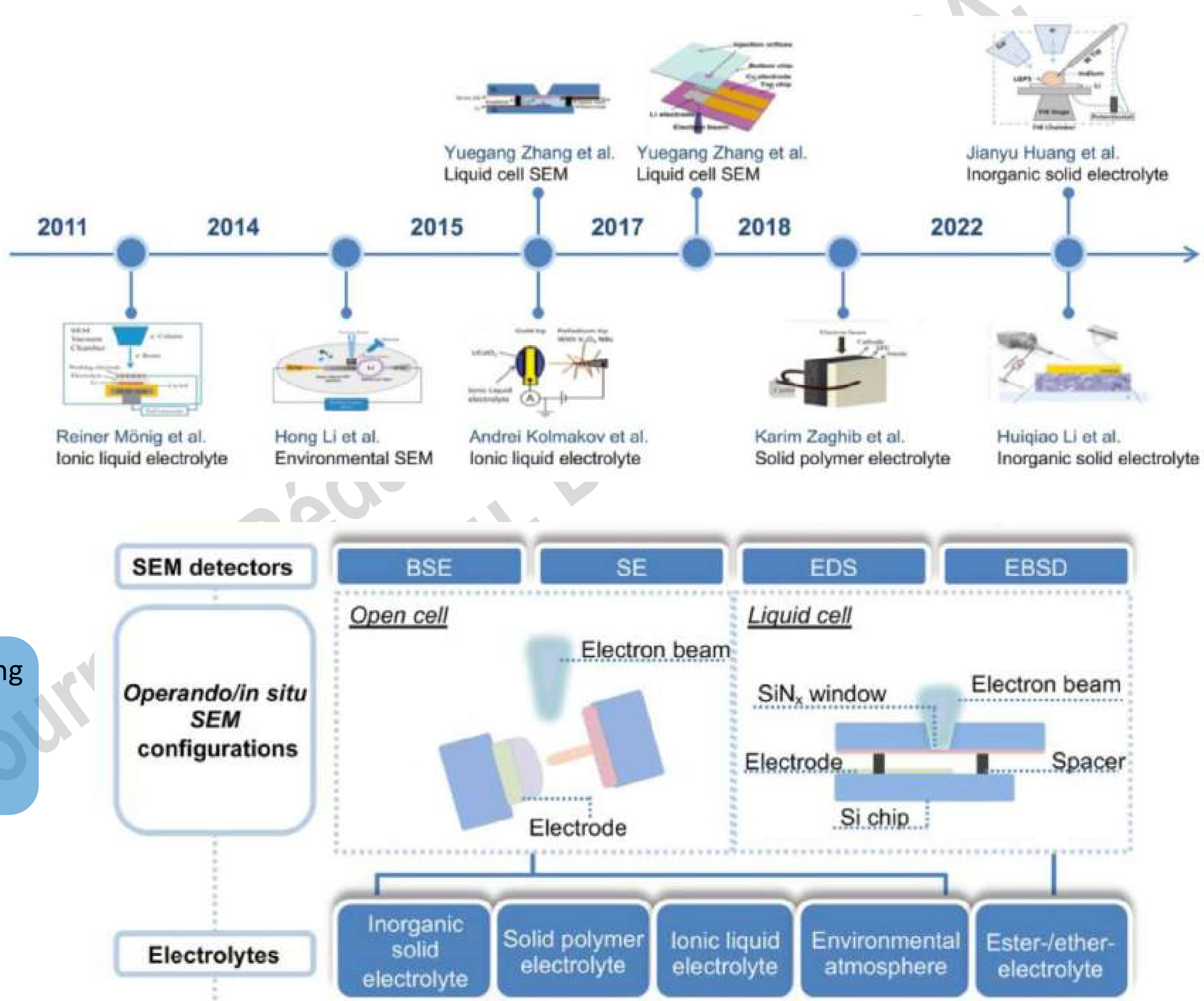

The cartogram of published papers related to *in situ*/operando techniques within the field of rechargeable batteries in recent years.
Data were collected from Web of Science in September 2020.

## *In situ* analysis of lithium rechargeable battery




*Lee et al. In situ techniques for Li-rechargeable battery analysis, Carbon Energy (2024)*

# *in situ*/Operando **SEM** for battery materials




Perspective of operando/*in situ* scanning electron microscope in rechargeable batteries; Shiyuan Zhou et al; Current Opinion in Electrochemistry: 41 (2023)

# *in situ*/operando SEM for battery materials

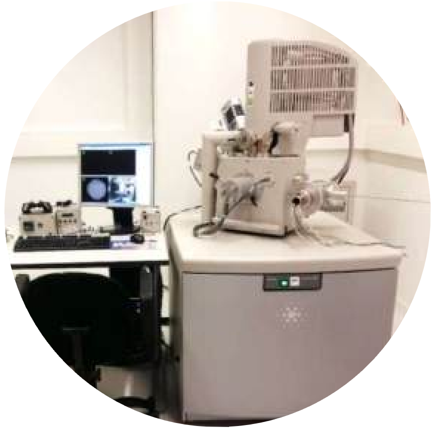
## Necessity of sealed air-tight sample-transfer modules


Dry room


Glovebox

Sample degradation upon exposure to air and humidity

e.g. Surface oxidation of LiMg alloy following air exposure


SEM


TEM

# *in situ*/Operando SEM for battery materials

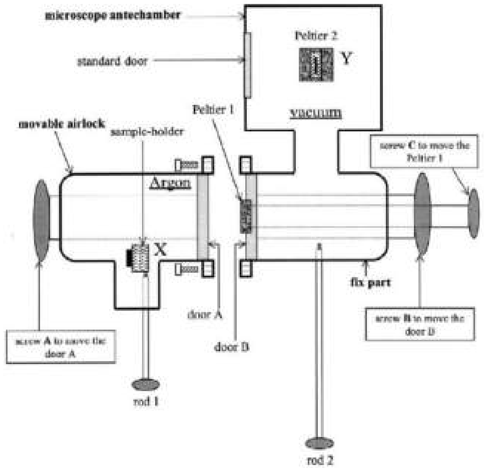
Development of a sample-transfer device for air-/moisture-sensitive materials at LRCS/UPJV

**1998: XL30-FEG**

Collaboration with Philips (FEI) to design and fabricate a sample-transfer system at LRCS/UPJV to observe air-sensitive samples in the SEM

**2008: Quanta 200 FEG ESEM**

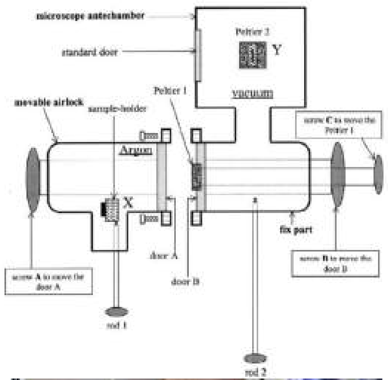
Use of sample transfer system and cycling battery under different auxiliary gas

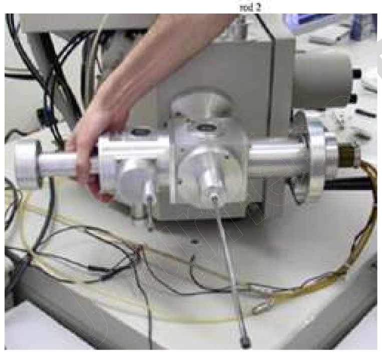




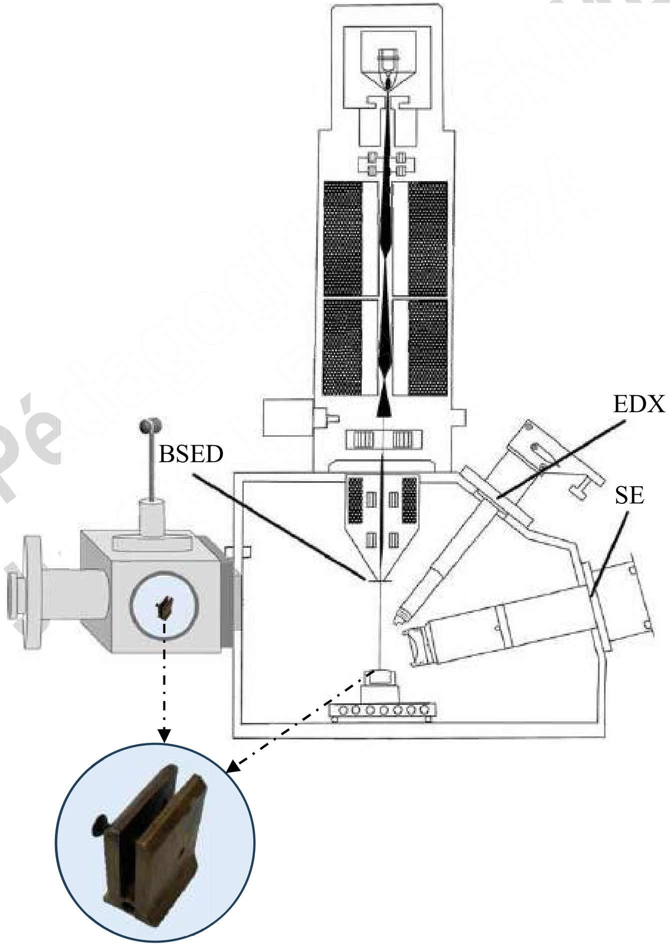
SEM imaging of the formation of copper vanadate particles upon cycling

# Sample transfer module for *in situ*/operando SEM



Glovebox → SEM




**Need for a New Version**

- Easy and efficient sample transfer
- Fitting various battery technologies, such as ASSB
- EDX analysis during cycling and use of micromanipulators
- Higher electrochemical reliability

↓

- Modification of the SEM chamber & electric connections
- Materials and fabrication

# Design and development of the *in situ*/operando module

**Carine Davoisne**

Neelam Yadav

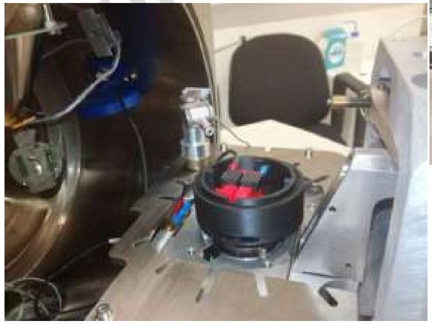
Melissa Herrmann

Defining Needs and Objectives

Conceptualizing and Prototyping with 3D Printing

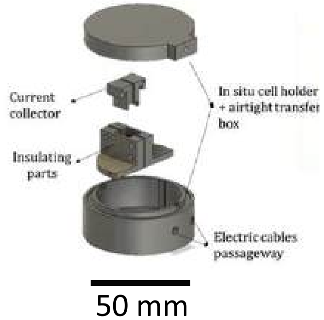
Compatibility and conformity with SEM

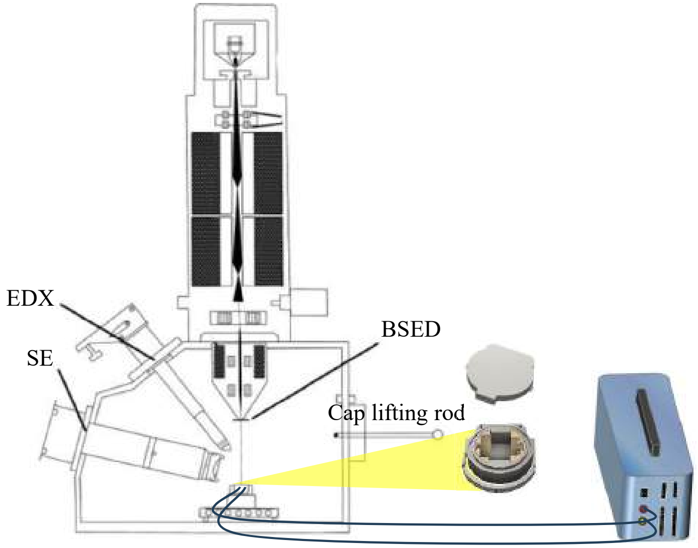
Manufacturing

PLA printed model

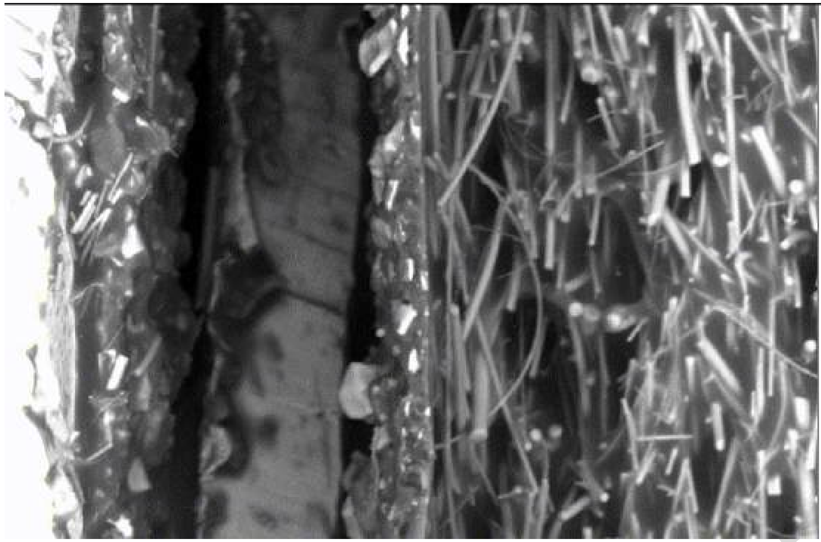
Electric connections and Stage movement

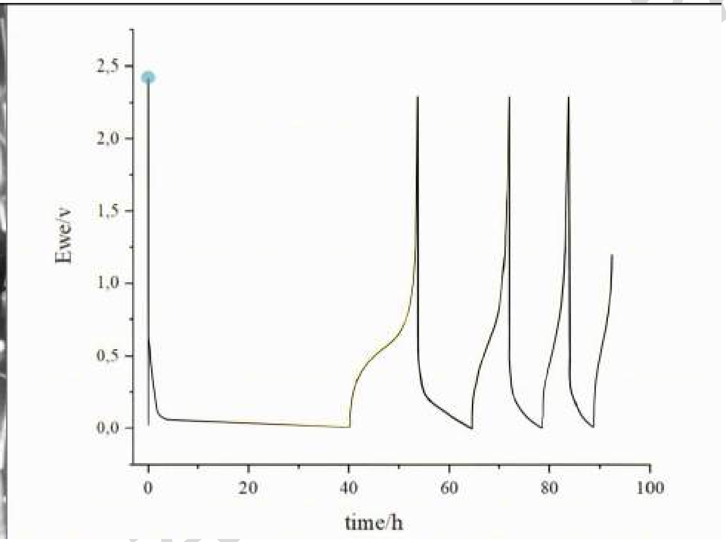


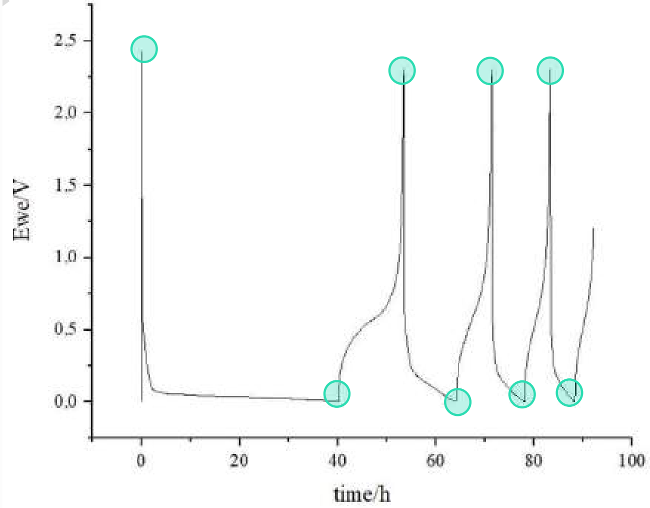



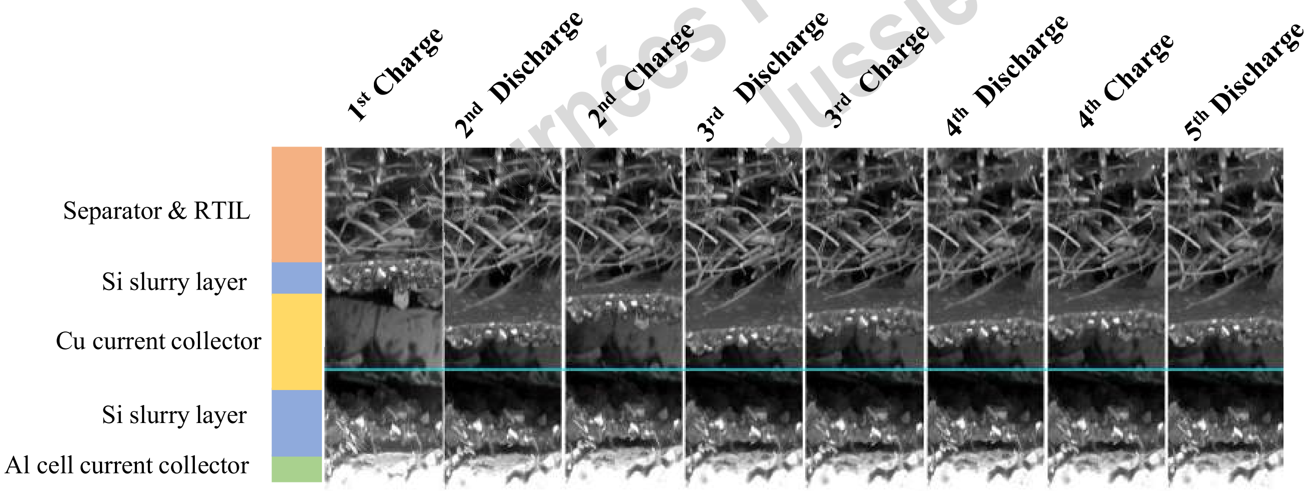
# Operando SEM

## Testing lithium-ion batteries (half cell) with silicon/graphite





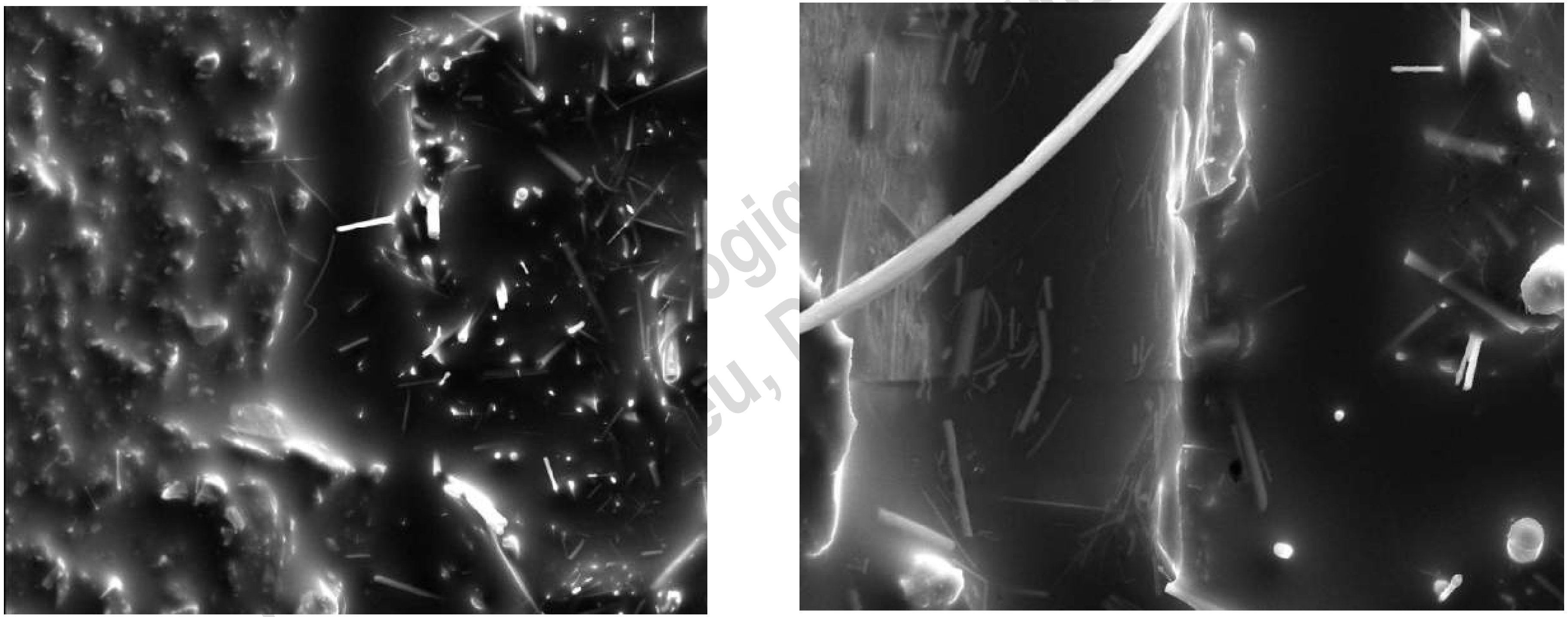




- Self Supported Electrode
- BMITFSI+LiTFSI 0,5M
- 2,62083 Si
- C/20= 0,463363mAh
- C/200= 0,046336 mAh

# Operando SEM

Testing lithium-ion batteries (half cell) with silicon/graphite

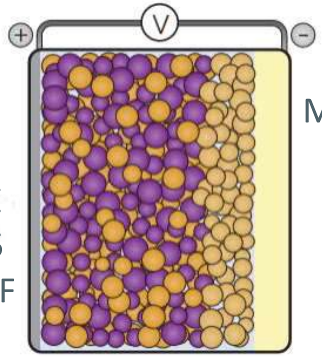


Difficulty in controlling experimental condition in SEM during cycling

# Operando SEM of All-Solid state batteries (ASSB)

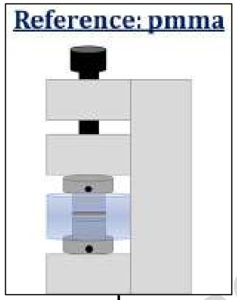
## Functionality test: Reliability and Consistency

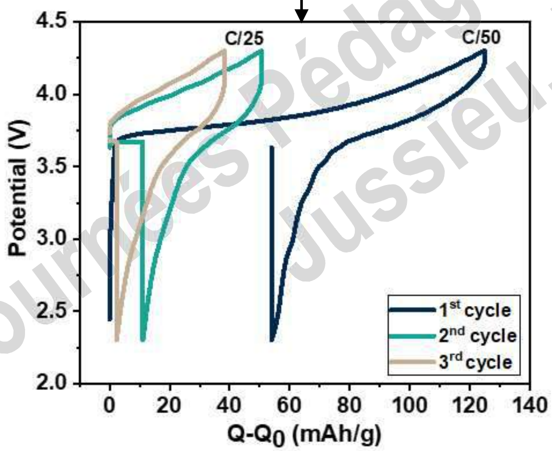
Cathode:
66,5% NMC
28,5% SE
2,5% C45
2,5% VGCF



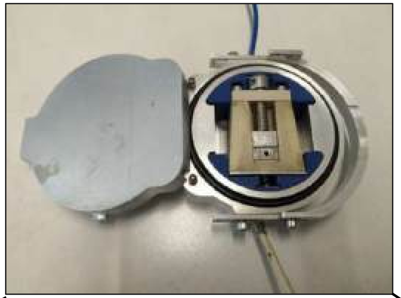

Anode:
Metallic Li

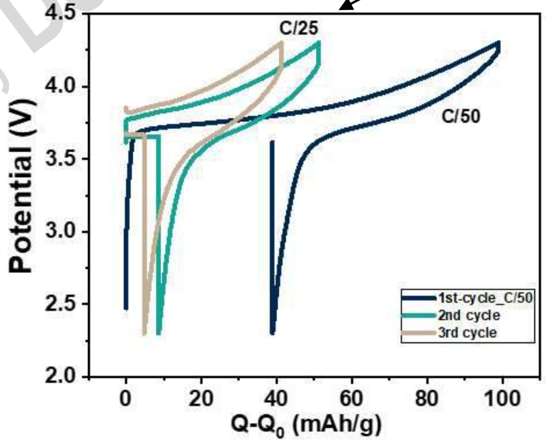
Solid electrolyte(SE): $Li_6PS_5Cl$ (LPSCl)



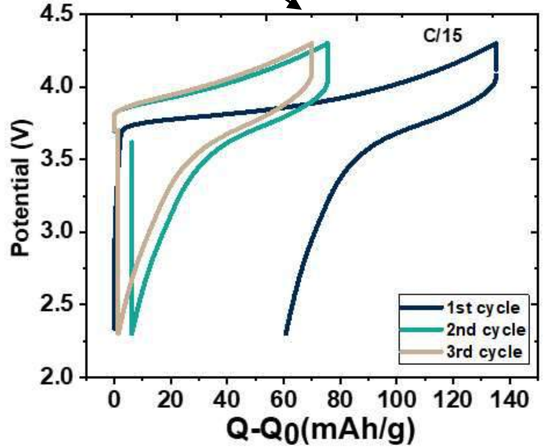




Reference system





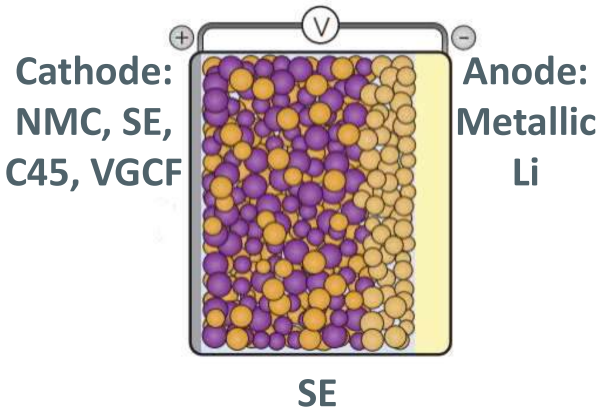

*Outside* SEM



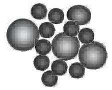

*Inside* SEM

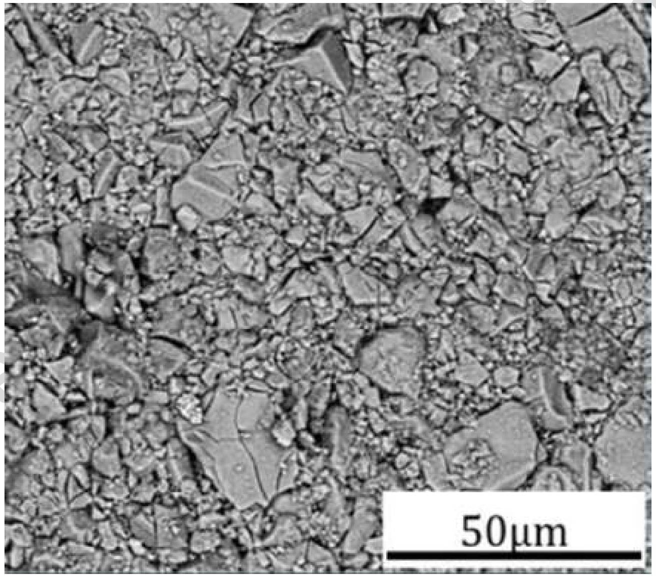
# Operando SEM of all-solid state batteries (ASSB)

## Effect of Solid Electrolyte (SE) particle size

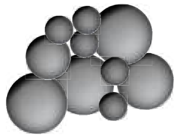


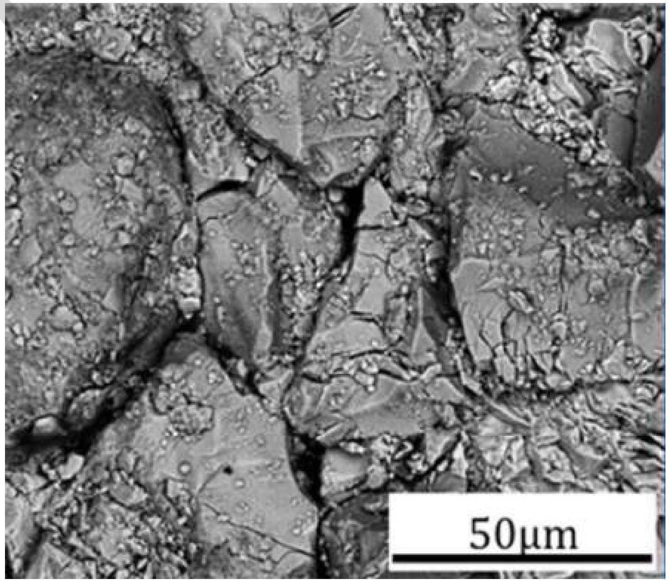

**0.5-20 µm**






**50-150 µm**

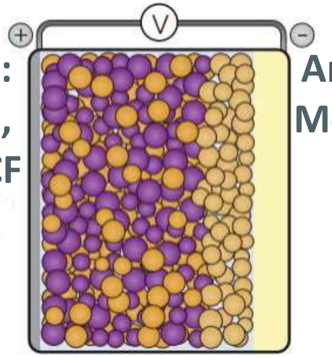





Commercial Solid electrolyte (SE):
$Li_6PS_5Cl$ (LPSCl)

# Effect of solid electrolyte particle size

Cathode: NMC, SE, C45, VGCF



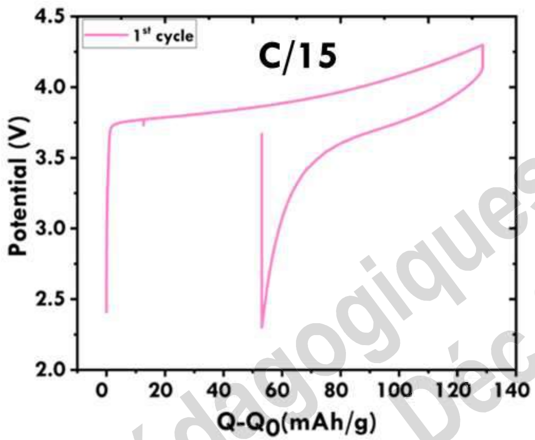

Anode: Metallic Li

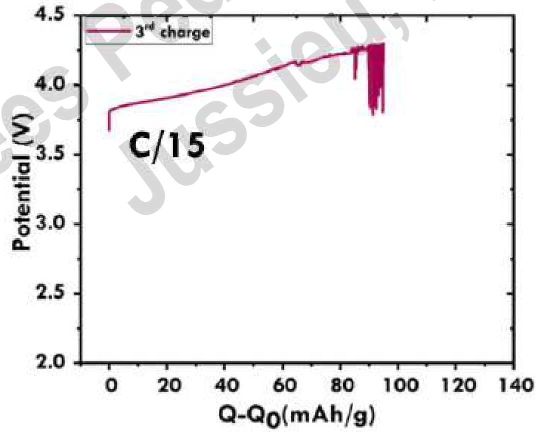
SE

Electrochemical behavior

Galvanostatic cycling
2.3 – 4.3 V

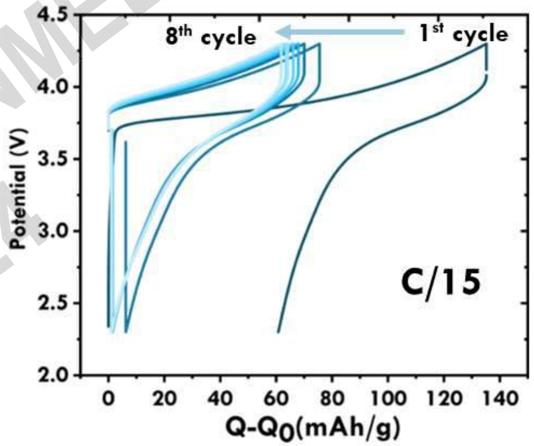
0,5-20 µm

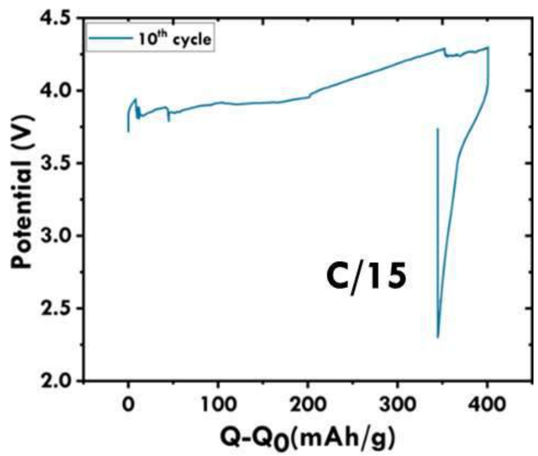


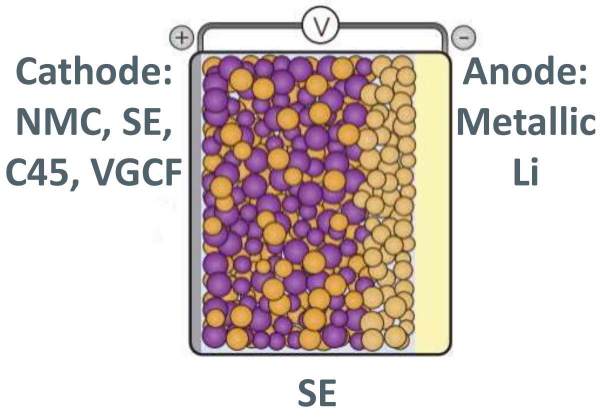

Fast short circuit

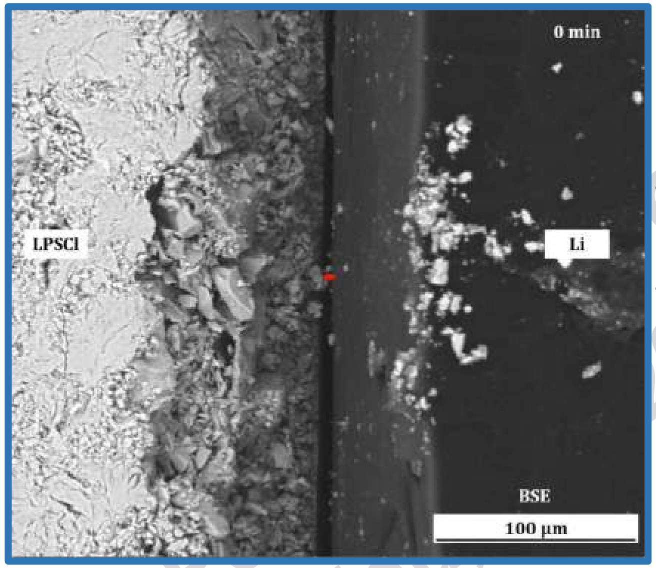
50-150 µm



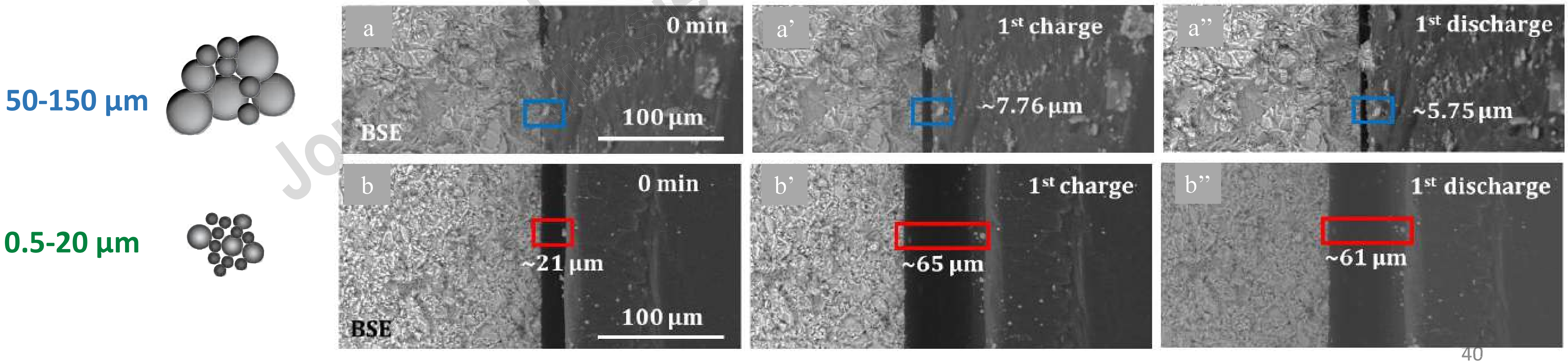



# Effect of solid electrolyte particle size: anodic interface evolution

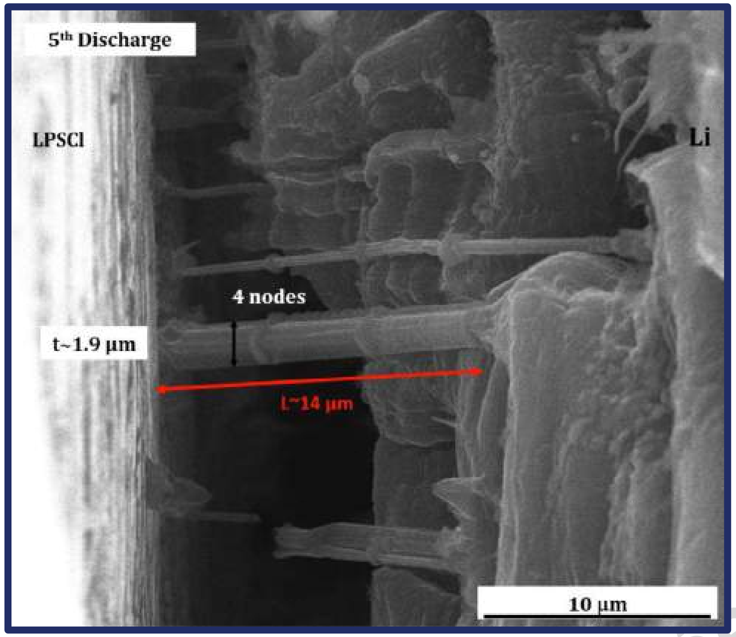


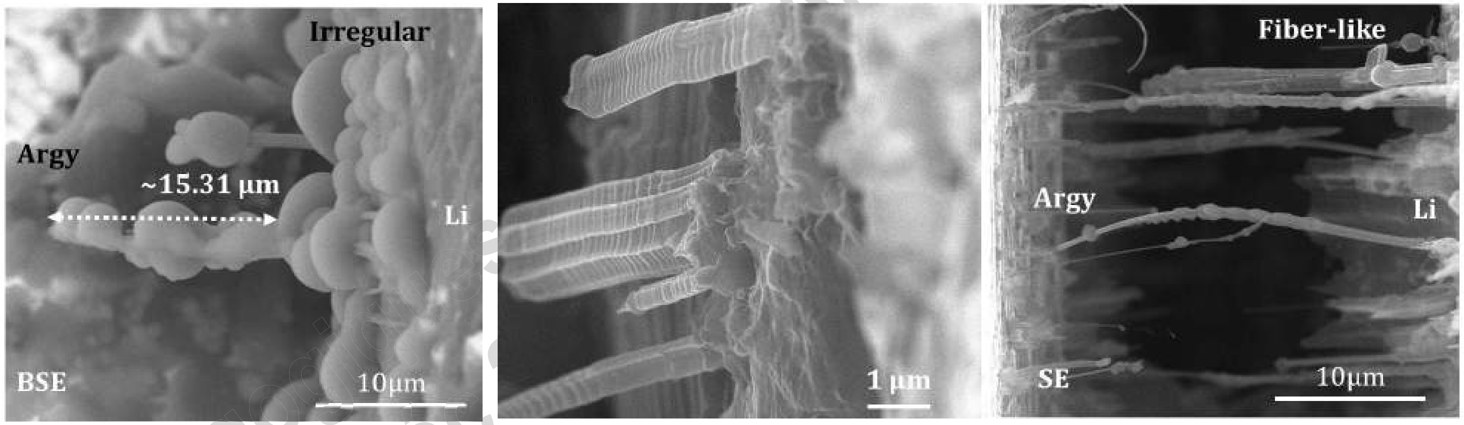



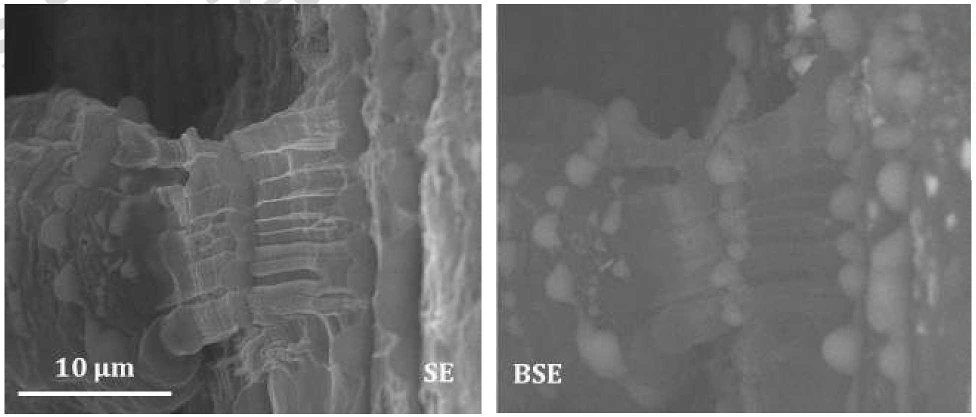

- Contact loss during charge
- Possible SE volume expansion/shrinkage

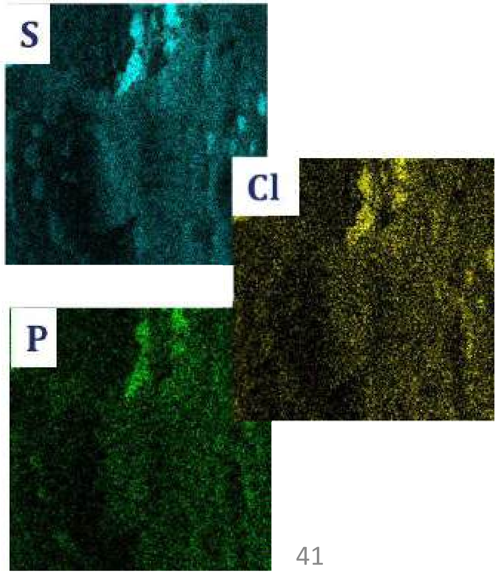


# Effect of solid electrolyte particle size: anodic interface evolution



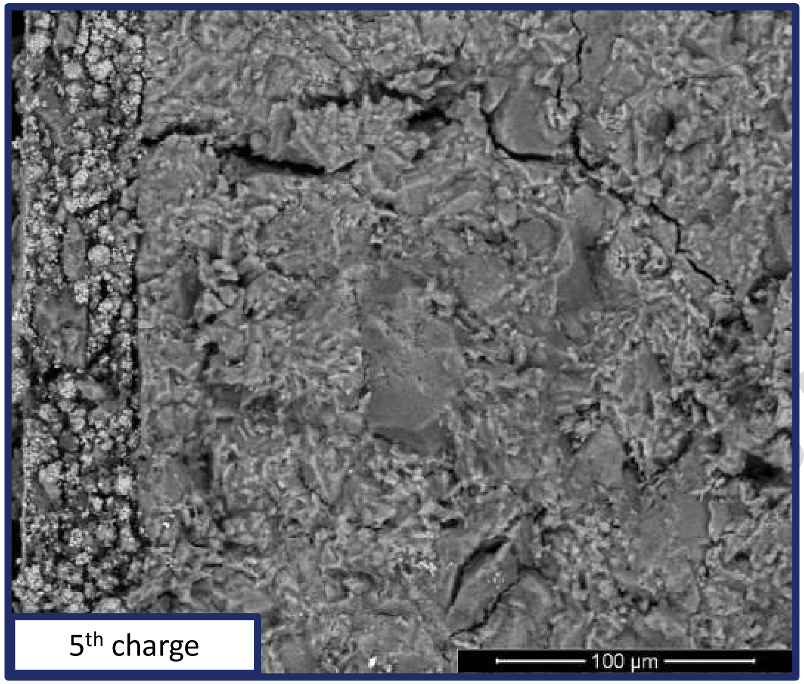



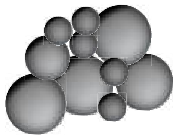



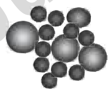

- Dendrites grow from lithium toward SE
- Different form of dendrite formation
- Presence of decomposition products

# Effect of solid electrolyte particle size: anodic interface evolution

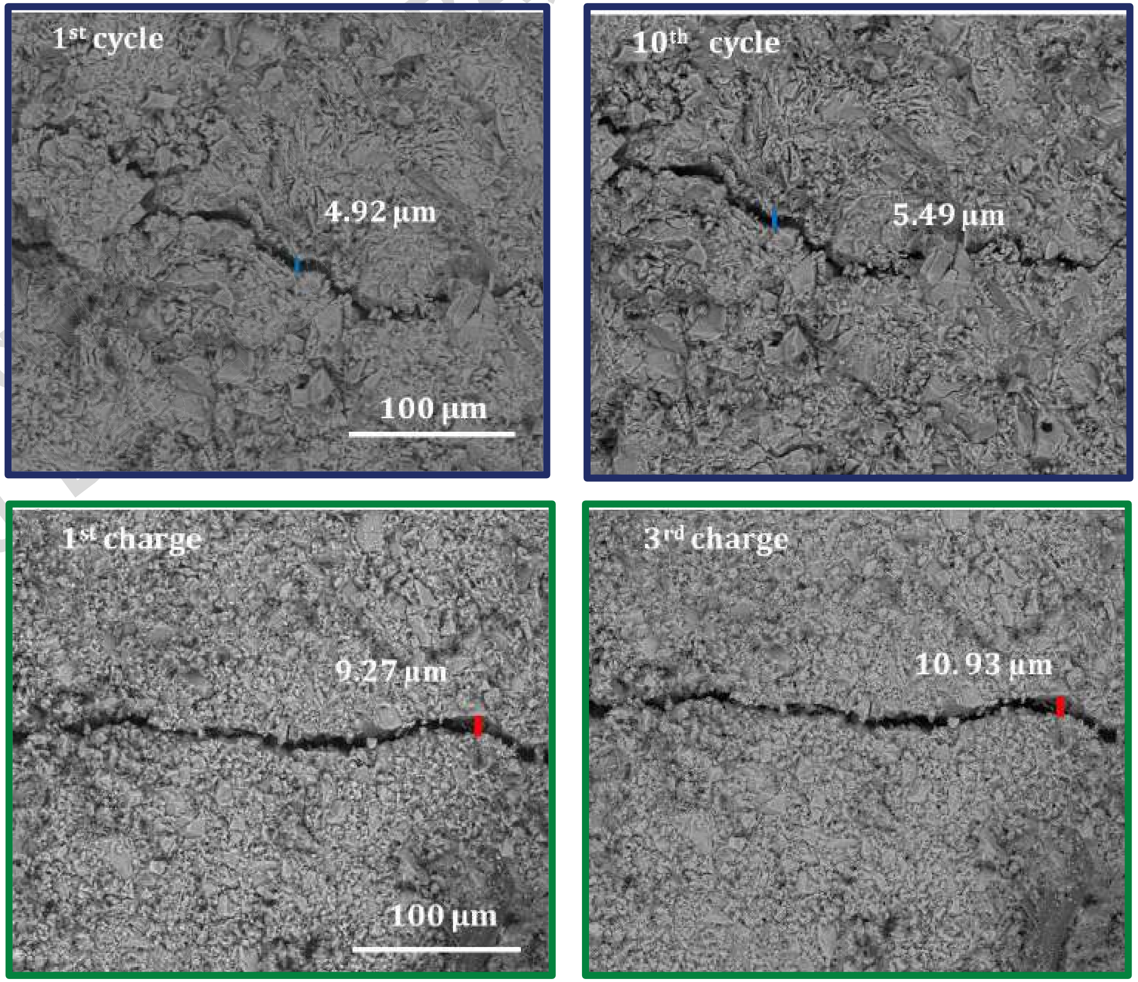


50-150 µm

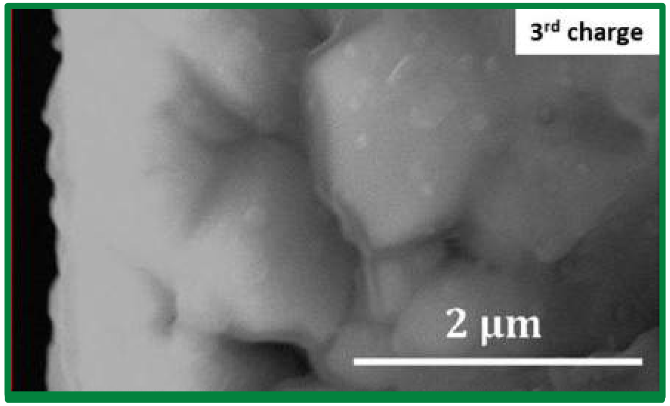


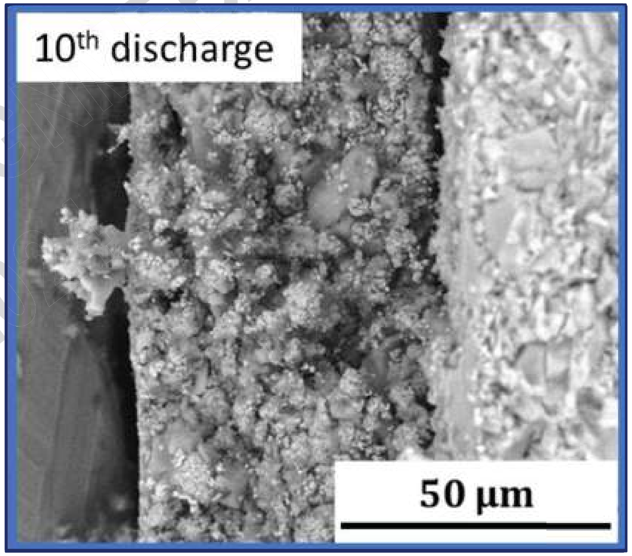
0.5-20 µm




Sinuous vs Linear cracking

# Effect of solid electrolyte particle size: cathodic interface evolution

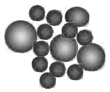


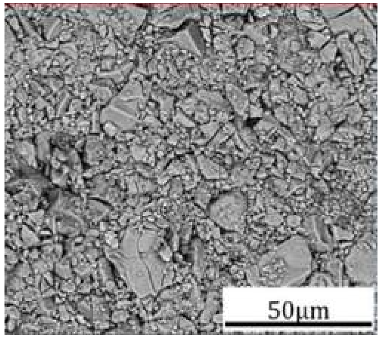

- 0,5-20µm: Pronounced SE degradation
- 50-150µm: Progressive cathode delamination from SE

# Effect of solid electrolyte particle size: conclusion

"Yes, size does matter!"

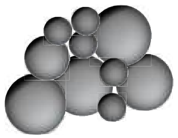


**0.5-20 μm**

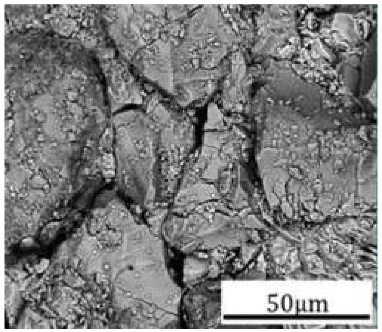



Linear cracks + Dendrites → Faster short circuit

Small particles → Greater anode – SE contact → Faster SE degradation



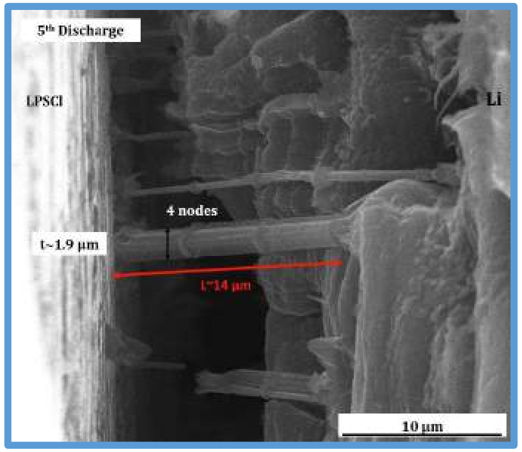
**50-150 μm**

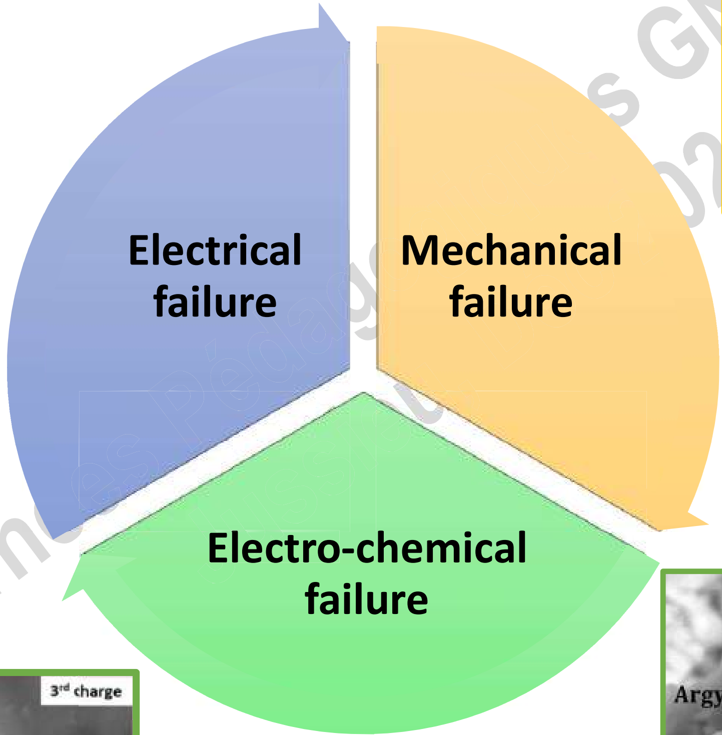


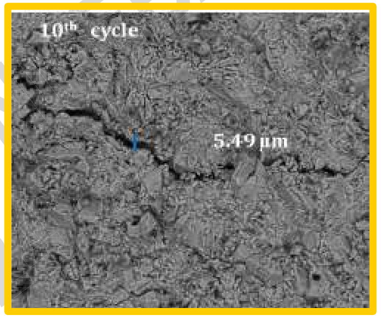

Sinuous cracks → Dendrites propagation prevented → Better cyclability

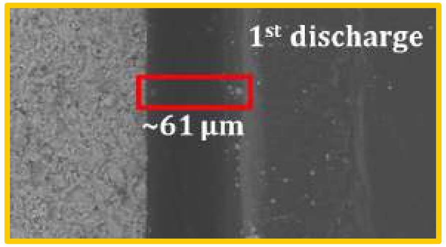
Cathode delamination → Progressive capacity loss

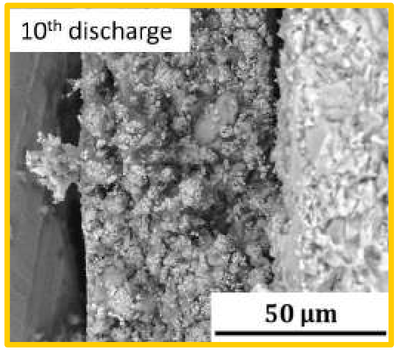
# Failure mode in sulfide-based all solid state batteries revealed by operando SEM

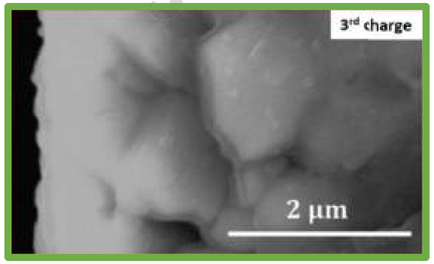


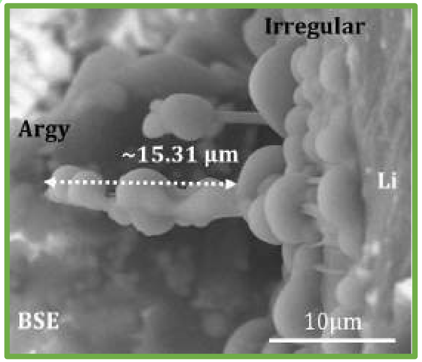



MERCI à VOUS!