



SAXS/WAXS Techniques for 1D, 2D, and 3D Mapping of Structural Changes in Battery Materials

Sandrine Lyonnard



www.europeanbatteryhub.eu



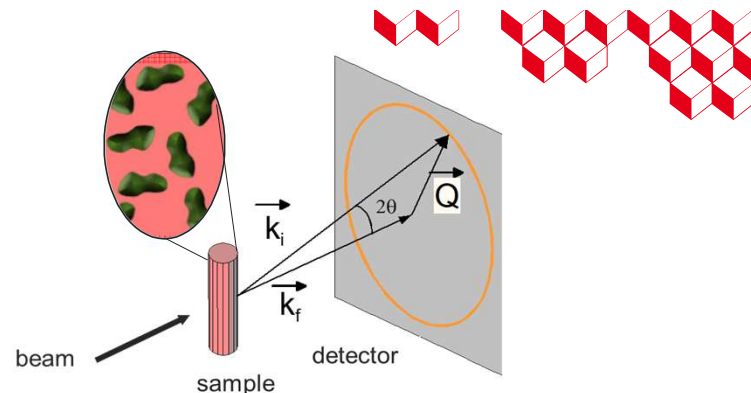
Outline

❖ I – SAXS TUTORIAL

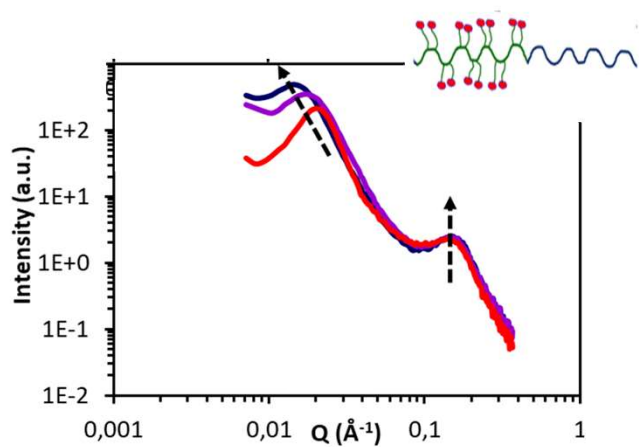
Basic principle of Small Angle Scattering techniques (SAXS, SANS)

❖ II – APPLICATIONS to battery research

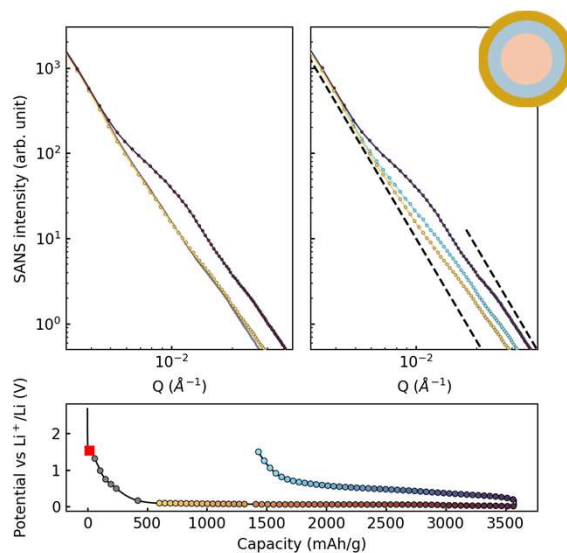
Nanostructured/Nanoparticles/Nanoporous materials



Polymer electrolytes

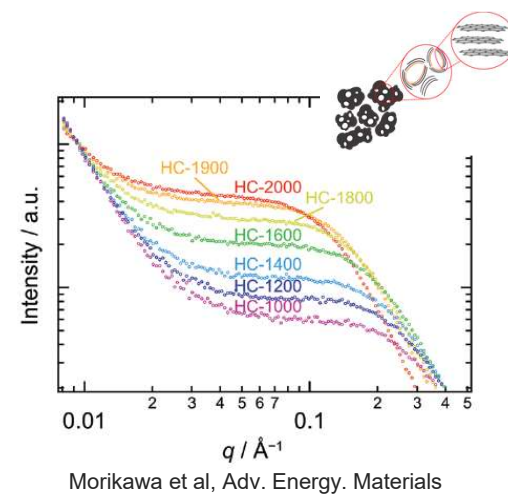


Silicon-based anodes for Li-ion



Courtesy of Xaver Brems

Hard carbons for Na-ion

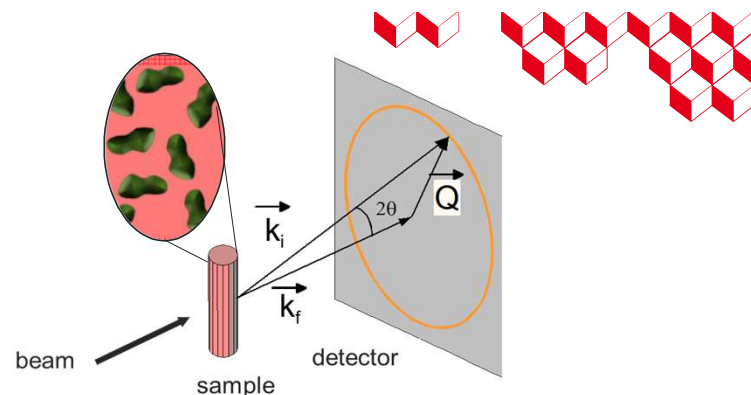


Morikawa et al, Adv. Energy. Materials

Outline

❖ I – SAXS TUTORIAL

Basic principle of Small Angle Scattering techniques (SAXS, SANS)



<https://www-ssrl.slac.stanford.edu/~saxs>

https://www.fhi.mpg.de/1075129/armin_hoell__anomalous_small-angle_x-ray_scattering__150116.pdf

<https://www.diamond.ac.uk/Instruments/Soft-Condensed-Matter/small-angle.html>

R. Heenan, ISIS Neutron Training Course Introduction to SANS

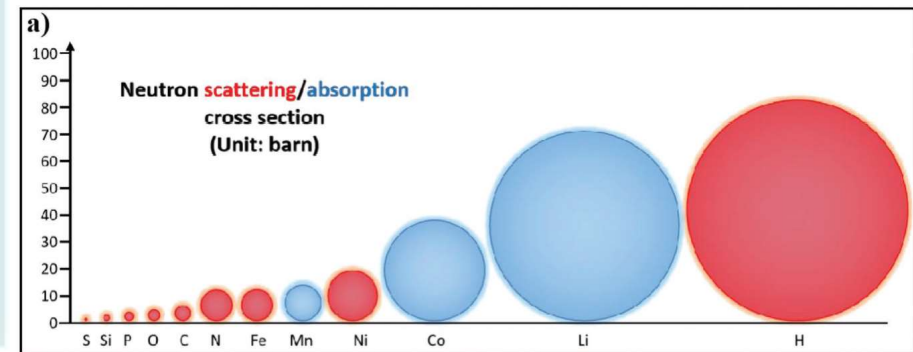
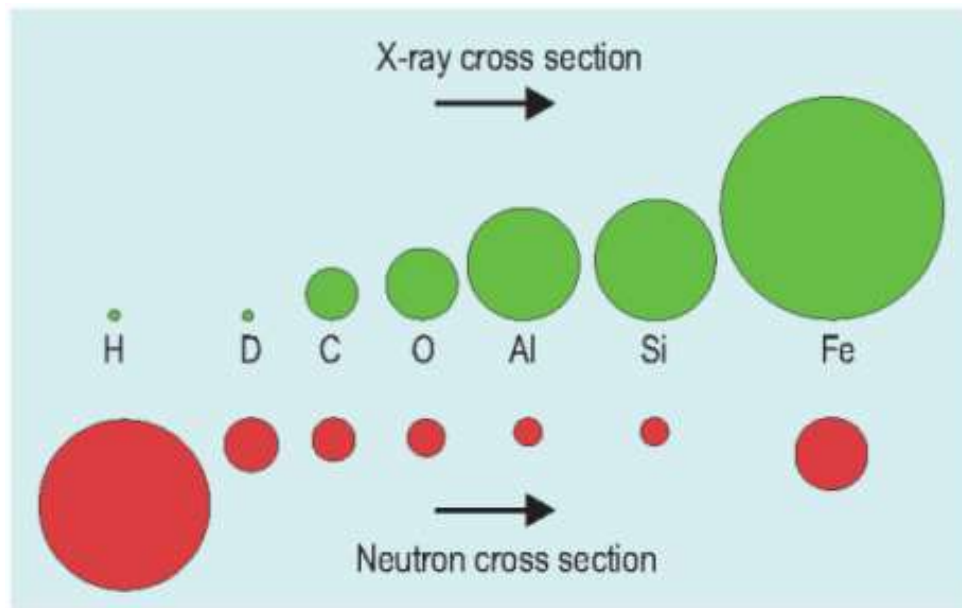
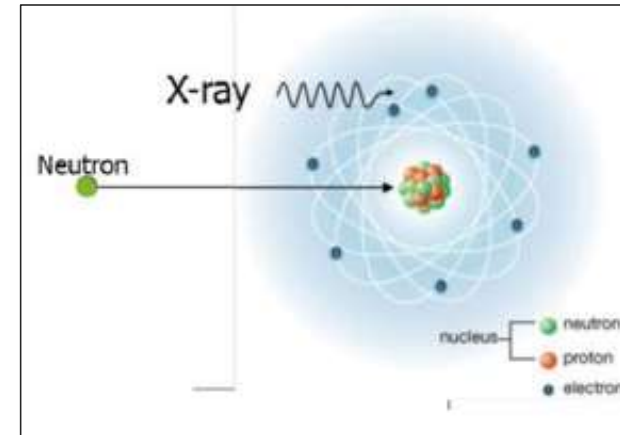
F. Cousin, Small Angle Neutron Scattering, EPJ Web of Conferences 104, 01004 (2015)

DOI: 10.1051/epjconf/201510401004

Basic principles of SAXS (SANS)

neutrons interact with nuclei while X-rays interact with e-

Scattering cross sections & absorption cross sections

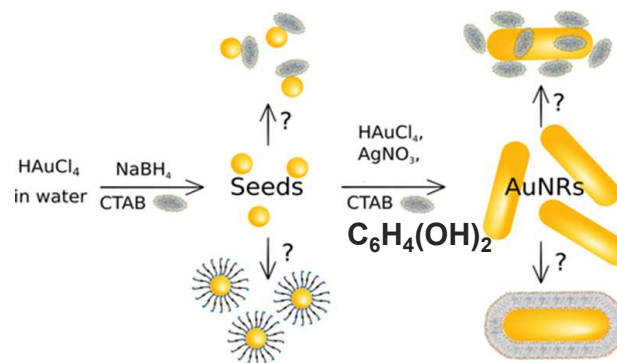


Adv. Energy Mater. 2020, 2000806

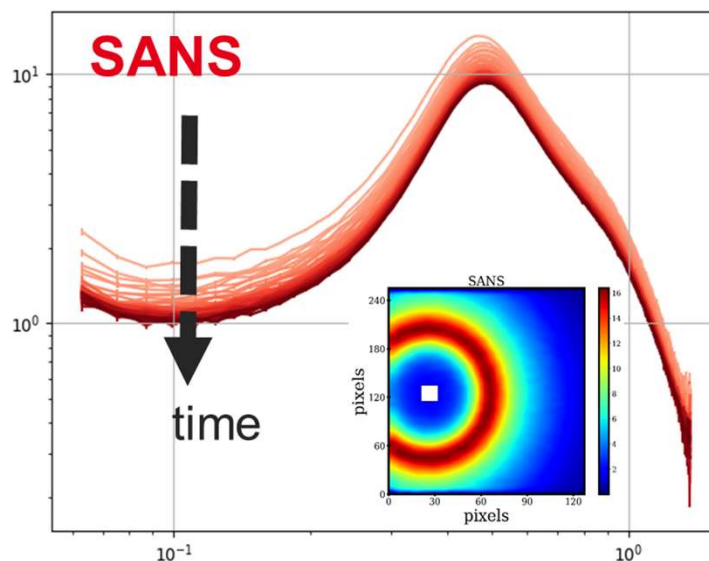
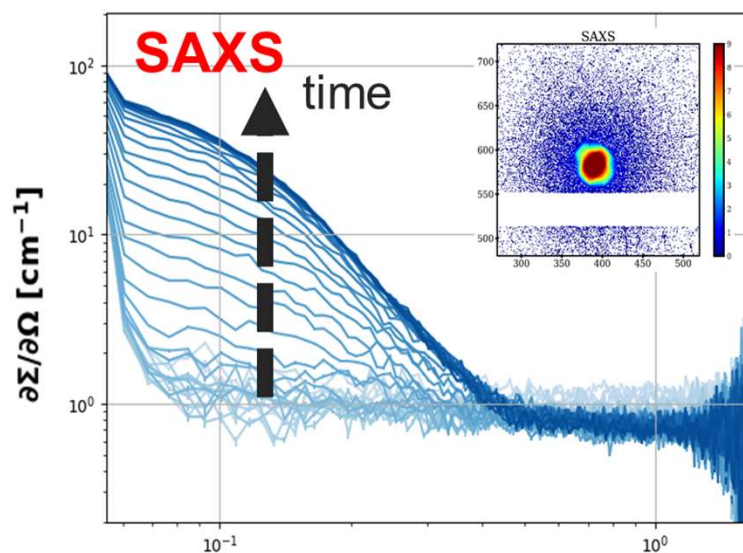
Basic principles of SAXS (SANS)

Hydroquinone synthesis of Au NPs:

Gold nanoparticles (Au NPs) synthesis begins with the gold precursor (HAuCl_4) which forms small seeds after reduction with the reducing agent NaBH_4 in the presence of cetyltrimethylammonium bromide (CTAB). The subsequent reduction of HAuCl_4 using Hydroquinone ($\text{C}_6\text{H}_6(\text{OH})_2$) in the presence of AgNO_3 , CTAB, and the seed particles leads to the formation of single crystalline Au NPs.



Temporal structural cross-correlation between organic stabilizing agent (CTAB micelles) and gold seeds? How do they cooperate in the formation of different size/shape of large stabilized gold nanoparticles?

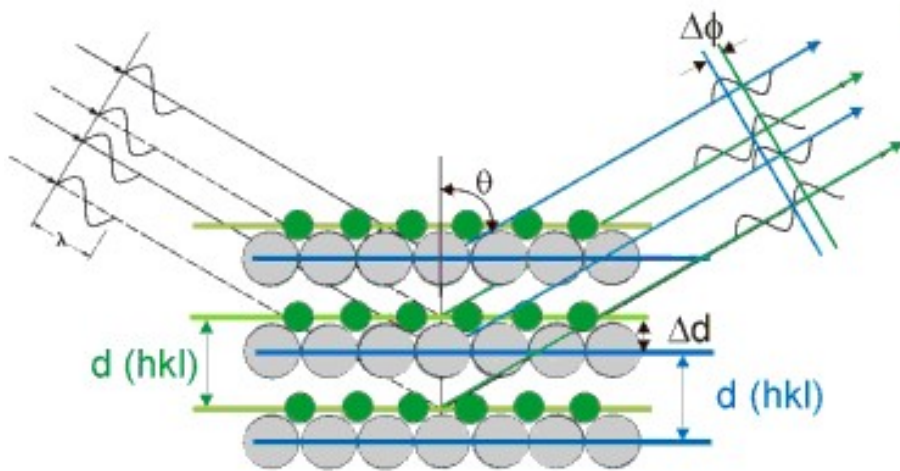


SAXS+SANS =
Complementary nanoscale structural information at two different contrast situations

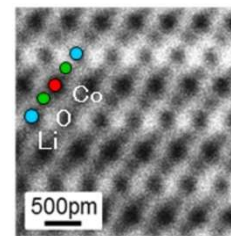
Time evolution of both SAXS and SANS 1d profiles during the in-situ reduction process of gold solution at 35°C.

Basic principles of SAXS/SANS

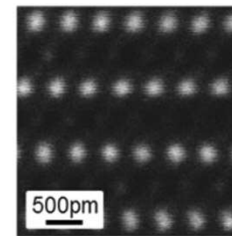
Note 1. Small Angle scattering is somehow a diffraction technique probing the wave interferences from nanoscale scattering objects ! Think about Bragg's law, not on atomic planes but at larger scales, e.g. atoms are replaced by colloids/particles/nanosized areas of the sample !



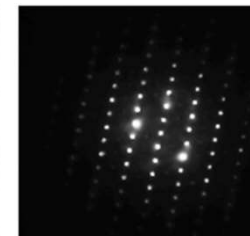
TEM image of a battery LCO cathode



ABF-STEM image



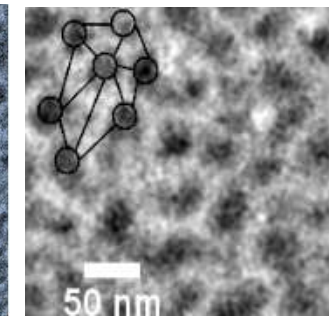
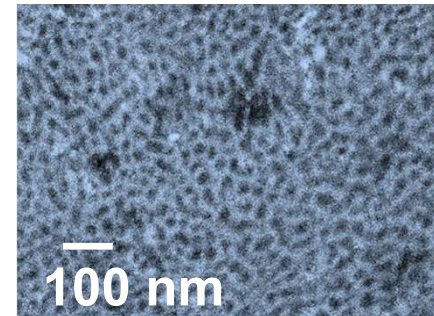
HAADF-STEM image



Electronic Diffraction Pattern

MST 材料科学技術振興財団
Foundation for Promotion of Material Science and Technology of Japan

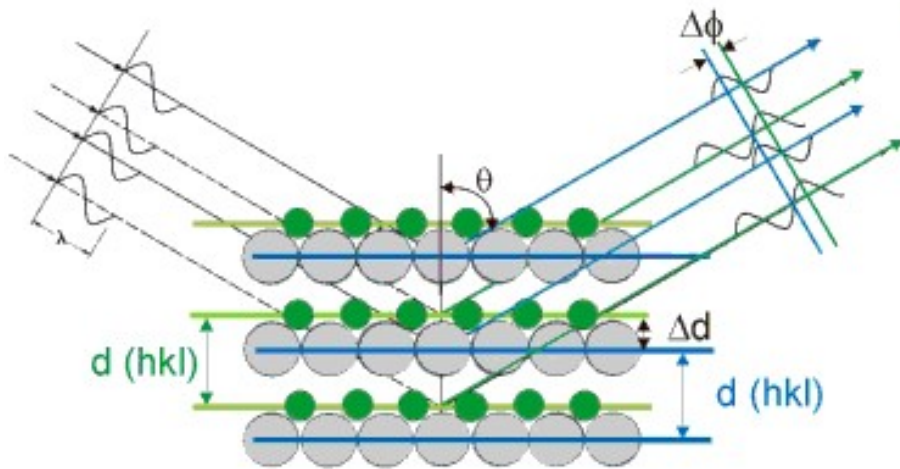
MEB image on a nanostructured polymer



Basic principles of SAXS/SANS



Note 1. Small Angle scattering is somehow a diffraction technique probing the wave interferences from nanoscale scattering objects ! Think about Bragg's law, not on atomic planes but at larger scales, e.g. atoms are replaced by colloids/particles/nanosized areas of the sample !



How can we look at « nano/microscale » interferences ?

$$2 d \sin \theta = n \lambda$$

d, distance probed, 1 – 1000 nm
large compared to λ

Wavelengths of Probe, of the order of
0.1 - 2 nm. Of the order of atomic
spacing. FIXED

λ fixed, d large:
 θ must be small!

-> Small Angle Scattering !

Basic principles of SAXS/SANS

A small angle experiment always works like that...

X-ray or neutron

Radiation sources

Lab X-ray generator ($\lambda = 0.1\text{-}0.2\text{ nm}$)

Synchrotron ($\lambda = 0.03\text{-}0.35\text{ nm}$)

Thermal neutrons ($\lambda = 0.2\text{-}1\text{ nm}$)

Elastic process and momentum transfer

$$\vec{k}_2 - \vec{k}_1 = \vec{Q} \quad , \quad |\vec{k}_1| = |\vec{k}_2|$$

$$|\vec{Q}| = 2|\vec{k}| \sin(\theta) = 4\pi \sin(\theta) / \lambda$$

Small angles $\theta < 5^\circ$ Q typically $[0.001 - 1 \text{ \AA}^{-1}]$

$$d = \frac{2\pi}{Q} \quad [6000 - 6 \text{ \AA}]$$

Magnitude of the scattering vector

$$|\vec{q}| = \frac{4\pi \sin(\theta)}{\lambda}$$

Bragg-equation

$$2d \sin(\theta) = \lambda$$

$$|\vec{q}| = \frac{2\pi}{d}$$

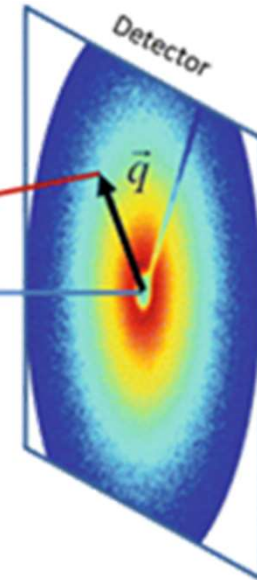
Threshold value:

$$|\vec{q}| \rightarrow 0$$

$$d \rightarrow \infty$$

Scattering also allows to investigate structures in the nm- and μm - range.

→ Small-Angle Scattering (SAXS, SANS, USAXS, USANS) ←



Basic principles of SAXS/SANS

A small angle experiment always works like that...

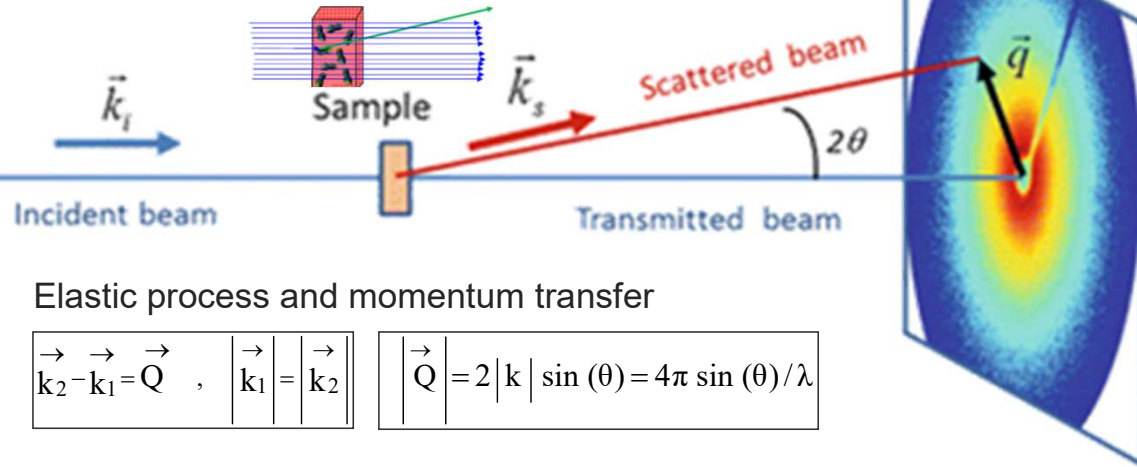
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Elastic process and momentum transfer

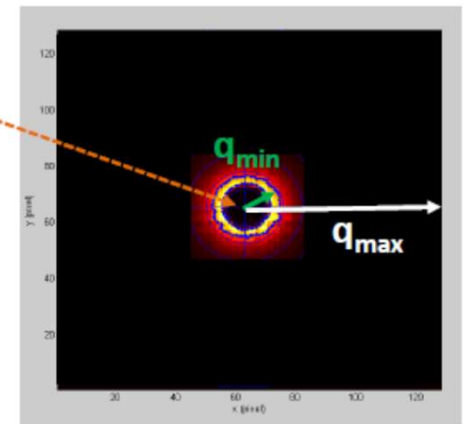
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The sample-detector distance L defines the smallest accessible $q_{\min}$

The detector size defines the maximum $q_{\max}$ accessible

Q-range is (L, λ) dependent

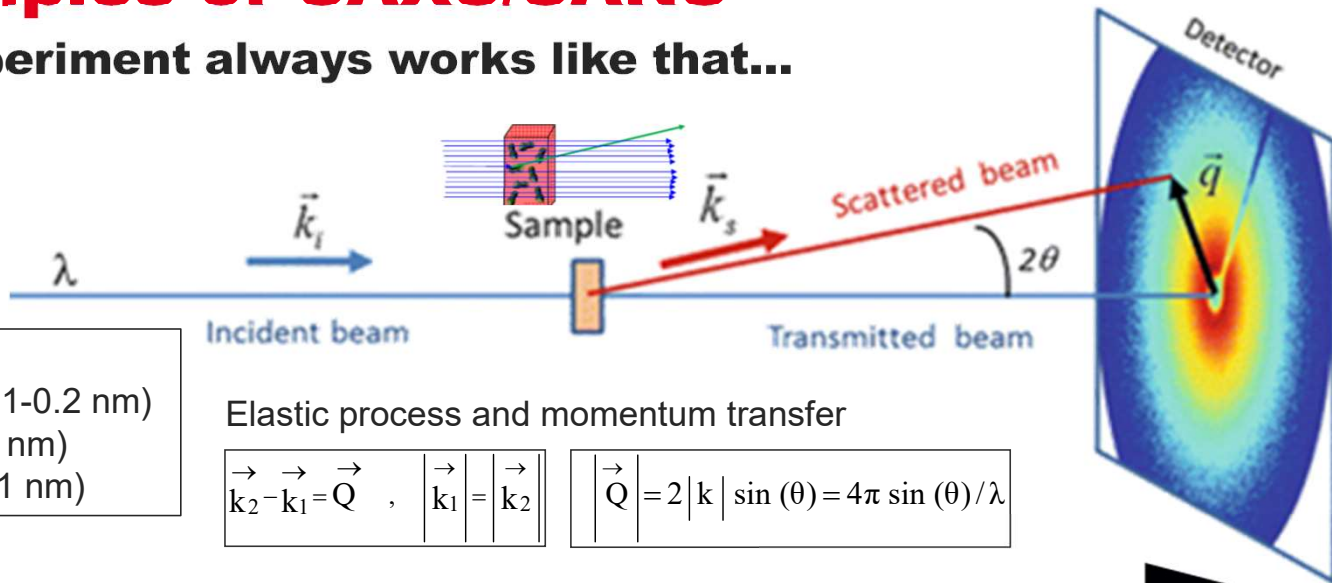
Beamstop



Basic principles of SAXS/SANS

A small angle experiment always works like that...

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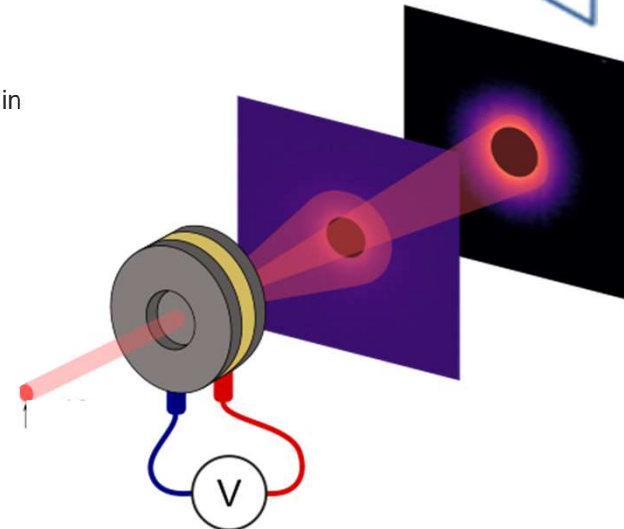
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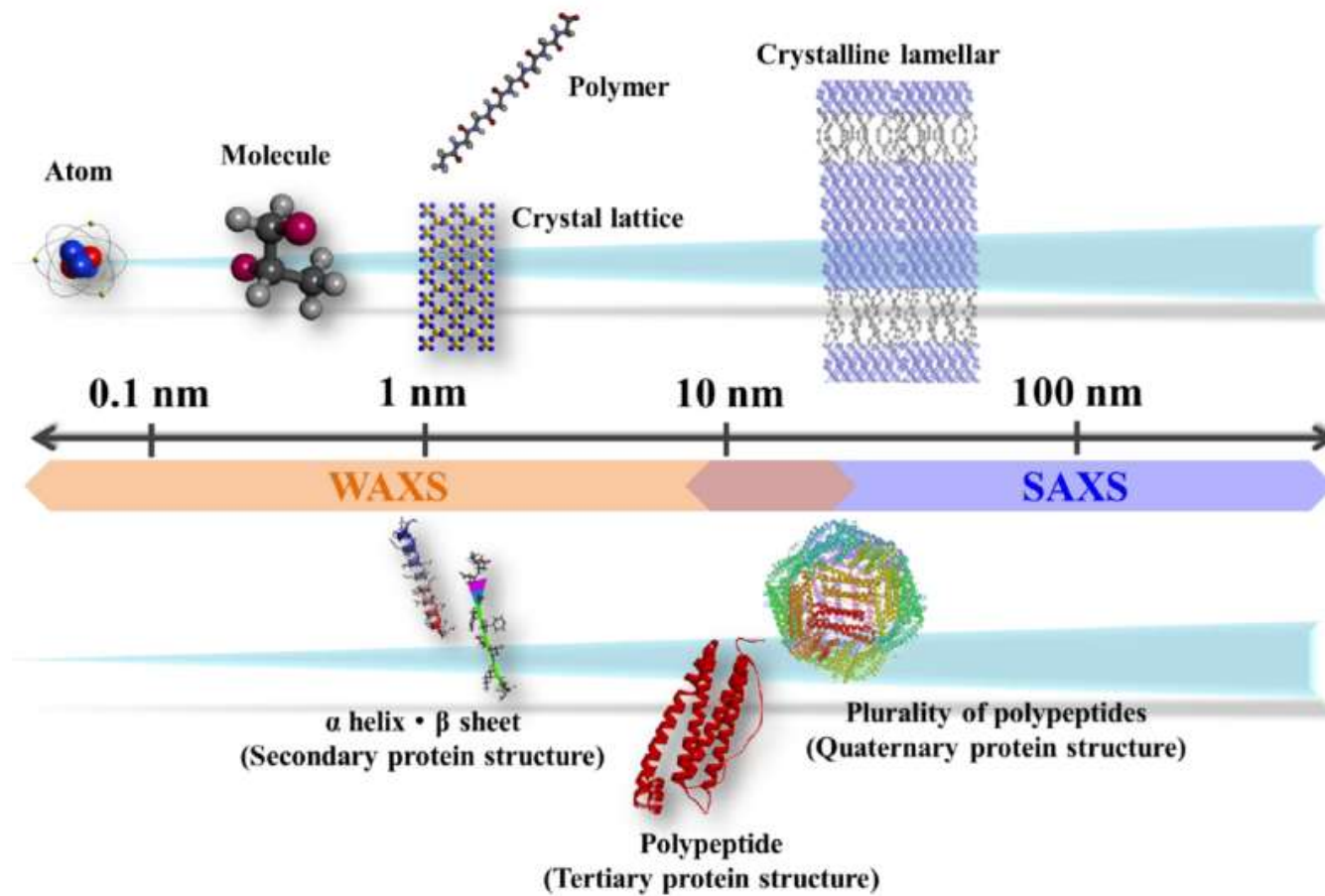
Q -range is (L, λ) dependent

To obtain an extended Q -range, detector is moved !



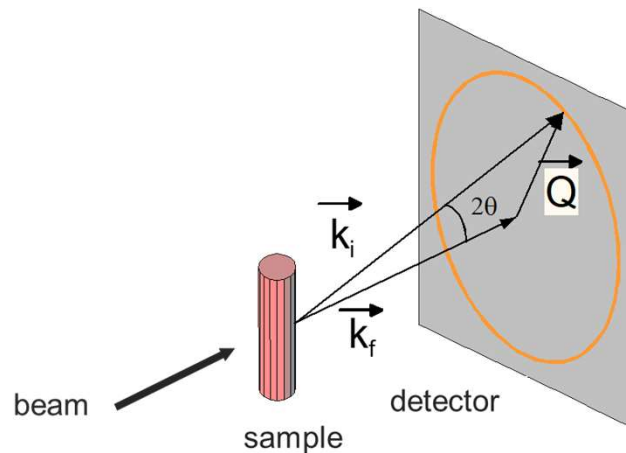
Basic principles of SAXS/SANS

Looking at matter / materials across extended nano-microscales

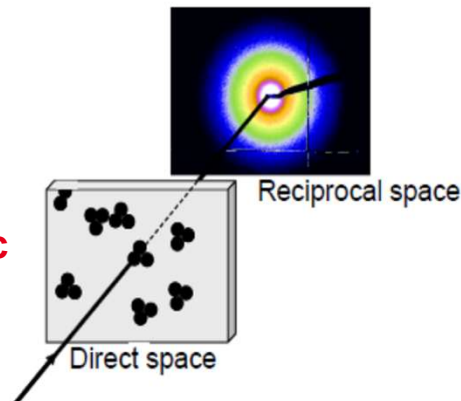


Basic principles of SAXS/SANS

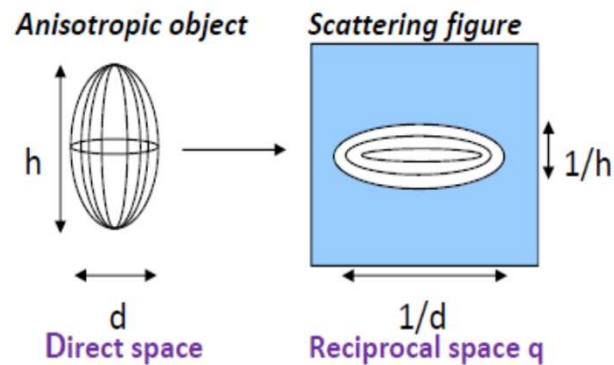
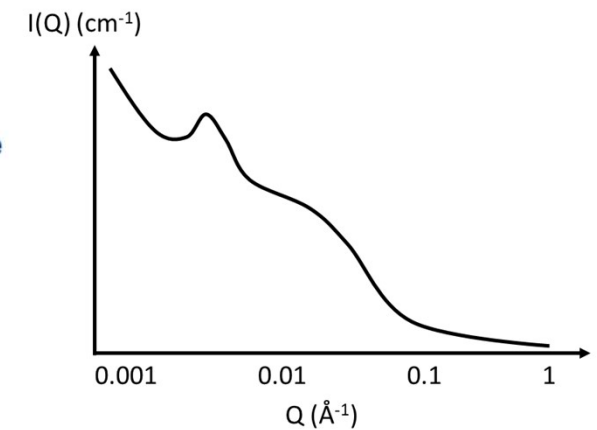
Note 2. Small Angle scattering measures a 2D intensity pattern vs Q



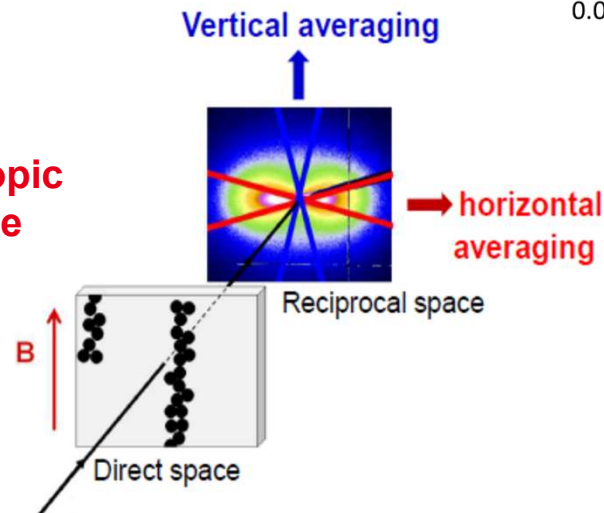
Isotropic sample



radial averaged intensity $I(Q)$



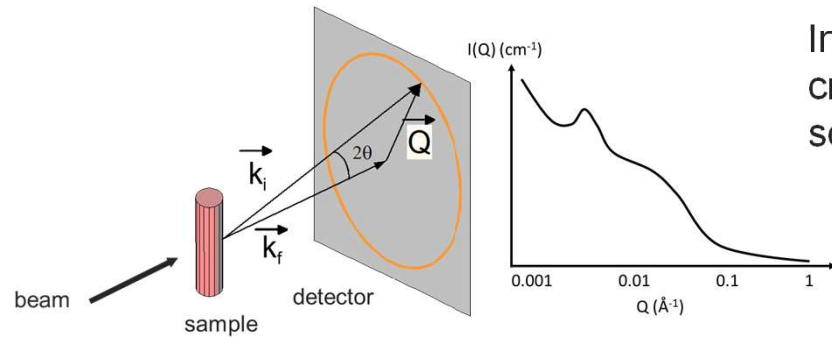
Anisotropic sample



Basic principles of SAXS/SANS



Note 3. SAXS is analytical (sometimes)



Intensity $I(Q)$ is the absolute scattering cross section $d\sigma(Q)/d\Omega$ in units of cm^{-1} = probability of a neutron of wavelength λ being scattered, per unit solid angle, at that Q .

Differential cross-section
= scattered intensity $I(Q)$

$$\frac{d\sigma}{d\Omega}(Q) = \frac{1}{N} \left| \int_{V_s} d\mathbf{r} \rho(\mathbf{r}) e^{i\mathbf{Q}\mathbf{r}} \right|^2 = \frac{1}{N} I(Q)$$

$$I(Q) = N \Delta\rho(r)^2 F(Q,r)^2 S(Q)$$

Scattering contrast $\Delta\rho$

Scattering length b of element i
concentration c_i , density ρ_i

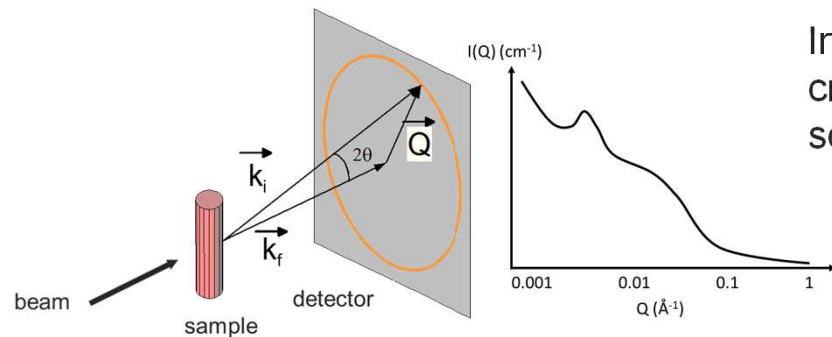
$$\Delta\rho(r) = \sum_i (b_i c_i \rho_i)_{\text{Phase1}} - \sum_j (b_j c_j \rho_j)_{\text{Phase2}}$$

Form factor $P(Q)$ size, shape of particle (we note $P(Q)=F(Q)^2$)

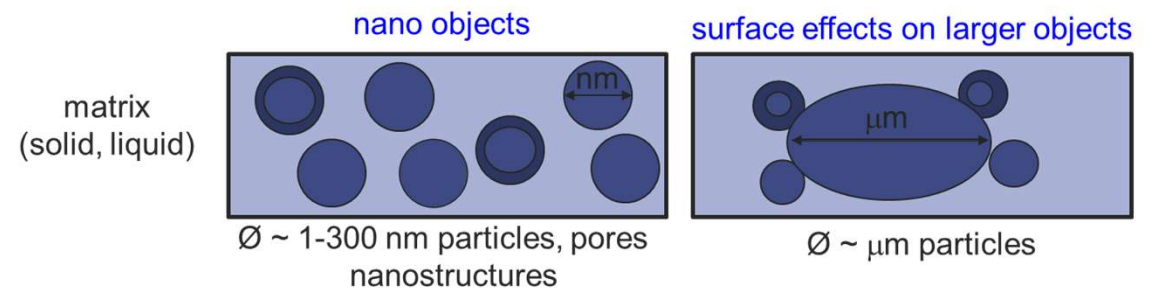
Structure factor $S(Q)$ arrangement of particles

Basic principles of SAXS/SANS

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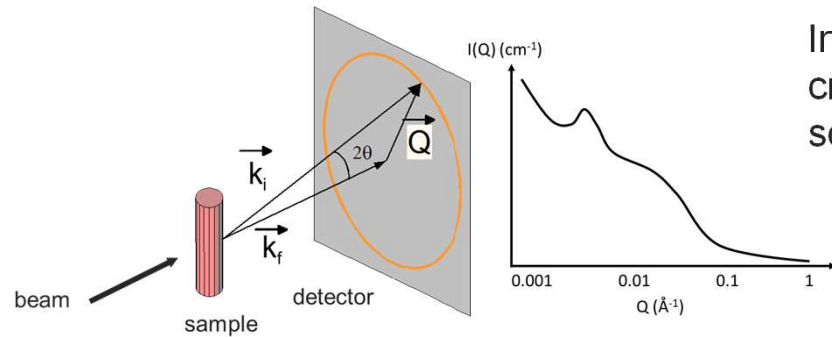
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Basic principles of SAXS/SANS



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Intensity $I(Q)$ is the absolute scattering cross section $d\sigma(Q)/d\Omega$ in units of cm^{-1} = probability of a neutron of wavelength λ being scattered, per unit solid angle, at that Q .

What do we measure experimentally ?

Counts in detector of area A at radius R and distance L from sample

$$I(R, \lambda) = I_0(\lambda) \cdot \frac{\partial \Sigma(Q)}{\partial \Omega} \cdot \Delta\Omega(R) \cdot t \cdot T(\lambda) \cdot \eta(\lambda)$$

Solid Angle $\Delta\Omega = A/L^2$

t = sample thickness

T = transmission

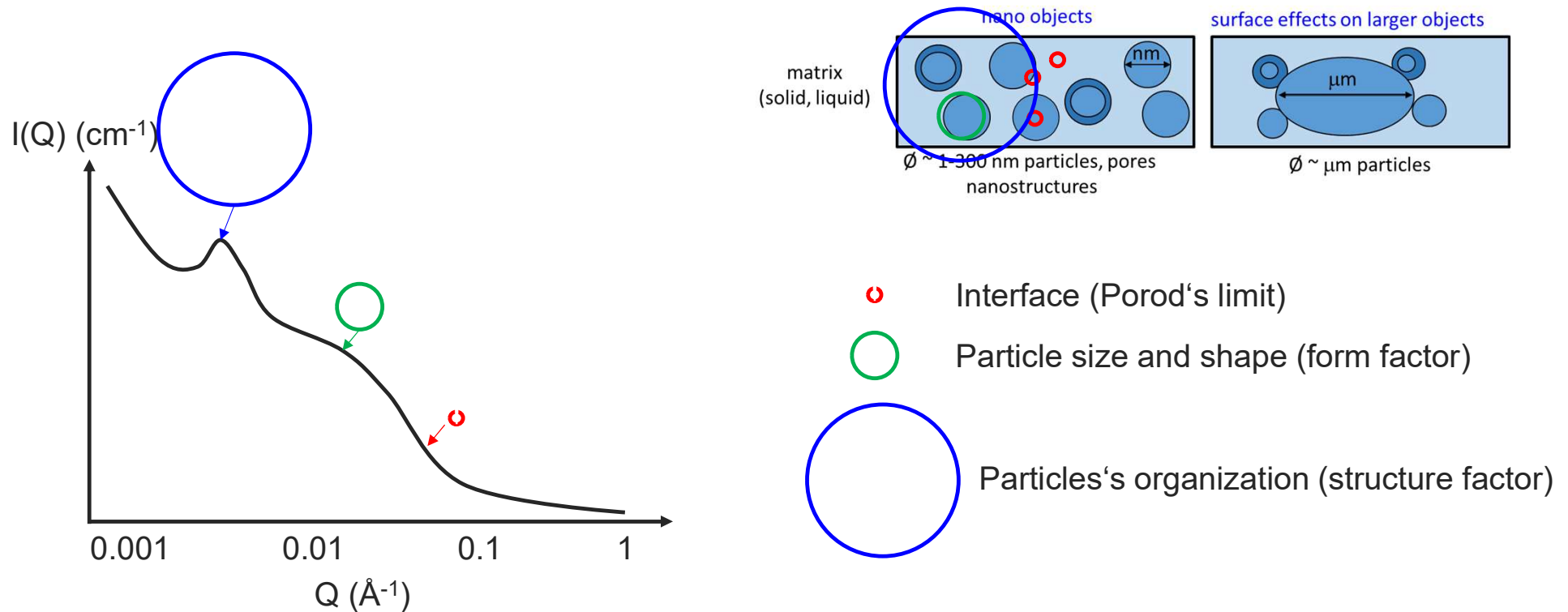
η = detector efficiency

$\tan(\theta) = R/L$

Basic principles of SAXS/SANS

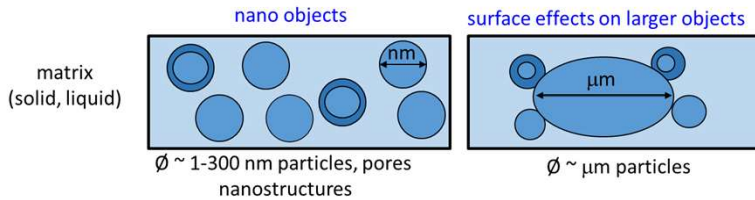


Note 4. SANS is like having a microscope with a magnifying glass of diameter $2\pi/Q$
You get a signal when you have a contrast !

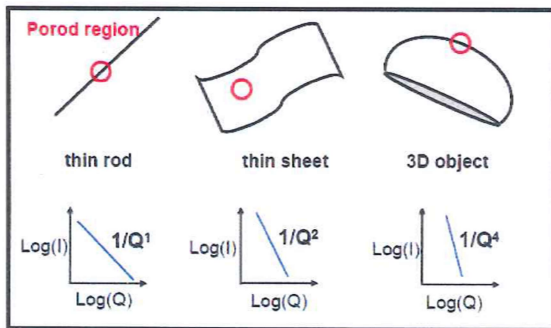


Interfaces

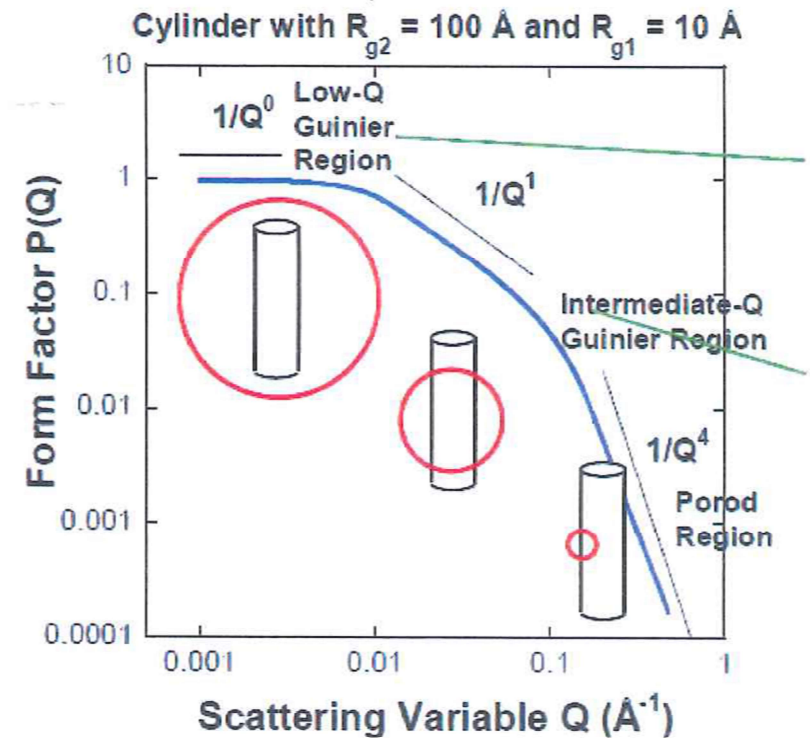
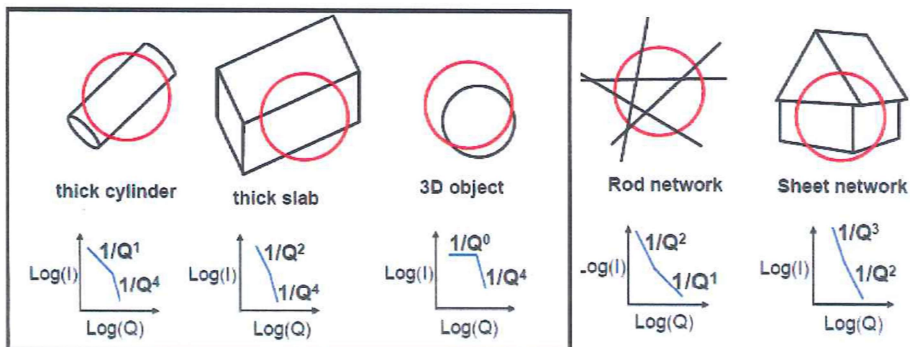
SANS/SAXS from disperse particles



Assortment of Porod Exponents

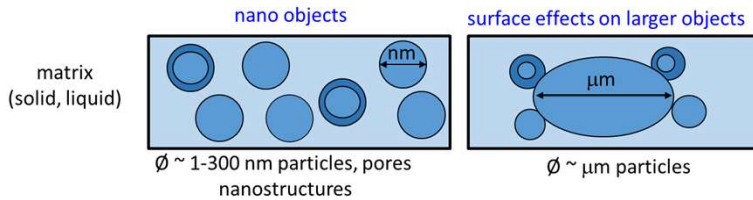


More Porod Exponents



Courtesy of Boualem Hammouda

Interfaces



Fractal aggregates or pores

$I(Q)$ from fractals give straight line regions on log-log plots
Ex : rocks, coals, cement, zeolites, silicas, battery electrodes !

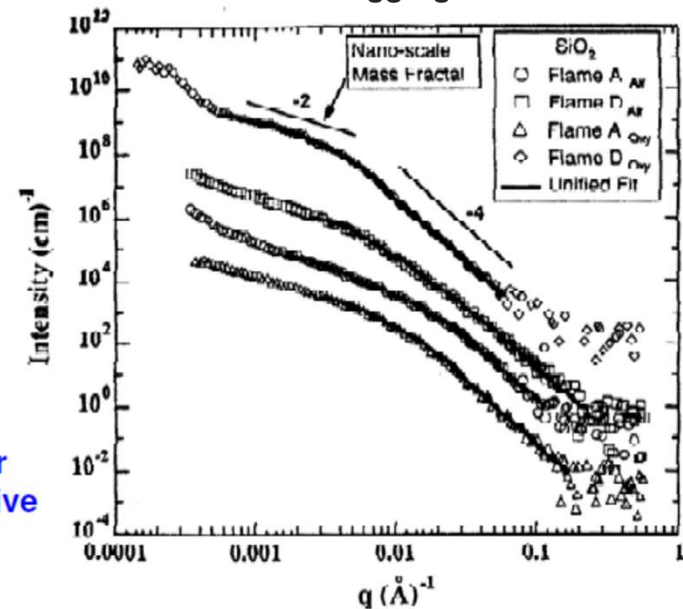
Volume or Mass Fractals give Q^{-d} where d ranges:

$d = 1$ – thin rods,
 $d \sim 1.8$ diffusion limited aggregation
(particles stick on first contact)
 $d \sim 2.1$ reaction limited aggregation
(some relaxation after sticking)
 $d = 3$ perfectly rough,

Surface fractals give $Q^{-(6-d)}$ where
 $d = 2$ - smooth i.e. Q^{-4} Porod law
up to $d = 3$ - perfectly rough.

Other scattering laws also give power laws in Q !!! Diffuse interfaces can give steeper than Q^{-4} , to Q^{-6}

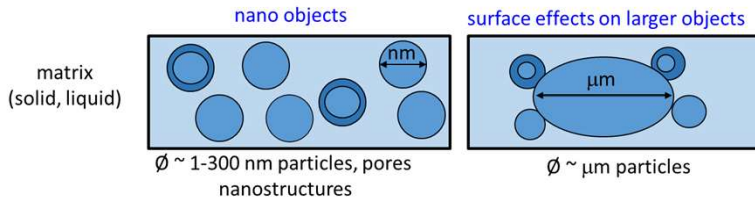
Fumed silica aggregates



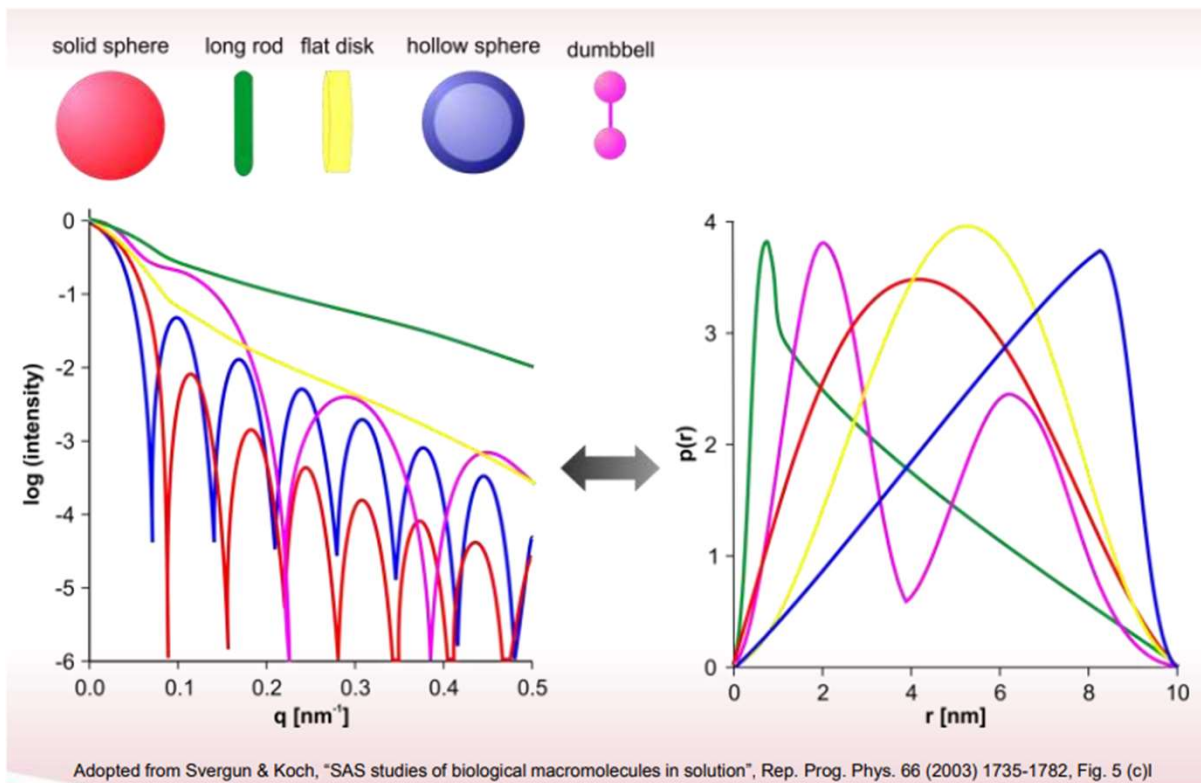
Slopes are meaningful !

J. Hyeon-Lee, Langmuir 14 (1998) 5751-5756

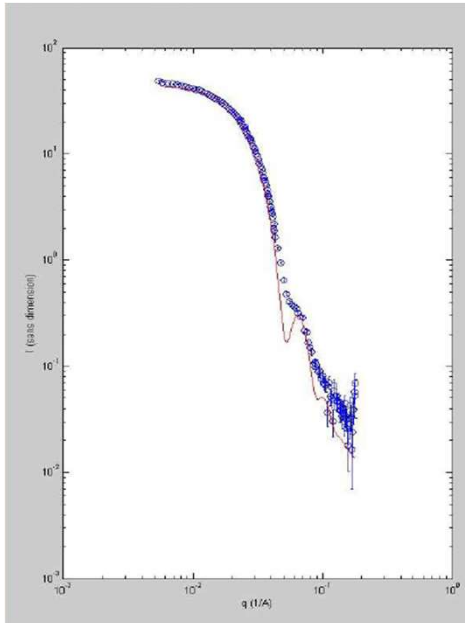
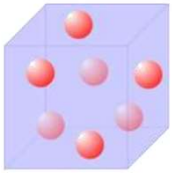
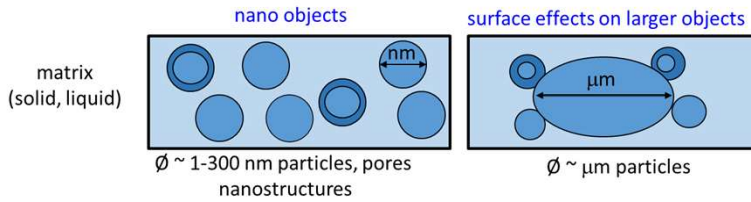
Form Factors P(Q)



Single objects (diluted suspensions / solutions) have very different SAXS fingerprints



Form Factors P(Q)



Dilute sample

Modelling : Form factor of sphere

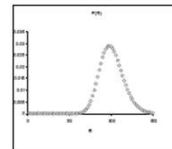
$$P_{\text{sphere}}(q, R) = \left[3 \frac{(\sin(qR) - qR \cdot \cos(qR))}{(qR)^3} \right]^2$$

Calculation of form factor with $R \sim 86 \text{ \AA}$

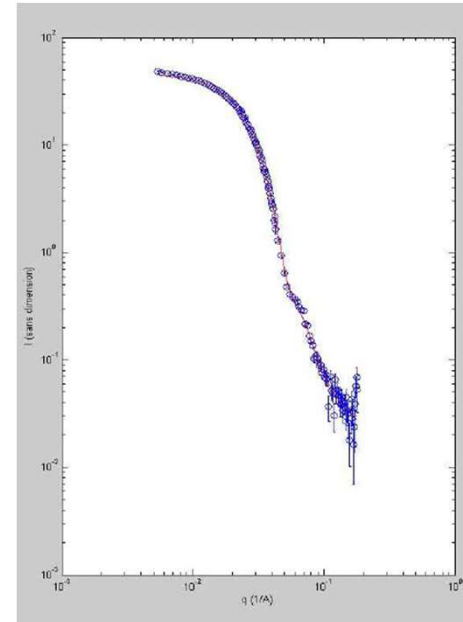
Why oscillations are not reproduced ?

- Polydispersity

$$P(R, R_0, \sigma) = \frac{1}{\sqrt{2\pi} R \sigma} \exp \left[-\frac{\ln \left(\frac{R}{R_0} \right)^2}{2\sigma^2} \right]$$



Log normal



Dilute sample

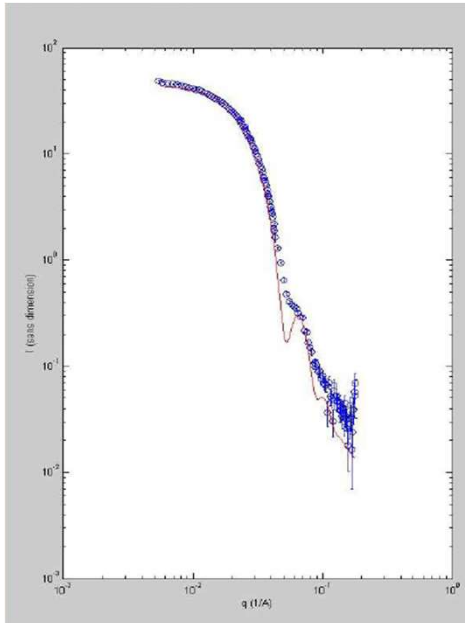
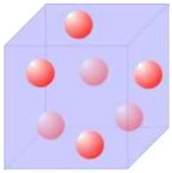
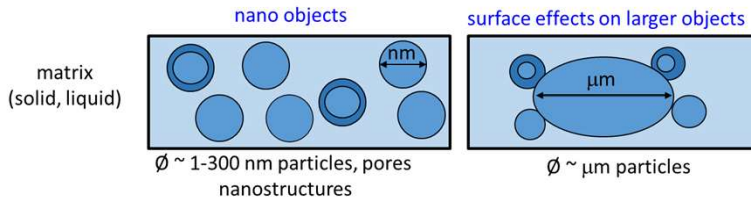
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$R = 72 \text{ \AA}, \sigma = 0.23$

Form Factors P(Q)



Dilute sample

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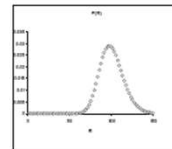
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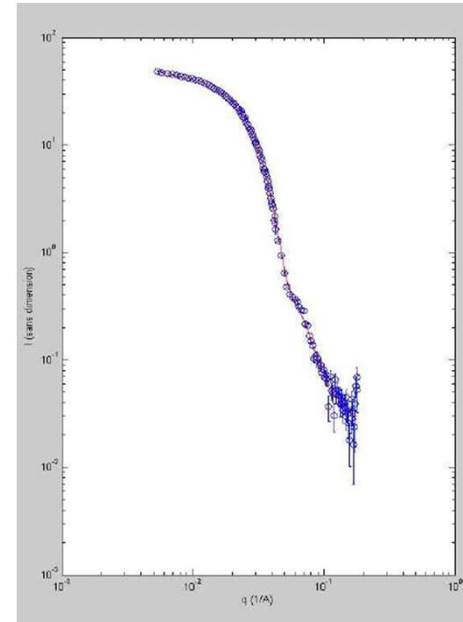
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Log normal



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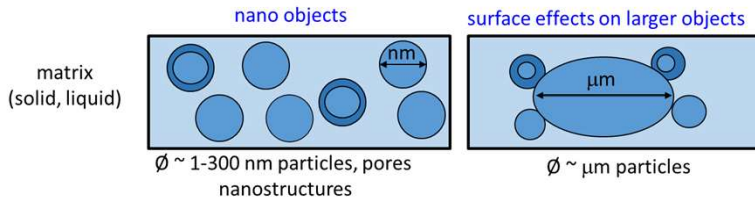
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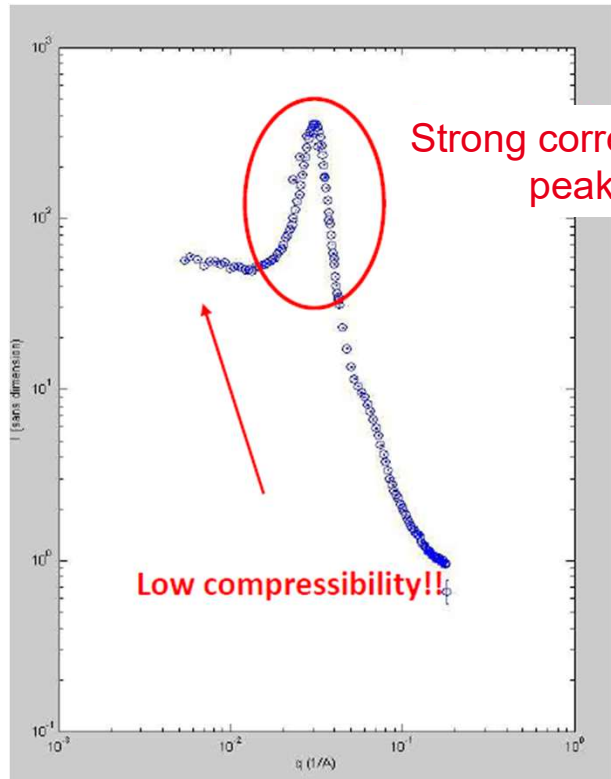
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$R = 72 \text{ \AA}, \sigma = 0.23$

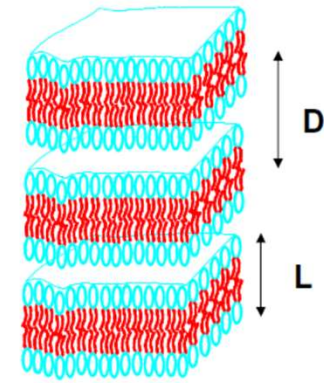
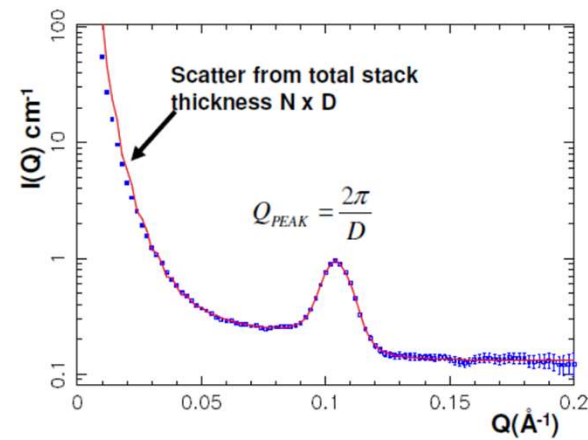
Form Factors P(Q)



Concentrated solution



Lamellar assemblies
Ex : 3% DPPC lipid in D2O

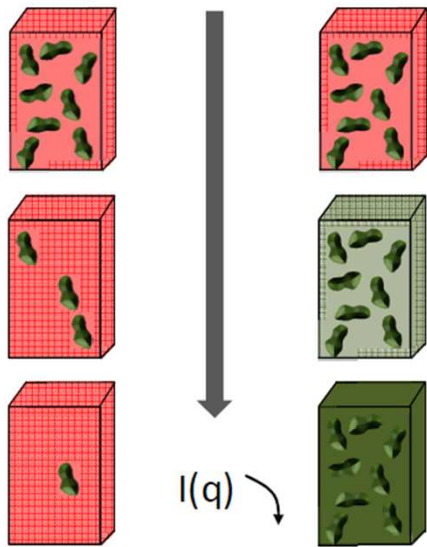


Fit has 18 layers of ($L = 4.64 \text{ nm}$ lipid + 1.32 nm water) $D = 5.96 \text{ nm}$
 $\sigma_D/D = 7\%$, $\sigma_L/L = 10\%$ (fixed)

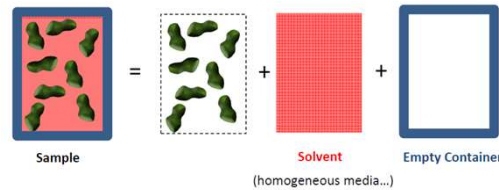
Practicalities

Samples must be concentrated enough with a sufficient contrast

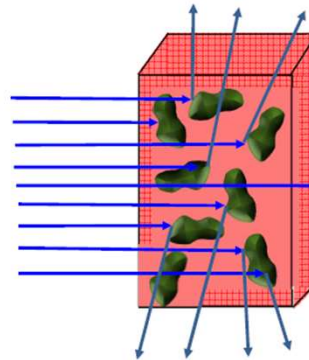
$$I(Q) \sim n \cdot \Delta\rho^2 \cdot P(Q) \cdot S(Q)$$



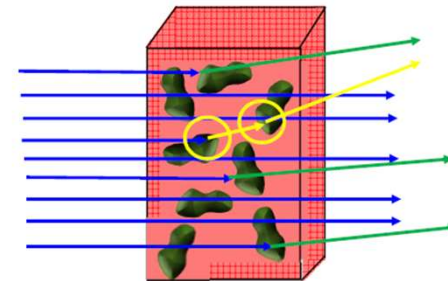
- 1) Choose X vs N
- 2) Choose set-up
- 3) Choose sample environment



Incoherent scattering ?



Multiple scattering ?



Adapt sample thickness

Calculate SLD prior to experiment

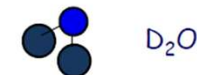
$$\rho_i = \sum_i \frac{b_i}{V} \quad V = \frac{d \cdot N_A}{M} \quad V_{H_2O} = \frac{M_{H_2O} \bar{V}_{H_2O}}{N_A}$$

$$b_H = -0.374 \cdot 10^{-12} \text{ cm}; b_D = 0.667 \cdot 10^{-12} \text{ cm}; b_O = 0.580 \cdot 10^{-12} \text{ cm}$$



$$\rho_{H_2O} = \frac{2b_H + b_O}{V_{H_2O}} = \frac{(5.81 - 3.74 \cdot 2) fm}{30 \text{ \AA}^3}$$

$$\rho_{H_2O} = -0.56 \cdot 10^{10} \text{ cm}^{-2}$$

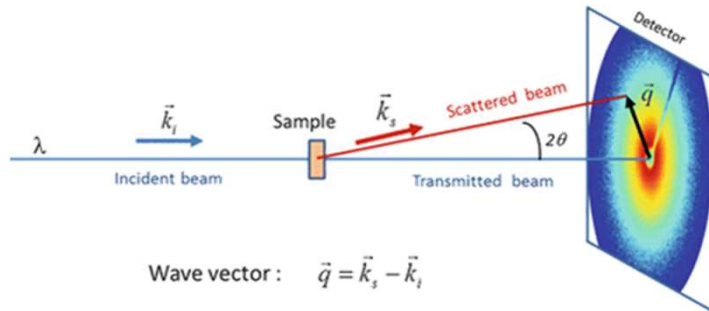


$$\rho_{D_2O} = \frac{2b_D + b_O}{V_{H_2O}} = \frac{(6.67 \cdot 2 + 5.81) fm}{30 \text{ \AA}^3}$$

$$\rho_{H_2O} = 6.38 \cdot 10^{10} \text{ cm}^{-2}$$

Courtesy of Fabrice Cousin

Practicalities

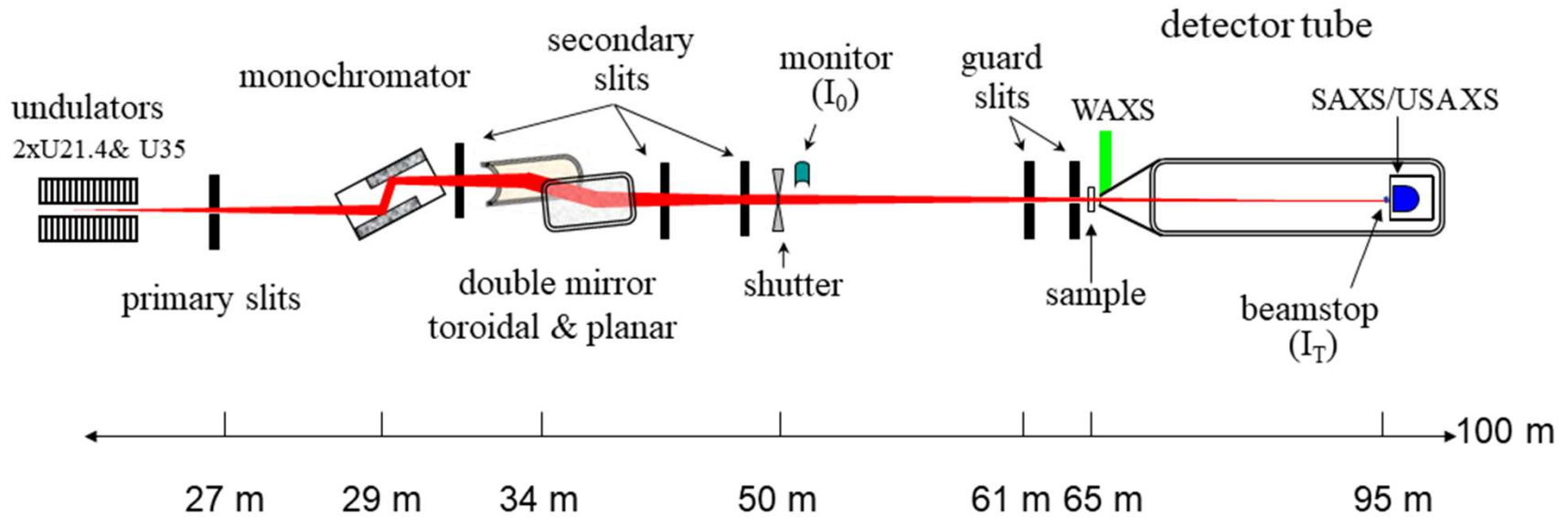


Lab-SAXS

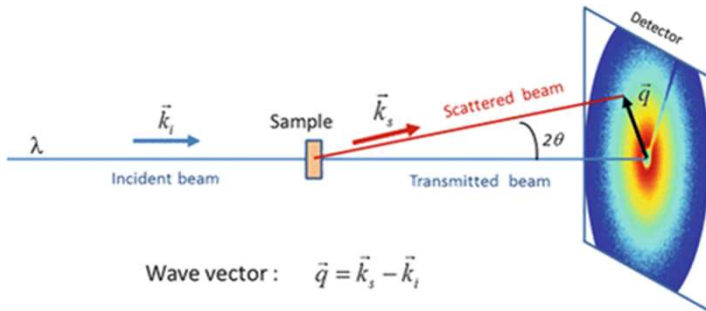


Synchrotron SAXS

ID02



Practicalities

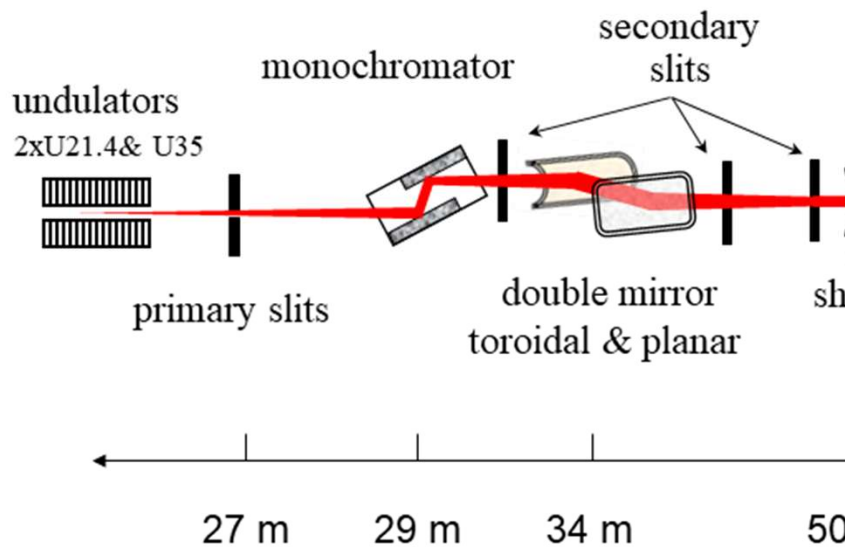


Lab-SAXS

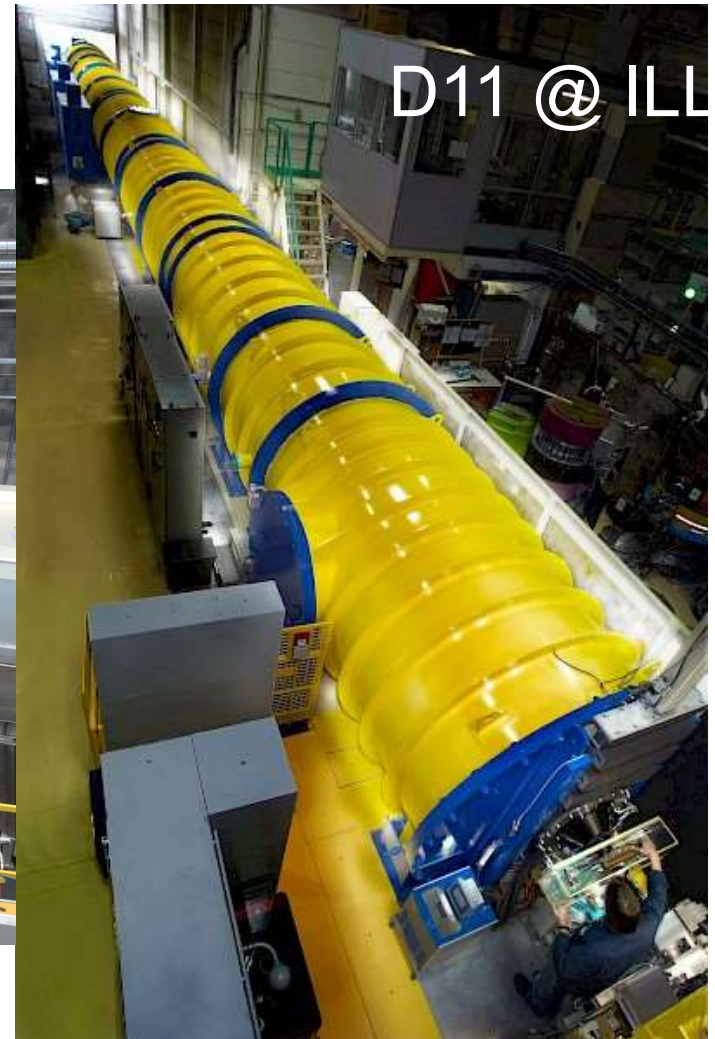
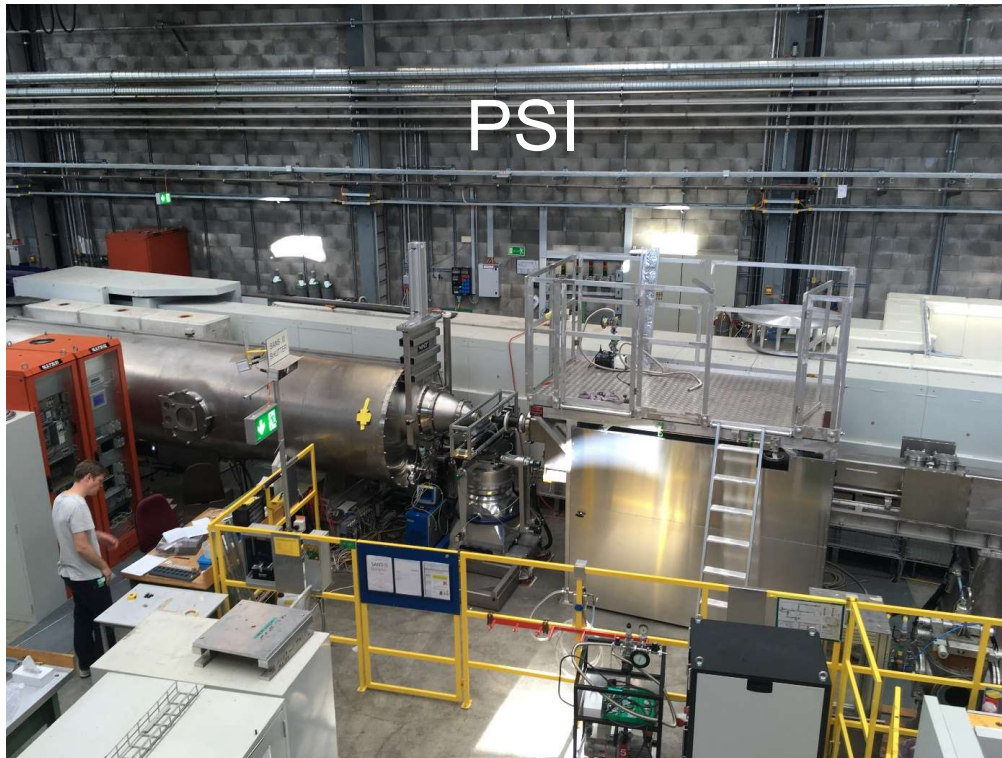


Synchrotron SAXS

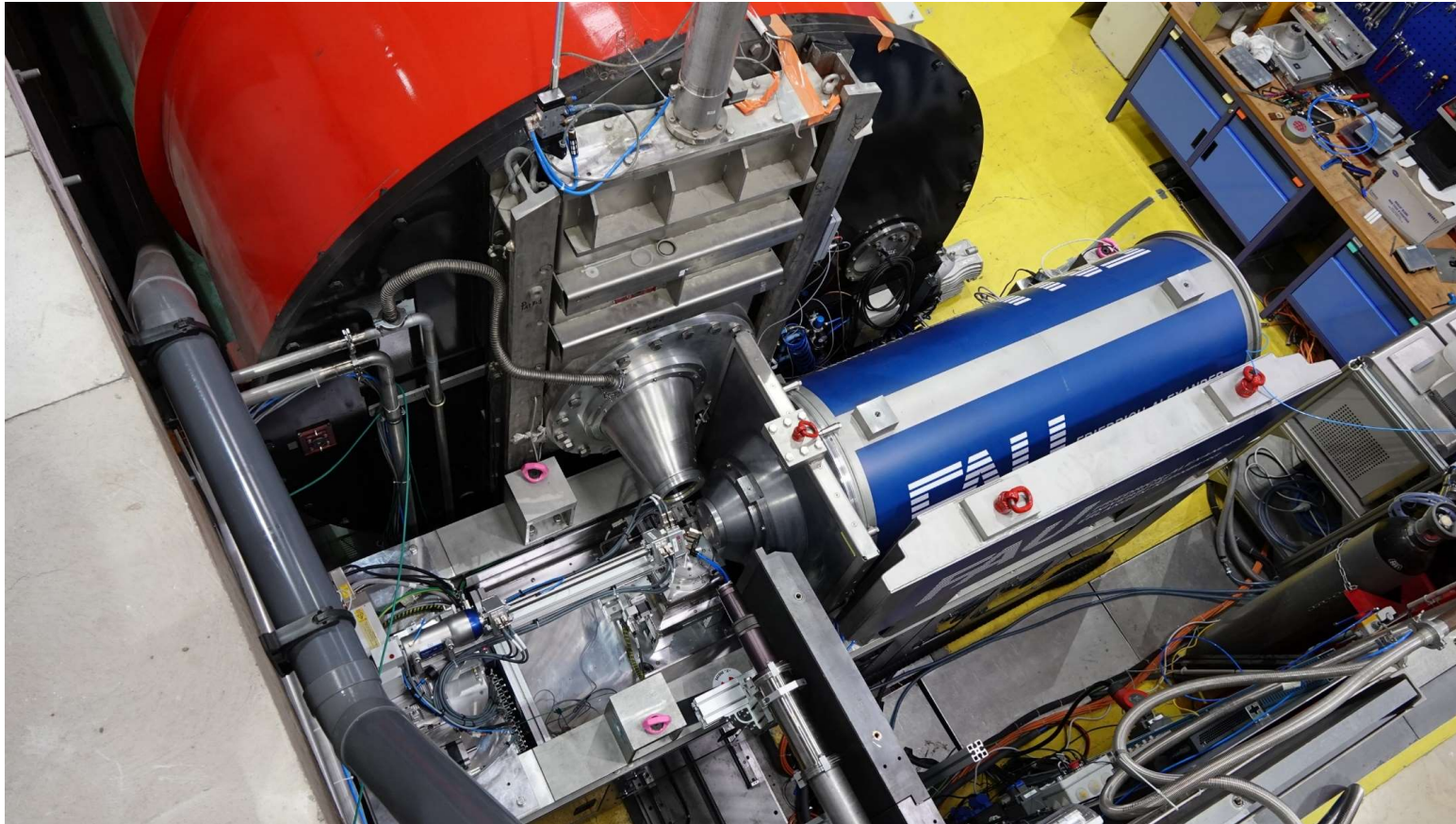
ID02



Practicalities



Coupled SAXS/SANS

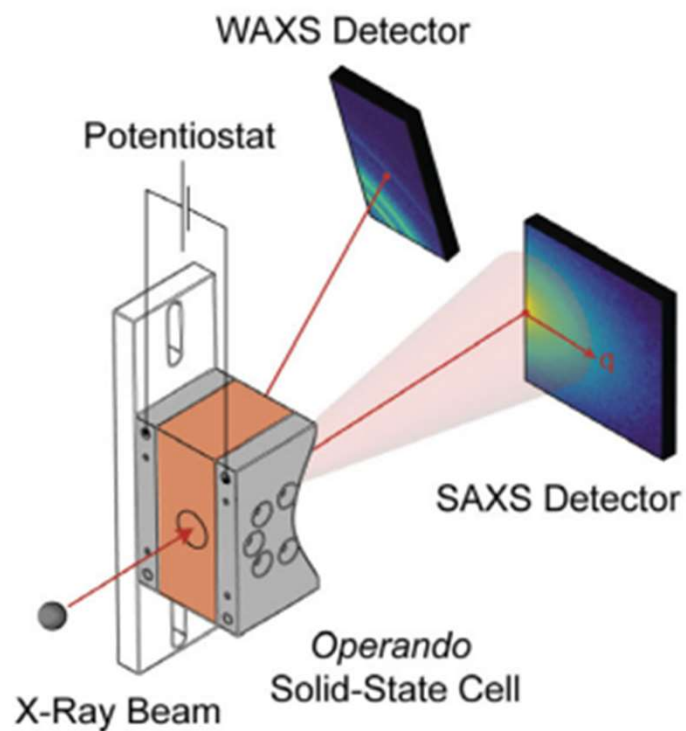


D22 spectrometer

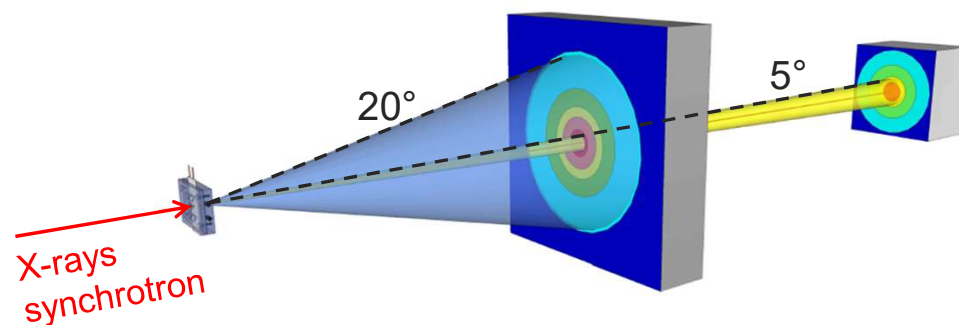


E. Metwalli, .., T. Unruh, *J. Appl. Cryst.* **53**, 722 (2020)

Coupled SAXS/WAXS

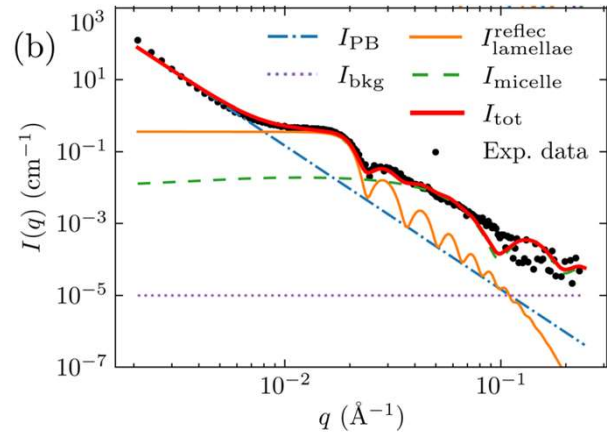
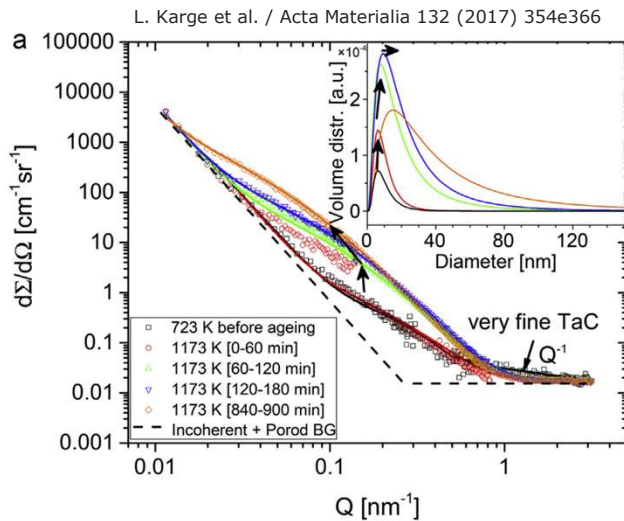


J-M. Von Mentlen et al, Batteries and supercaps, 2025, e202500428

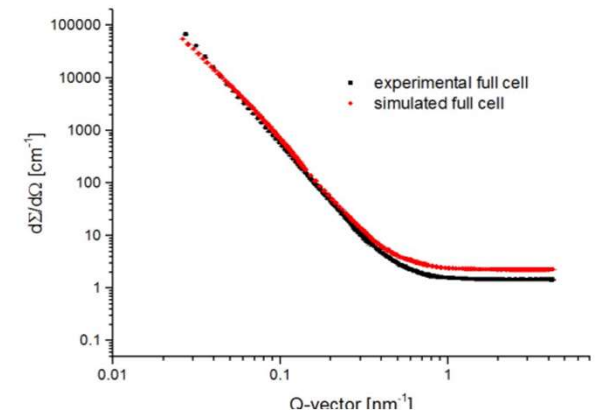


C. Berhaut et al, ACS Nano (2019), 13, 10, 11538-11551

SAXS in batteries...not always easy !



Julien Lamolinarie et al Soft Matter, 2022, 18, 8733



Stefan Seidlmayer et al 2015 J. Electrochem. Soc. 162 A3116

Few reviews

A. Black et al, Synchrotron radiation based operando characterization of battery materials, Chem. Sci., 2023, 14, 1641

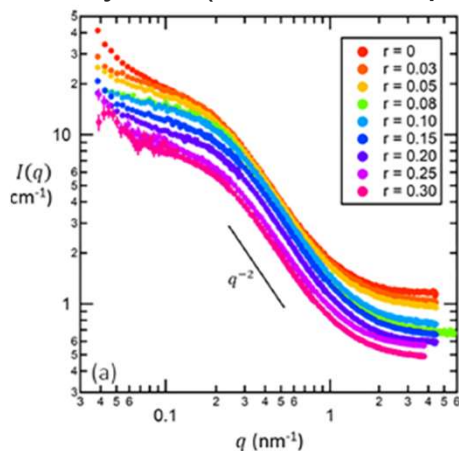
L. Fang et al, Synchrotron small-angle X-ray scattering technique for battery electrode study, Nano Energy, 2024, 121, 109255

W. Cheng et al, Recent advances in battery characterization using in situ XAFS, SAXS, XRD, and their combining techniques: From single scale to multiscale structure detection, Exploration, 2023, DOI: 10.1002/EXP.20230056

Main applications of SAXS/SANS in batteries

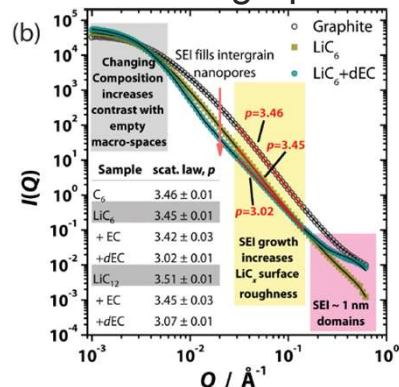


Polymer (blends, composites)



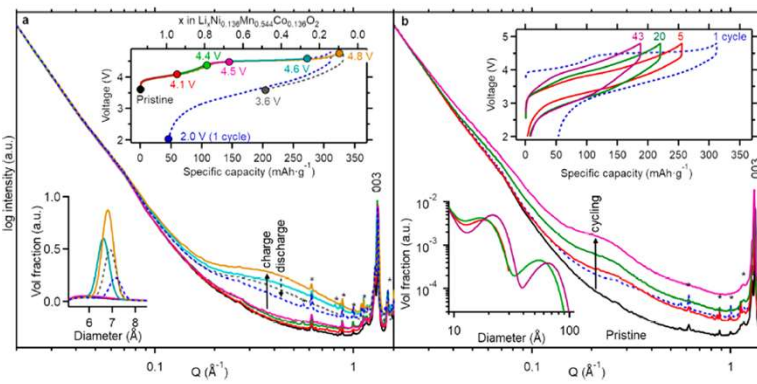
W.S. Loo et al, Macromolecules 2019, 52, 8724–8732

SEI on graphite



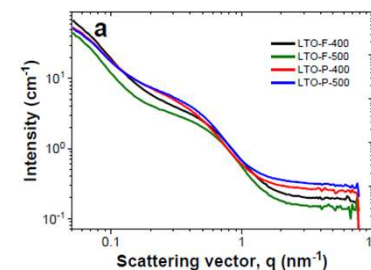
R.L. Sacchi et al, J. Phys. Chem. C 2015, 119, 9816–9823

LNMO



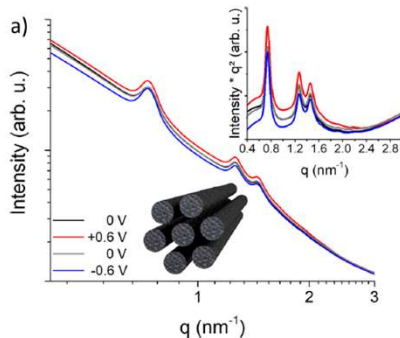
Grenier et al, <https://doi.org/10.1021/jacs.1c00497>

LTO interfaces



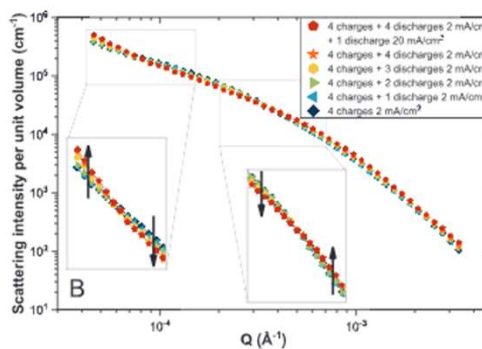
C.J. Jafta et al, 10.1002/cssc.202000802

Porous Carbon



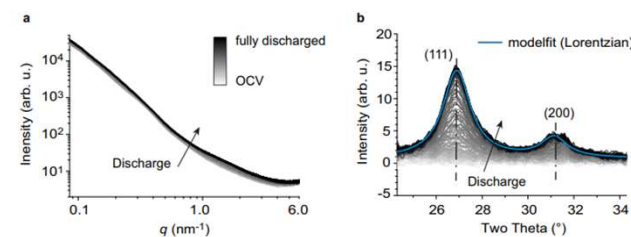
C. Kocswara et al, ACS Appl. Mater. Interfaces 2019, 11, 42214–42220

Lithium metal batteries



C. Didier et al, Adv. Energy Mater. 2023, 13, 2301266

Lithium sulphur batteries



C. Prehal et al, Nature Communications | (2022) 13:6326

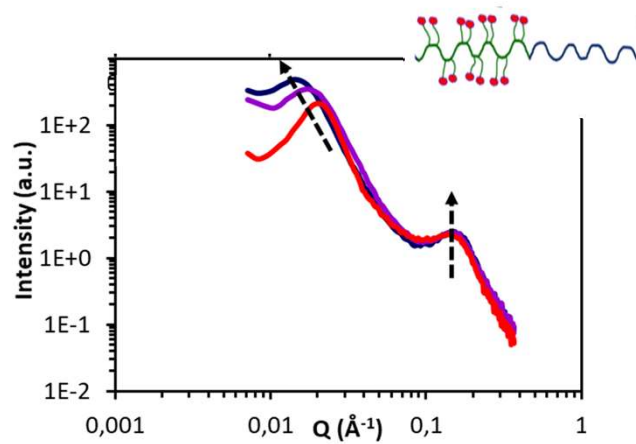


N. Paul et al, Journal of The Electrochemical Society, 166 (6) A1051-A1054 (2019)

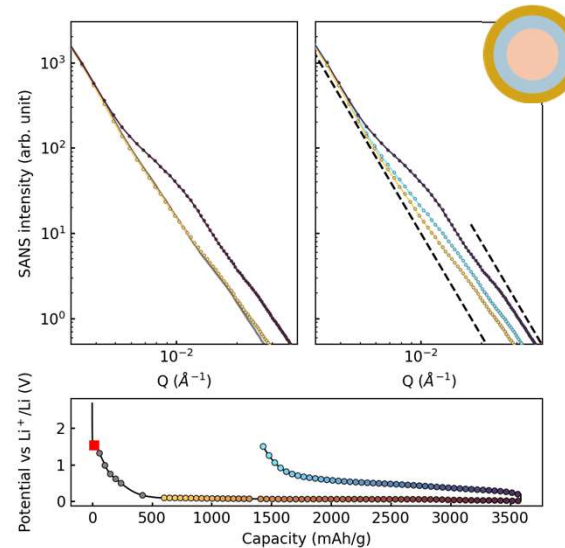
Main applications of SAXS/SANS in batteries



Polymer electrolytes

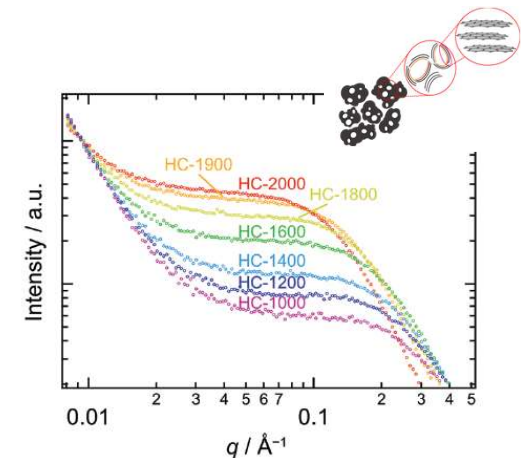


Silicon-based anodes for Li-ion



Courtesy of Xaver Brems

Hard carbons for Na-ion

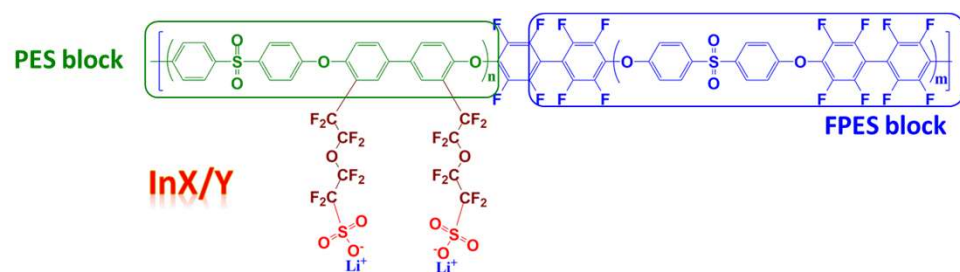


Morikawa et al, Adv. Energy. Materials

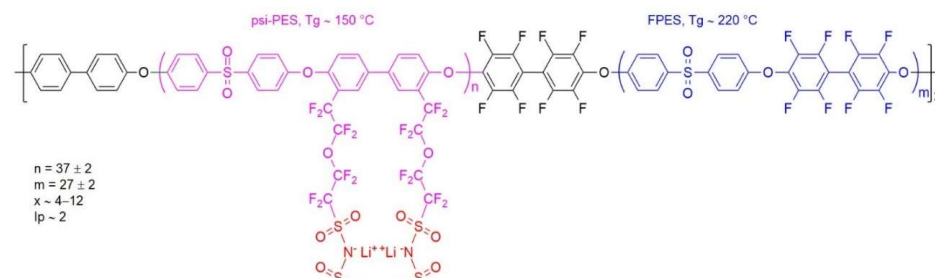
#1 Nanostructure of block copolymer membranes

A platform of single-ion conductors

H⁺ conducting fuel cell membranes



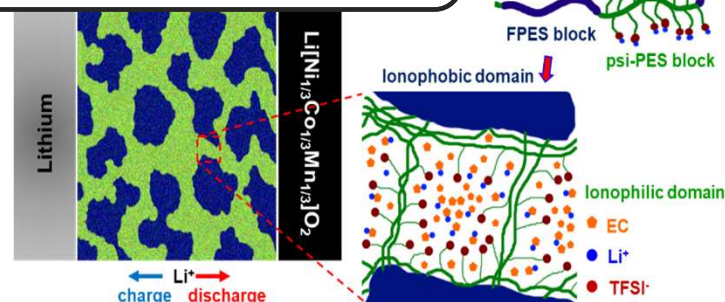
Li⁺ conducting polymer electrolyte for Li-ion batteries



How do the transport properties relate to the nanostructure and chemical architecture ??

IEC series					
In2.5/5	2.500	5.000			
In5/5	5.000	5.000			
In7.5/5	7.500	5.000	1.56	In15/15	15.000
					15.000
					1.32

- L. Assumma, H.-D. Nguyen et al., *J. Polym. Sci. Part A Polym. Chem.* **53** (2015) 1941–1956
 O. Danyliv et al, *Macromolecules*, **49** (11), pp 4164–4177 (2016)
 H.-D. Nguyen et al, *ACS Appl. Mater. Interfaces* 2017, **9** (2), 1671–1683.
 HD. N'guyen et al, *ACS Applied Energy Materials* 2018, **1** (2), pp 355–367
 HD. N'guyen et al, *ChemSusChem* 2020 Feb 7;13(3):590-600.

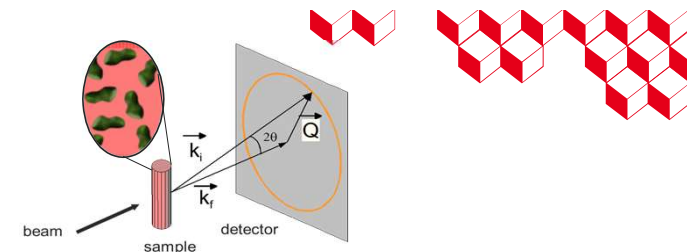
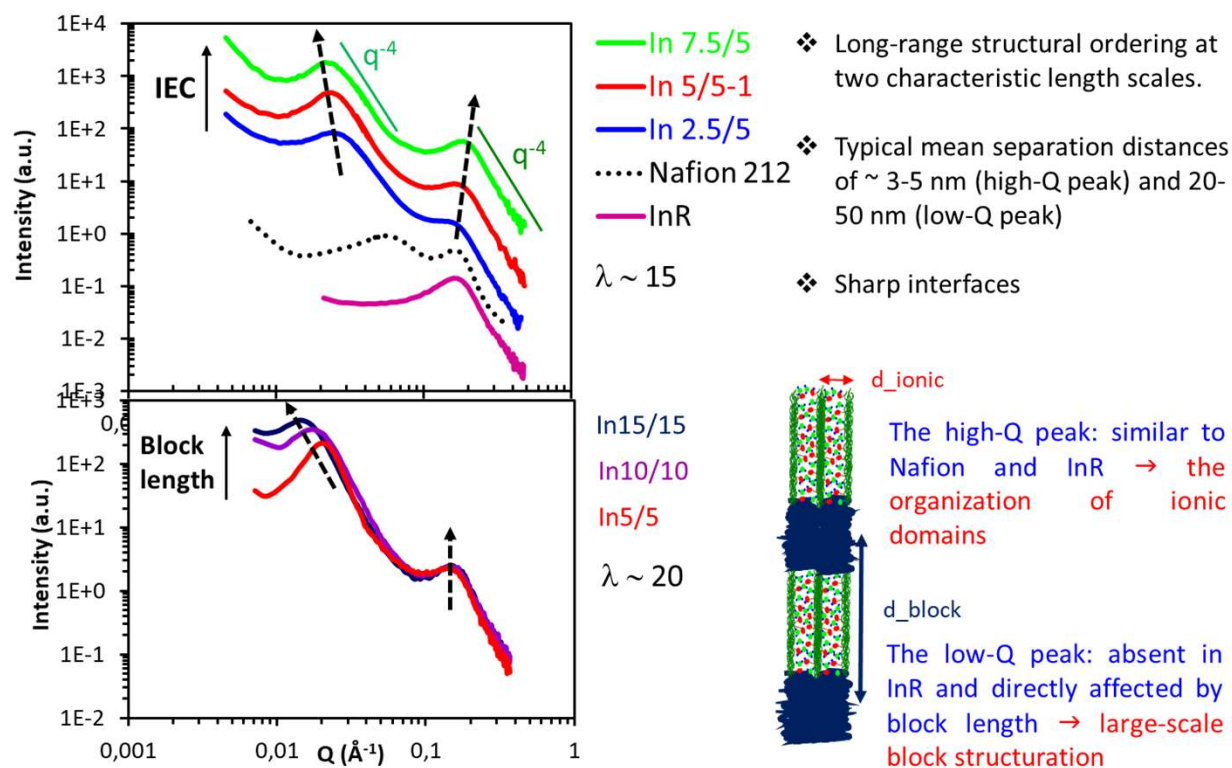


- Nguyen, H-D et al. *Energy & Environmental Science*, 2018, **11**, 3298-3309.
 A. Mayer et al, *ACS Macro Letters*, 2022, **11**(8), 982-990

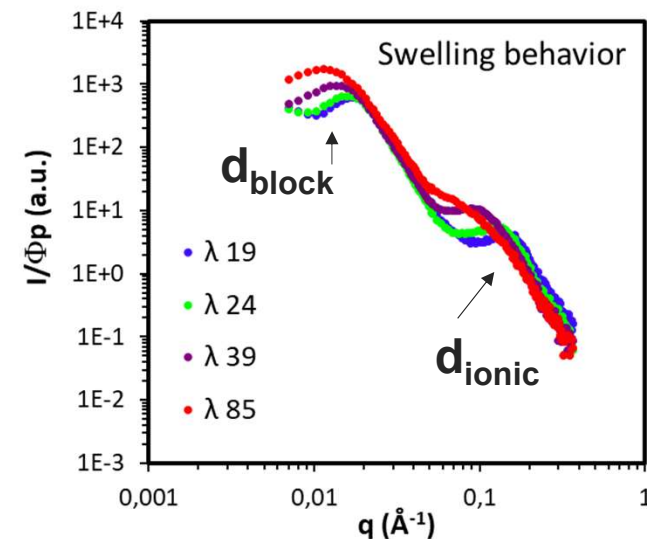
#1 Nanostructure of block copolymer membranes

Microstructure by SANS

Effect of chemical design on nanostructure



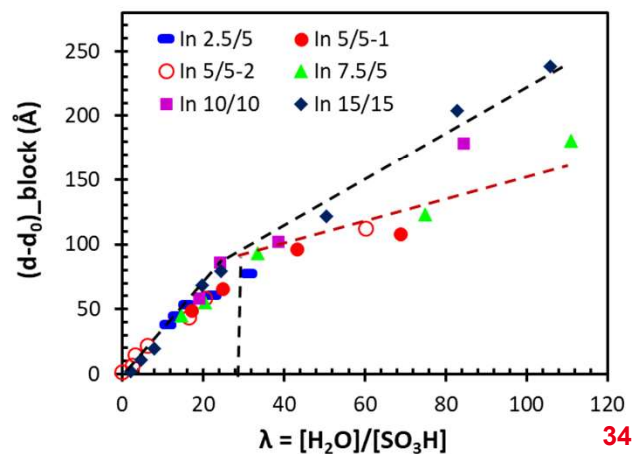
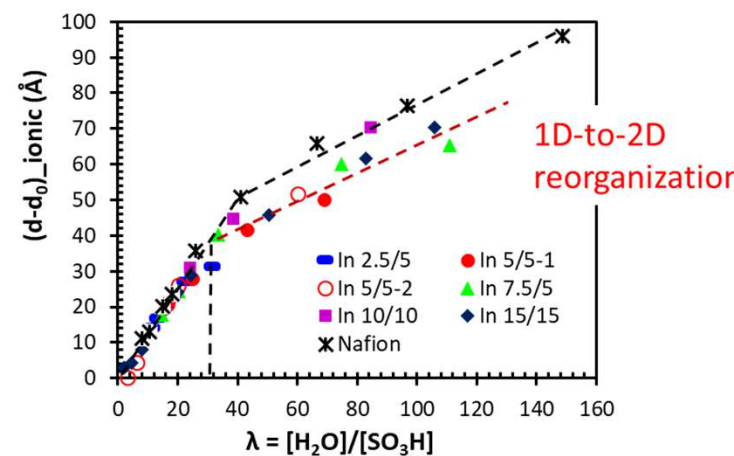
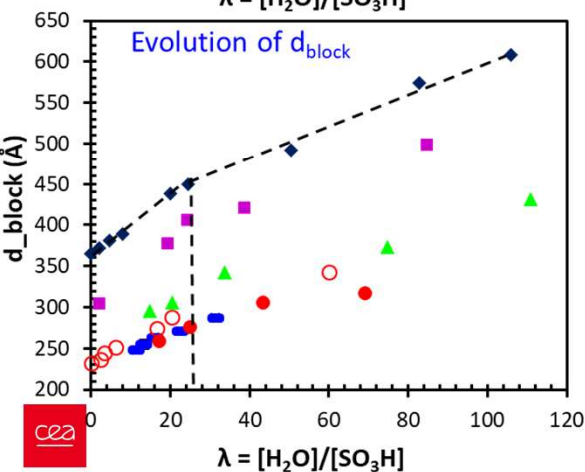
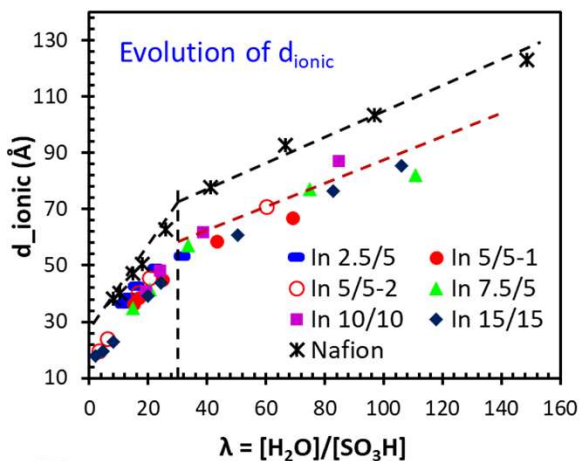
Effect of water content





#1 Nanostructure of block copolymer membranes

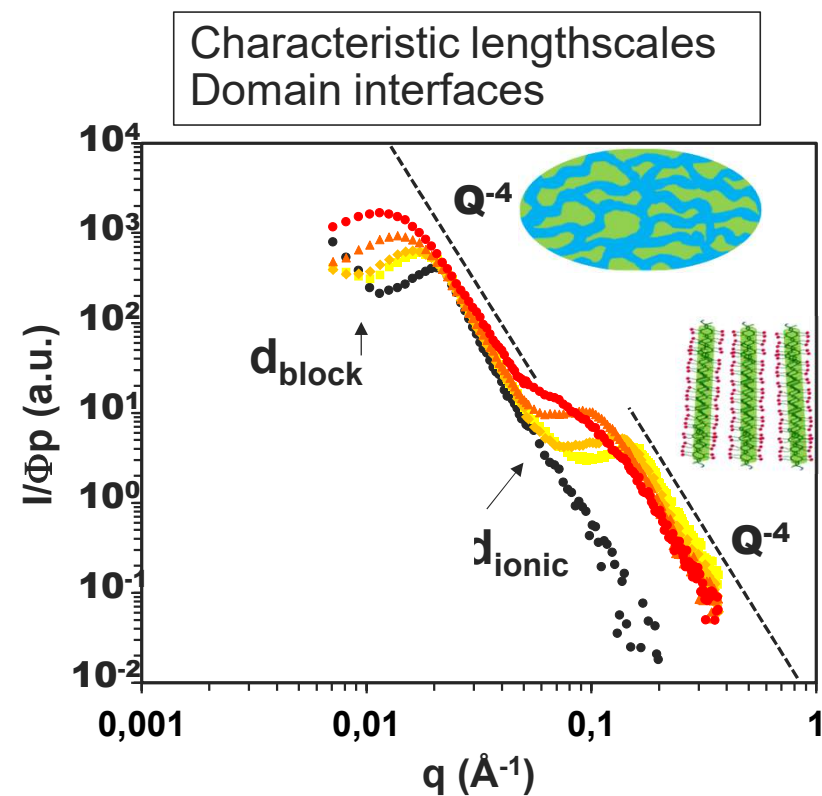
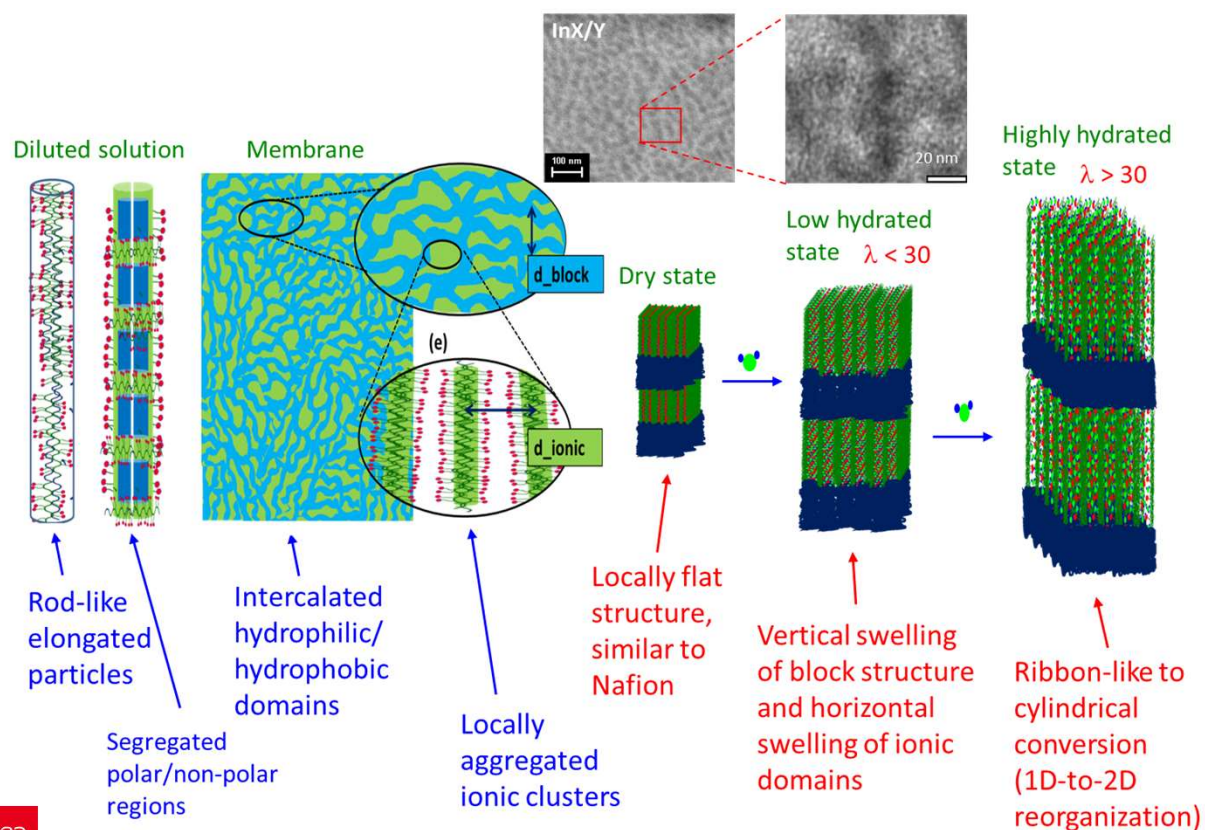
Microstructure by SANS





#1 Nanostructure of block copolymer membranes

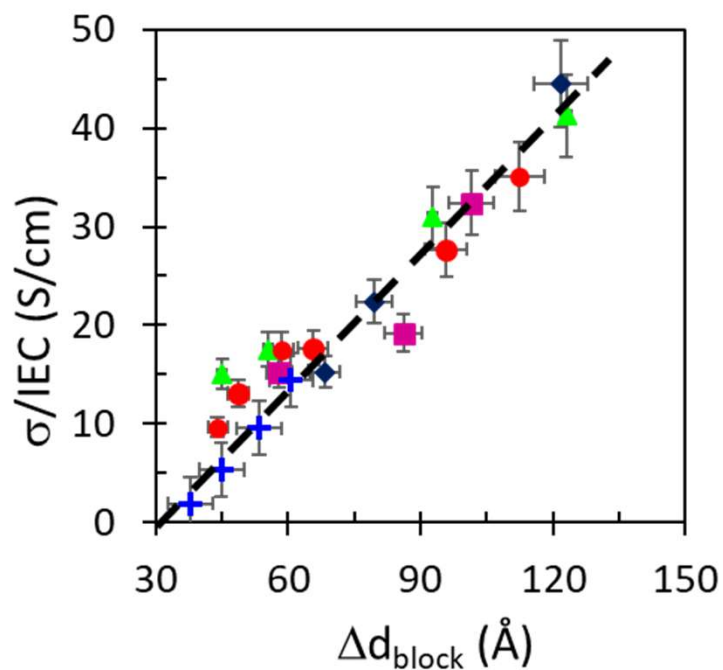
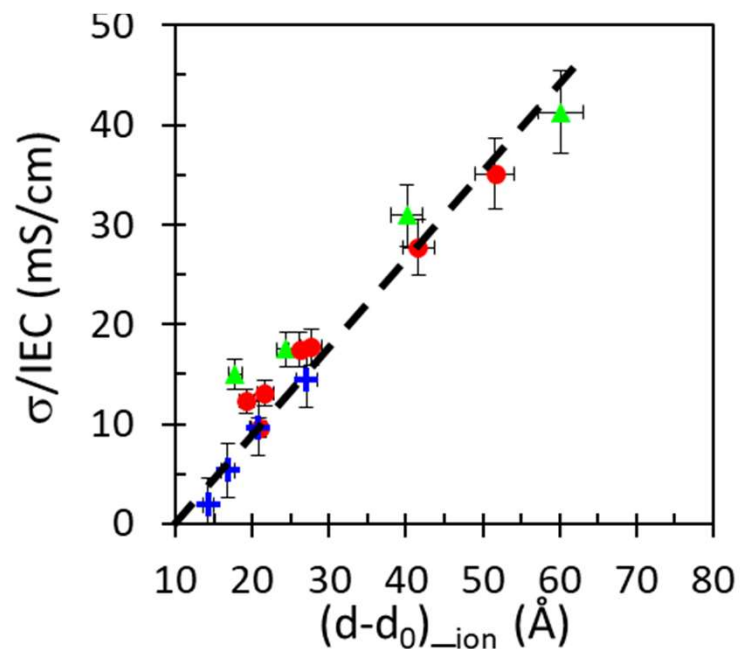
SANS allowed to « picture » the complex multi-scale structure of these materials ! (but many samples were needed to vary parameters and obtain the key features)





#1 Nanostructure of block copolymer membranes

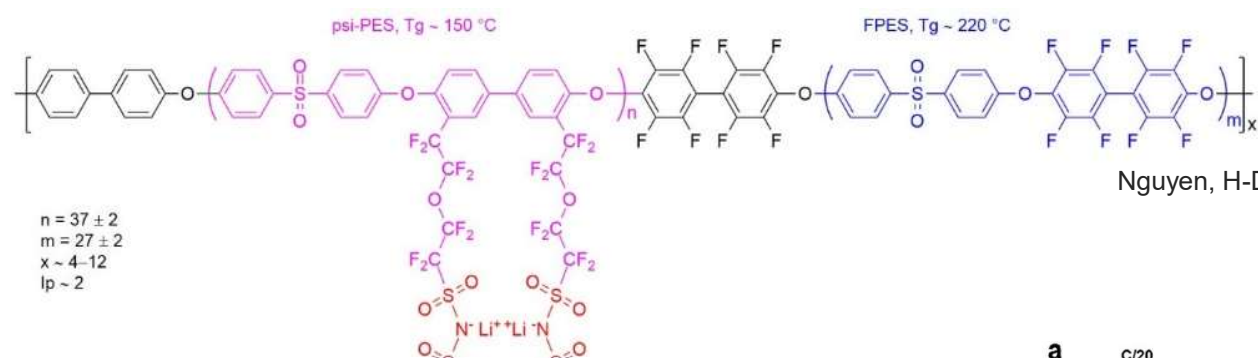
We could correlate the nanostructure (characteristic distance extracted by SAXS/SANS using $d=2\pi/Q$) to the transport properties (ionic conductivity) and extract « universal laws » that can be used to guide materials design.





#1 Nanostructure of block copolymer membranes

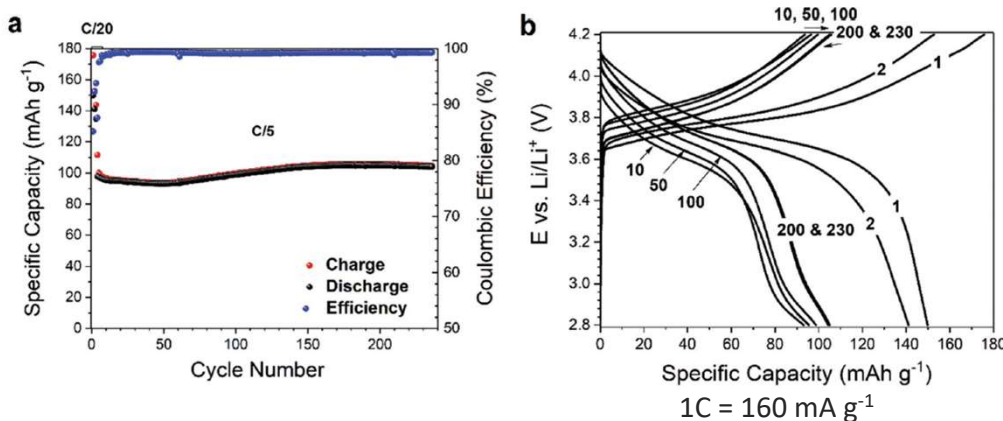
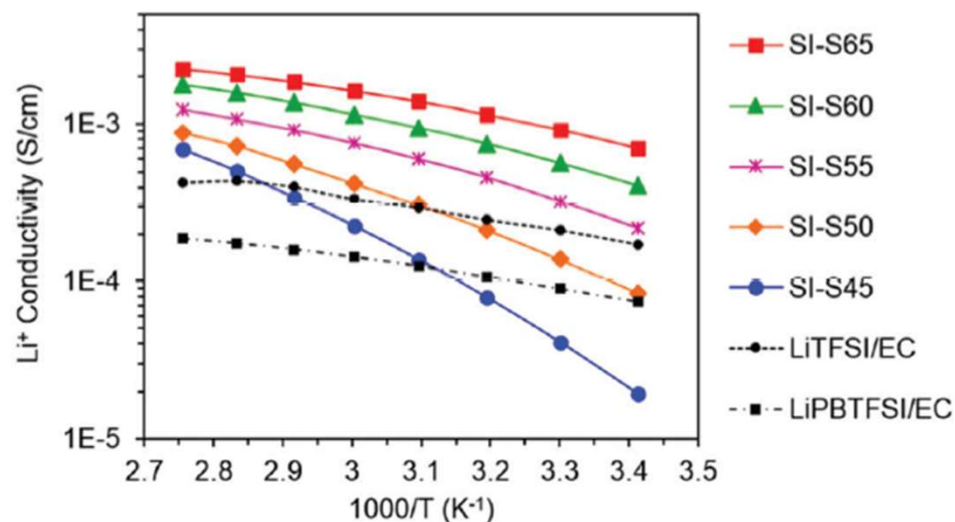
The Li⁺ conducting single-ion polymer



Single-ion Multi-block copoly(arylene sulfone) + Ethylene Carbonate (wt% from 45 to 65)

Nguyen, H-D et al. *Energy & Environmental Science*, 2018, 11, 3298-3309.

SI-S55 in Li/NCM cells at 40°C



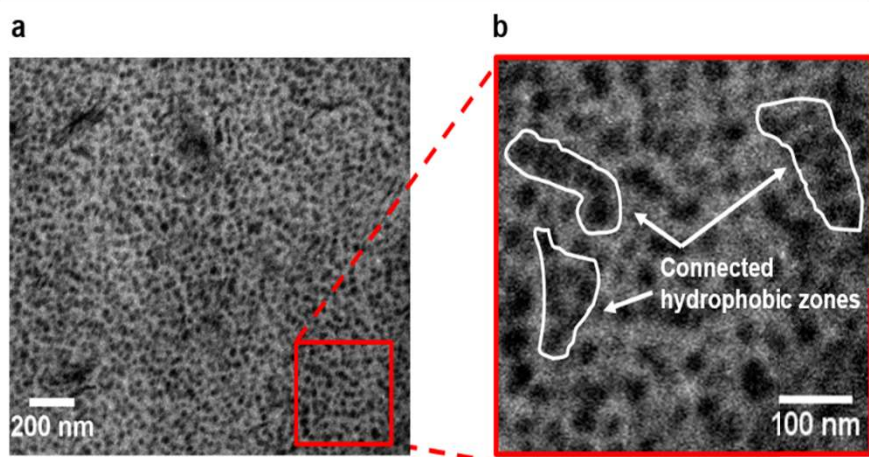
Excellent single-ion conductivity and cycling stability for high-energy Lithium/Li[Ni_{1/3}Co_{1/3}Mn_{1/3}]O₂ batteries.



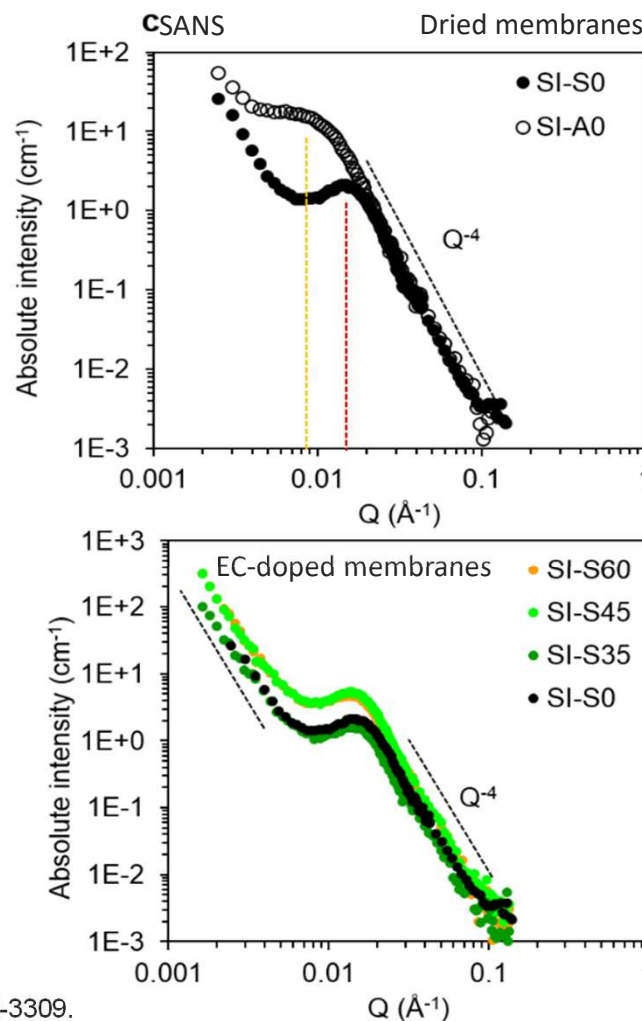
#1 Nanostructure of block copolymer membranes

The Li⁺ conducting single-ion polymer

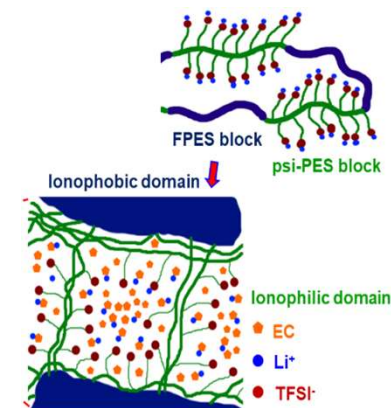
Self-assembling, nanophase-separated morphology



FE-SEM of dry membrane showing hydrophilic (white) and hydrophobic (black) domains

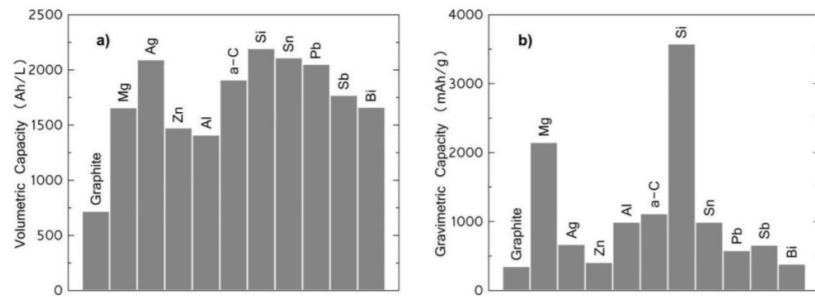


Homogeneously dispersed rigid hydrophobic nano-domains of about 20–40 nm in size, embedded in and chemically bonded to the EC plasticized ionophilic domains



#2 Operando investigation of silicon-based anodes for batteries

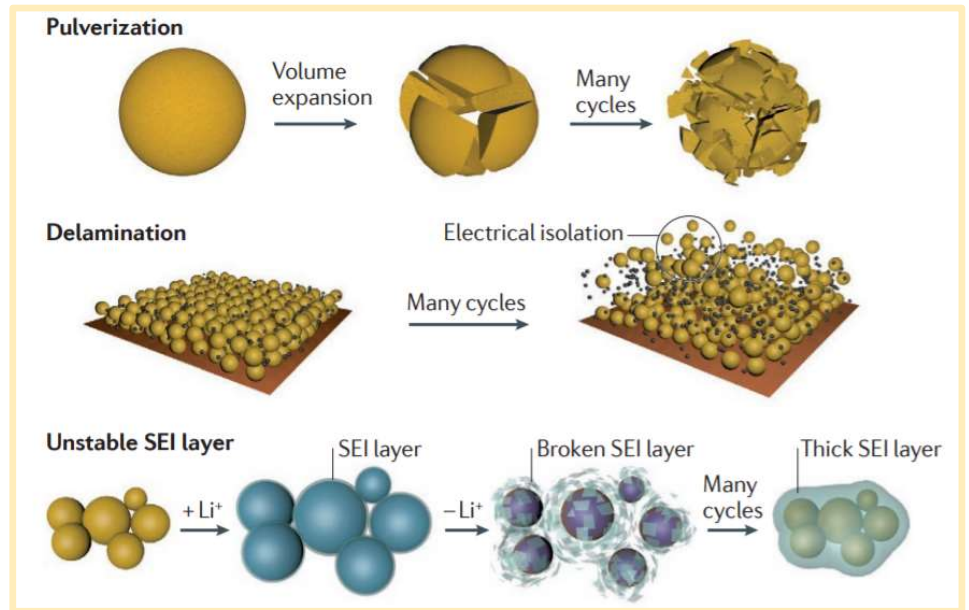
Si = best gravimetric and volumetric capacity



Anode	graphite	silicium
Theoretical specific capacity(mAh/g)	372	3579
Potential vs Li/Li+ (V)	0,1	0,4
Type	Intercalation	Alliage
Lithiated phases	LiC ₆	Li ₁₅ Si ₄

Obrovac, M. N. & Chevrier, V. L. *Chem. Rev.* **114**, 11444–11502 (2014).

**High first-cycle irreversible capacity +
Alloying process: 300% volume expansion**



J. W. Choi, D. Aurbach, *Nature Reviews Materials*. **1**, 1–16 (2016).

- ◇ **Nanoparticles, nanowires, nanostructured materials**
- ◇ **Particles dispersed in a conductive matrix**
- ◇ **Dual-phase composite materials**

#2 Operando investigation of silicon-based anodes for batteries

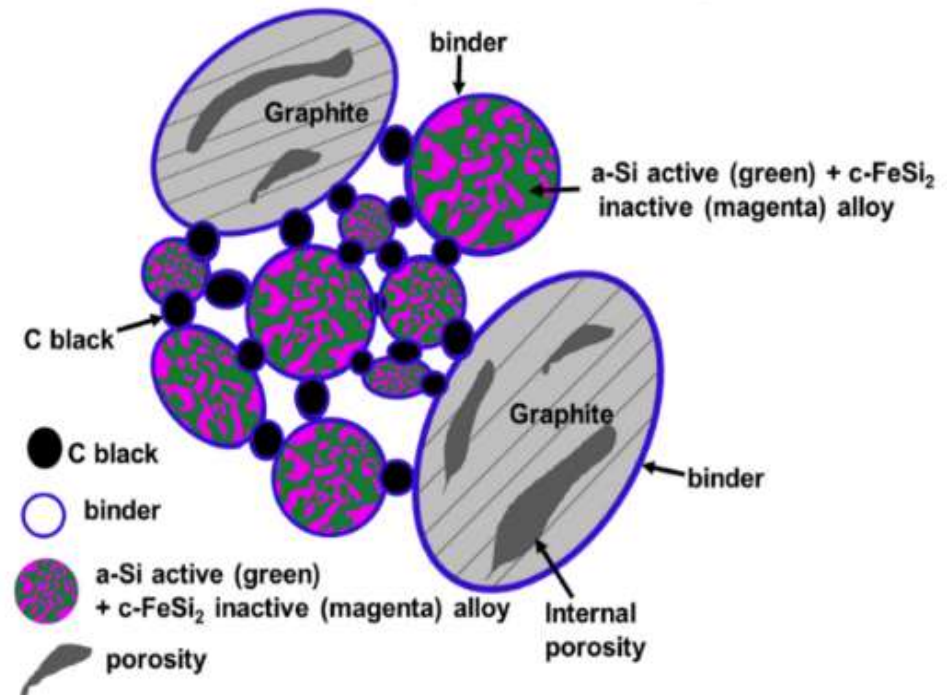
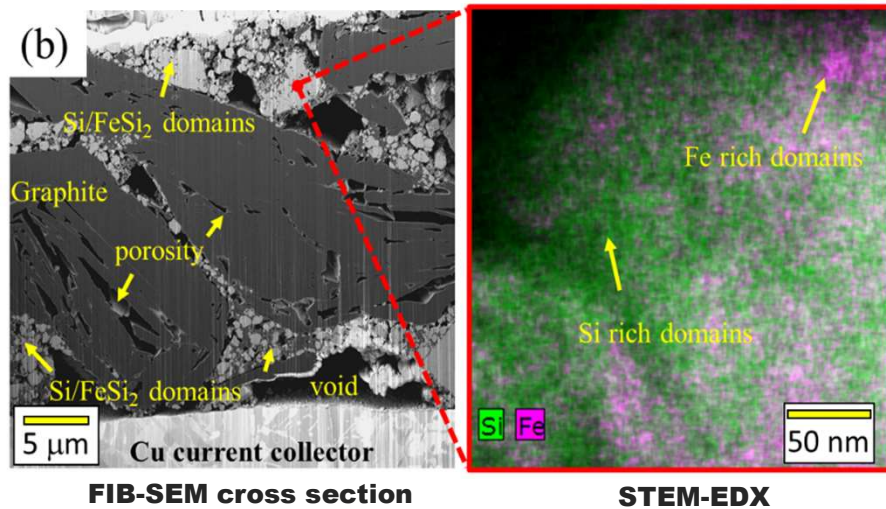
Si-FeSi₂ / Graphite composite anode

◇ 50% L20772, 41% graphite, 7%LiPAA, 2% Super P

L20772 : 20% graphite, 25% a-Si, 55% c-FeSi₂

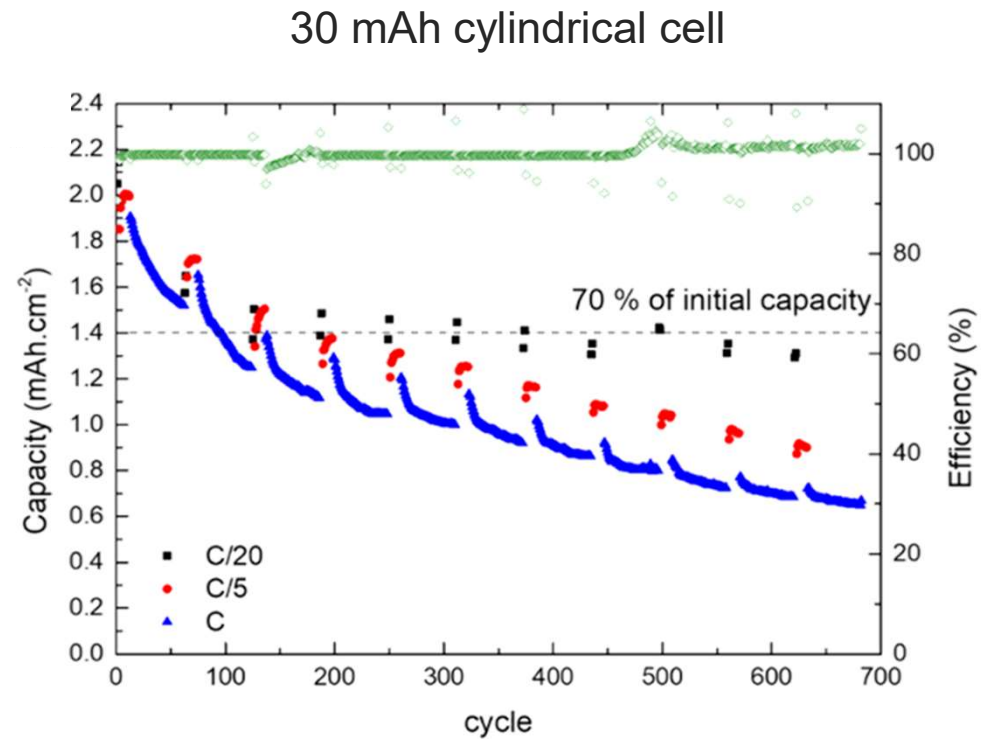
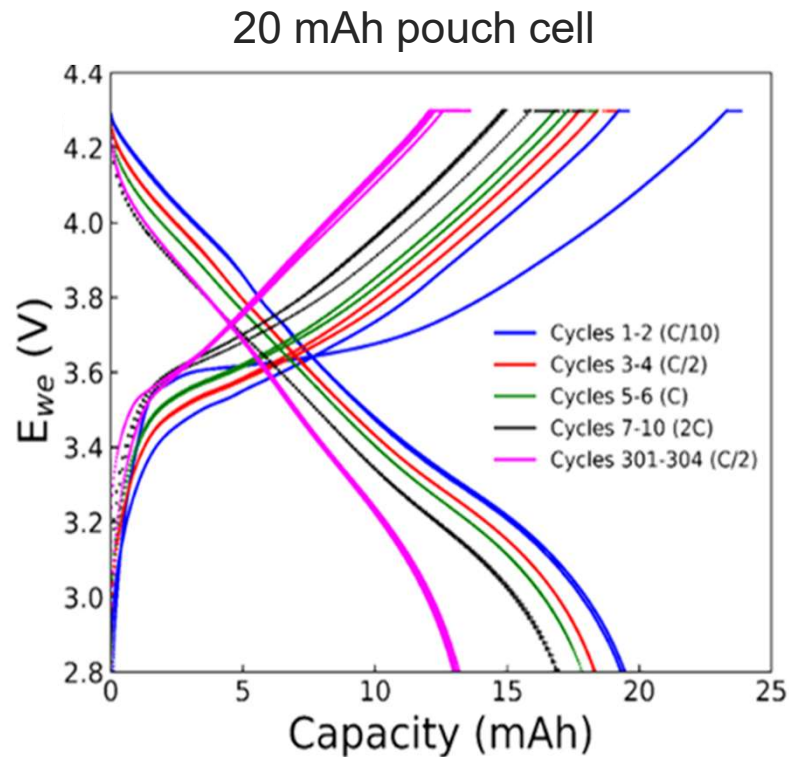
◇ Large graphite chunks (1-50 mm ; Smaller composite a-Si / c-FeSi₂ microparticles (100 nm to 5 mm), which are nanostructured

◇ c-FeSi₂ is a ductile, conductive and close to inactive phase



#2 Operando investigation of silicon-based anodes for batteries

Loss of capacity in full cells (against NMC)

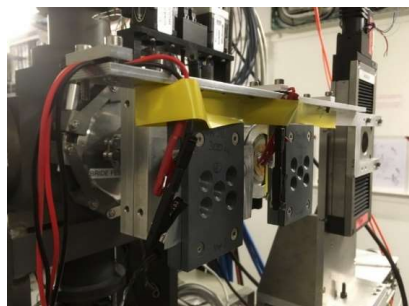


#2 Operando investigation of silicon-based anodes for batteries

1D - SAXS

◇ 20 mAh pouch cells using a-Si/c-FeSi₂/Gr / NMC622 (loading 2.4 and 2 mAh. cm⁻²)

Lithiation & Aging Mechanism



ACS NANO

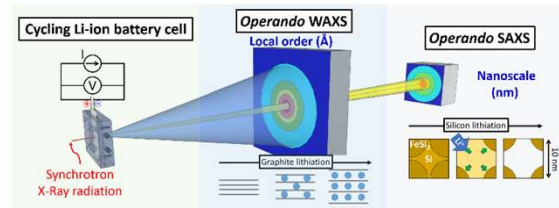
Cite This: ACS Nano 2019, 13, 11538–11551

www.acsnano.org

Multiscale Multiphase Lithiation and Delithiation Mechanisms in a Composite Electrode Unraveled by Simultaneous Operando Small-Angle and Wide-Angle X-Ray Scattering

Christopher L. Berhaut,^{*,1} Diana Zapata Dominguez,² Praveen Kumar,³ Pierre-Henri Jouneau,² Willy Porcher,³ David Aradilla,^{1,4} Samuel Tardif,^{5,6} Stéphanie Pouget,^{*,2} and Sandrine Lyonnard^{*,1,6}

ARTICLE



2D scanning μ SAXS

◇ Swagelok cells (half-cell against Li) using a-Si/c-FeSi₂/Gr / NMC622

Loading 2.4 mAh.cm⁻²

Depth-resolved charge dynamics

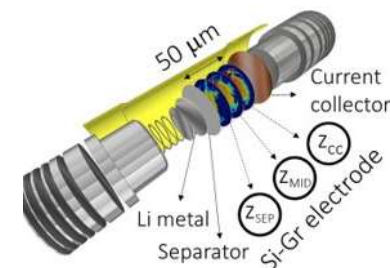


RESEARCH ARTICLE

ADVANCED ENERGY MATERIALS
www.advenergymat.de

Charge Dynamics Induced by Lithiation Heterogeneity in Silicon-Graphite Composite Anodes

Christopher L. Berhaut, Marta Mirolo, Diana Zapata Dominguez, Isaac Martens, Stéphanie Pouget, Nathalie Herlin-Boime, Marion Chandesris, Samuel Tardif, Jakub Drnec,^{*} and Sandrine Lyonnard^{*}



3D SAXS-CT

◇ 30 mAh industry-grade cylindrical cells

3D heterogeneities and defects



Energy & Environmental Science

ROYAL SOCIETY OF CHEMISTRY

PAPER

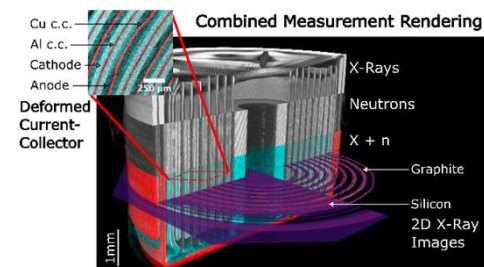
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The origins of critical deformations in cylindrical silicon based Li-ion batteries†

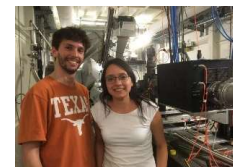
Cite this: DOI: 10.1039/d4ee00590b

Erik Lübke,^{*,a} Lukas Helfen,^{*,a} Phil Cook,^b Marta Mirolo,^b Valentin Vinci,^b Ove Korjus,^{*,c} Bernd Fuchsichler,^d Stefan Koller,^d Roland Brunner,^{*,e} Jakub Drnec,^{*,b} and Sandrine Lyonnard^{*,c}

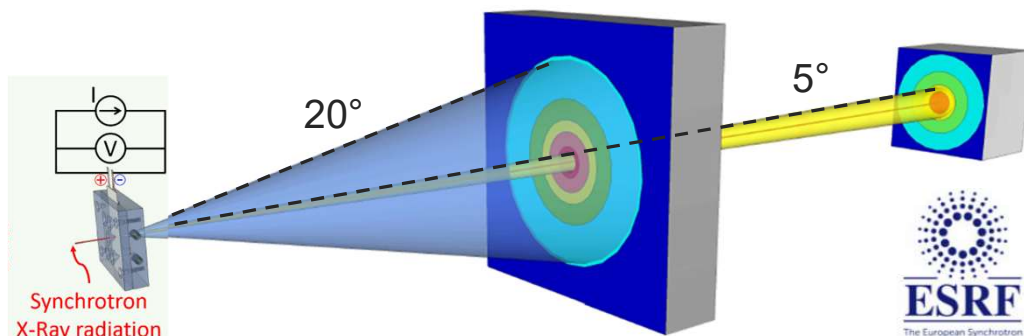


#2 Operando investigation of silicon-based anodes for batteries

Reaction & degradation mechanisms in pouch cells

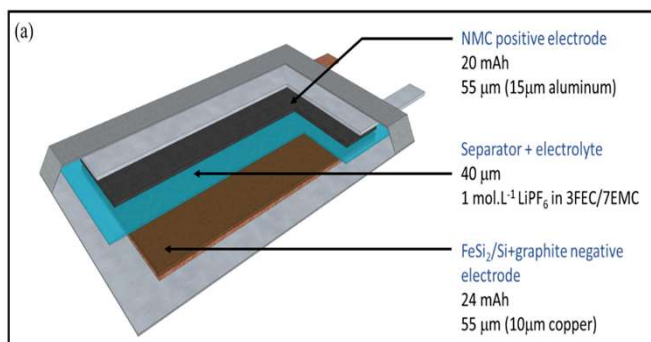


Christopher Berhaut
Diana Zapata-domínguez

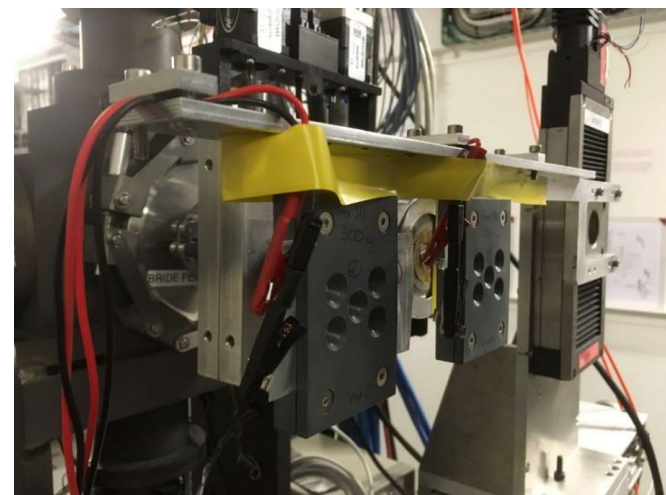
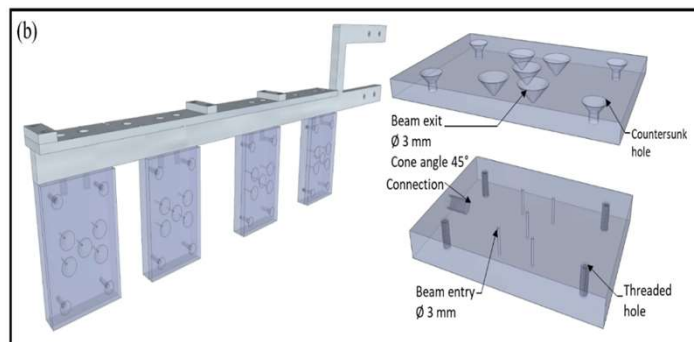


French Beamline BM02 @ ESRF
A unique combined WAXS/SAXS set-up

Cycling in full cell (pouch geometry)

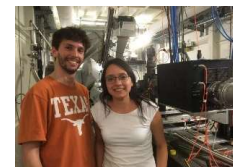


Operando experiments on several cells simultaneously (pristine and aged)

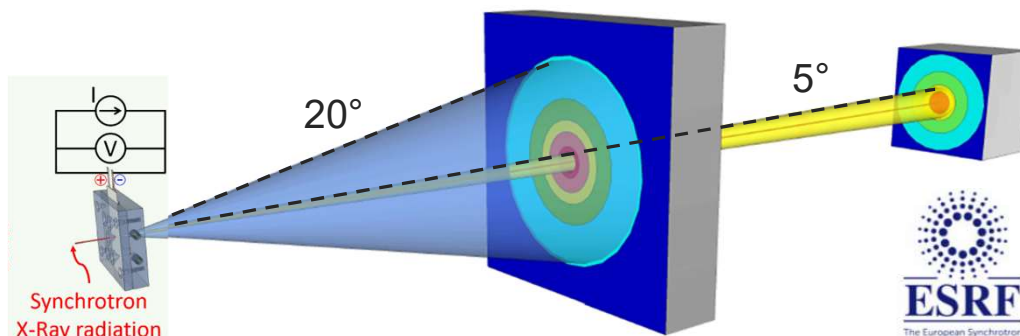


#2 Operando investigation of silicon-based anodes for batteries

Reaction & degradation mechanisms in pouch cells

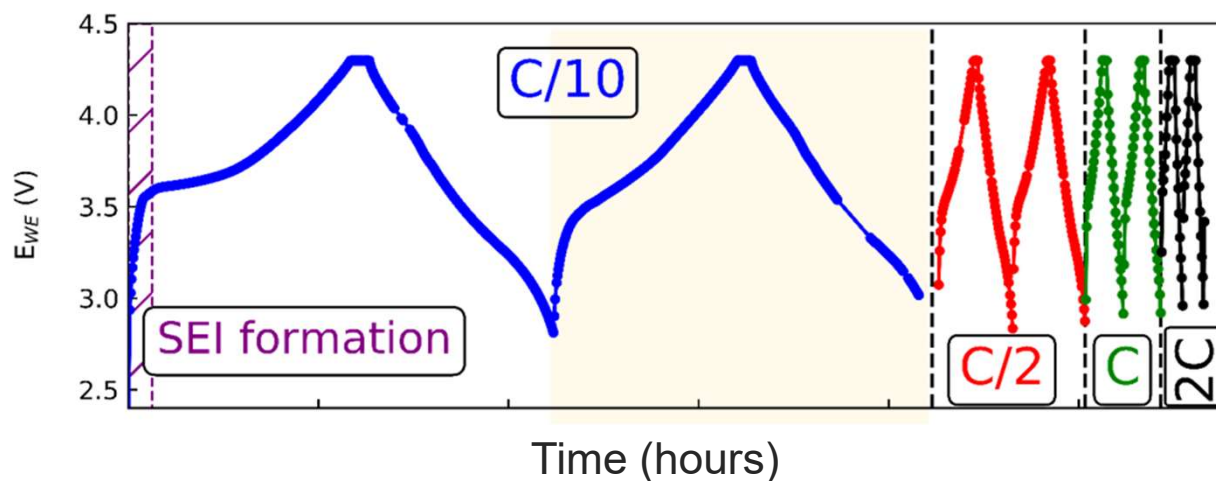


Christopher Berhaut
Diana Zapata-domínguez



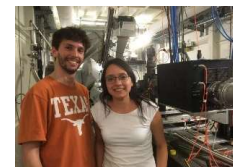
French Beamline BM02 @ ESRF
A unique combined WAXS/SAXS set-up

Several cycles at
different C-rates in fresh
and aged cells

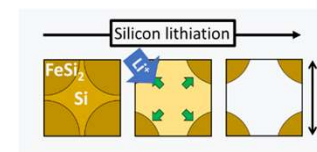
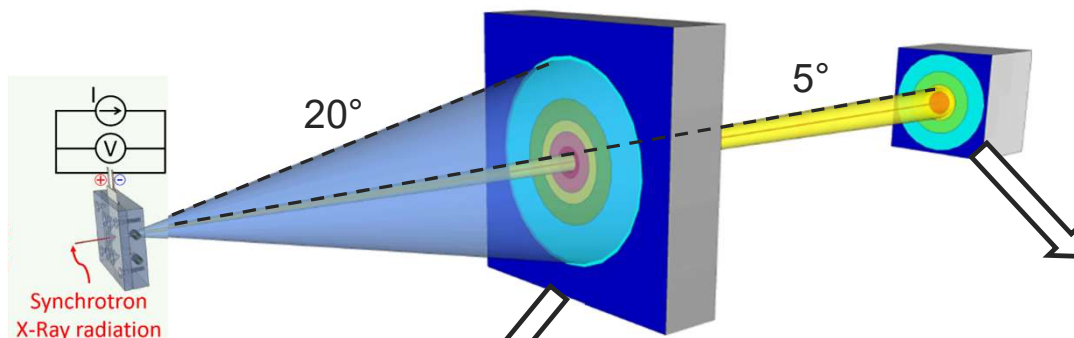


#2 Operando investigation of silicon-based anodes for batteries

Reaction & degradation mechanisms in pouch cells

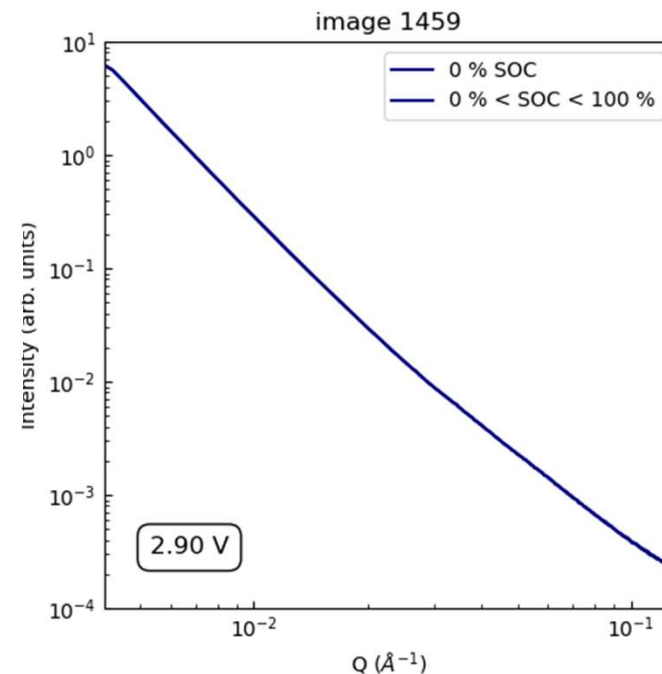
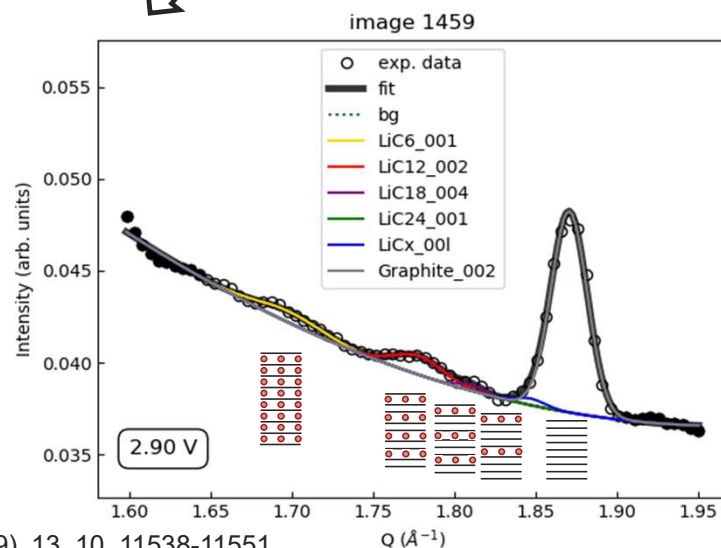
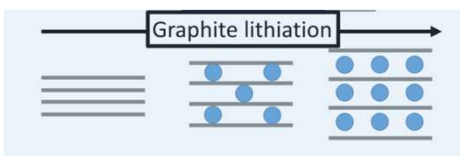


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Diana Zapata-domínguez



SAXS
Nanoscale - Silicon

WAXS
Atomic scale -
Graphite



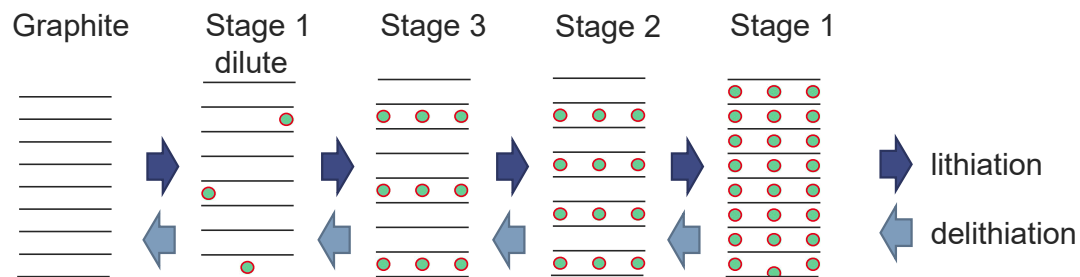
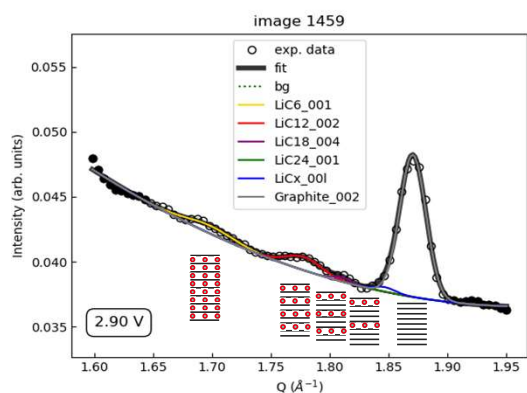
C. Berhaut *et al*, ACS Nano (2019), 13, 10, 11538-11551

#2 Operando investigation of silicon-based anodes for batteries

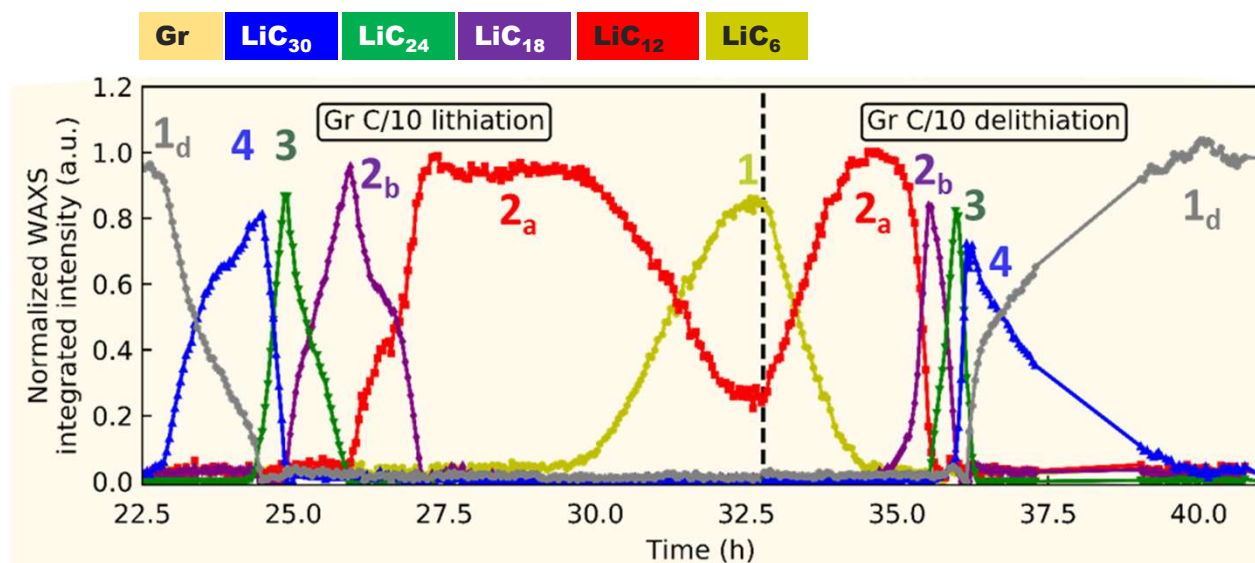
Reaction & degradation mechanisms in pouch cells

WAXS data analysis

Real-time diffraction peaks



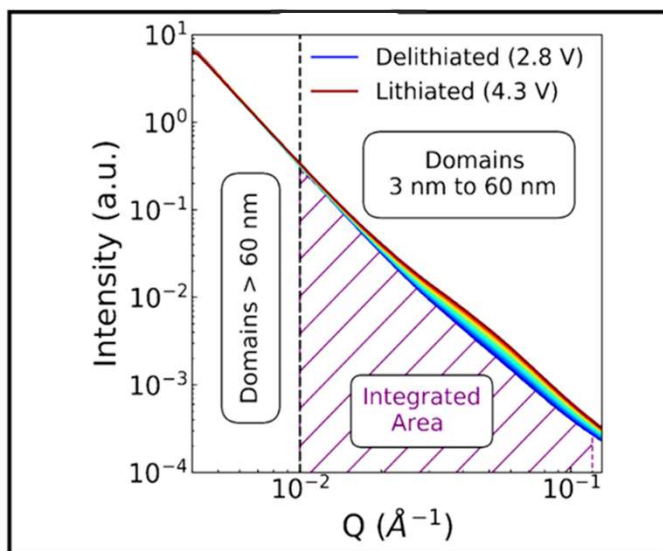
Lithiated phases Li_xC_6



#2 Operando investigation of silicon-based anodes for batteries

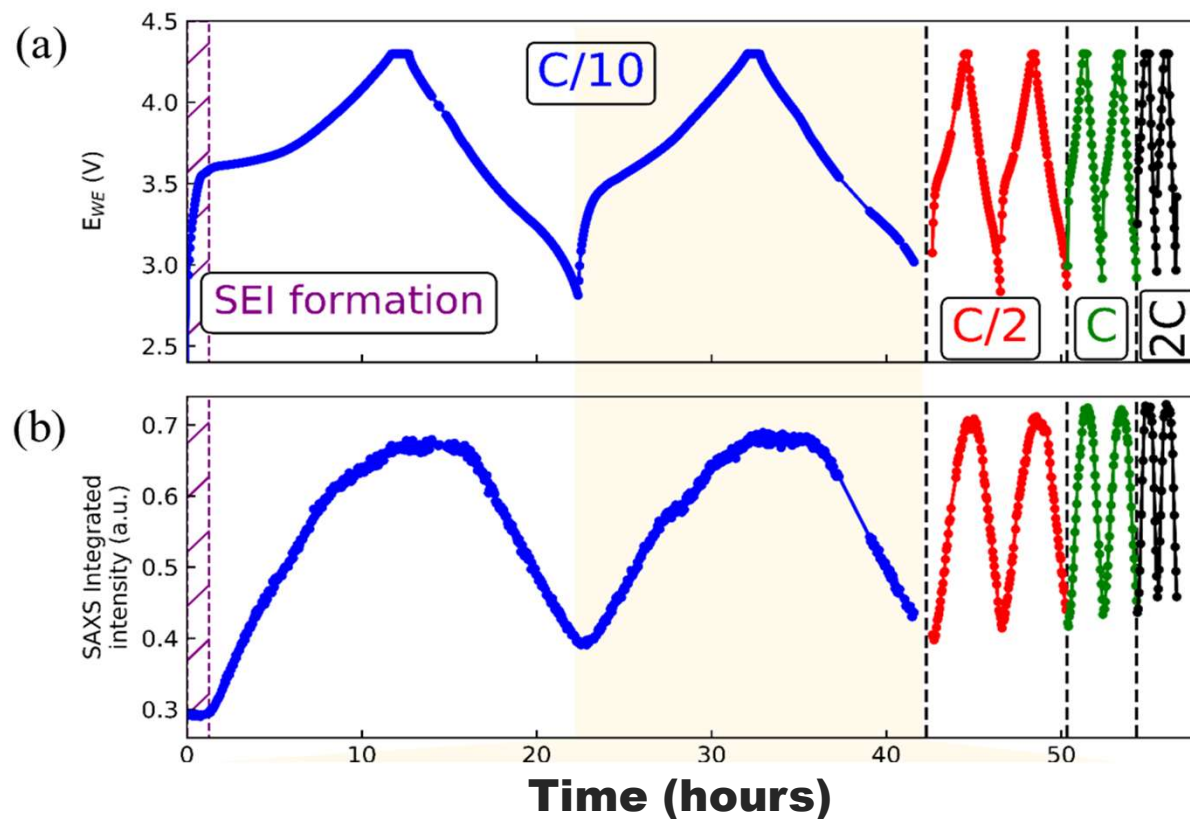
Reaction & degradation mechanisms in pouch cells

SAXS data analysis



Electrochemistry

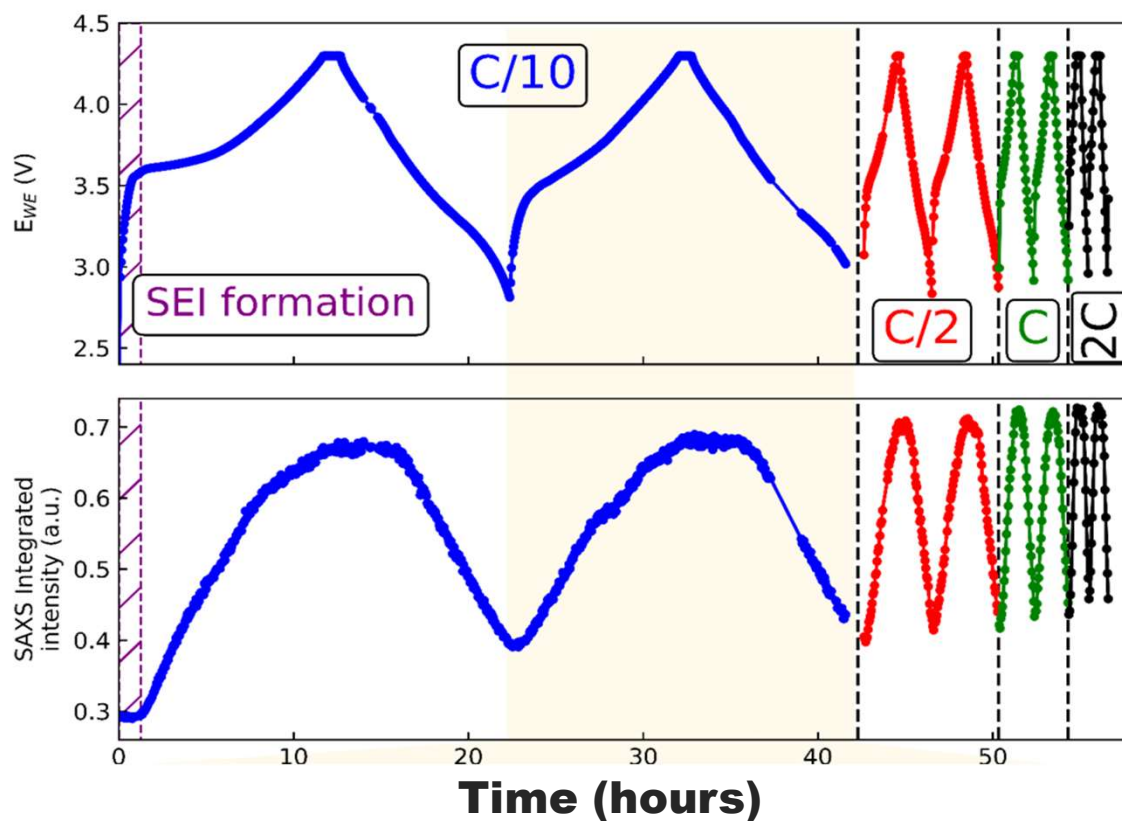
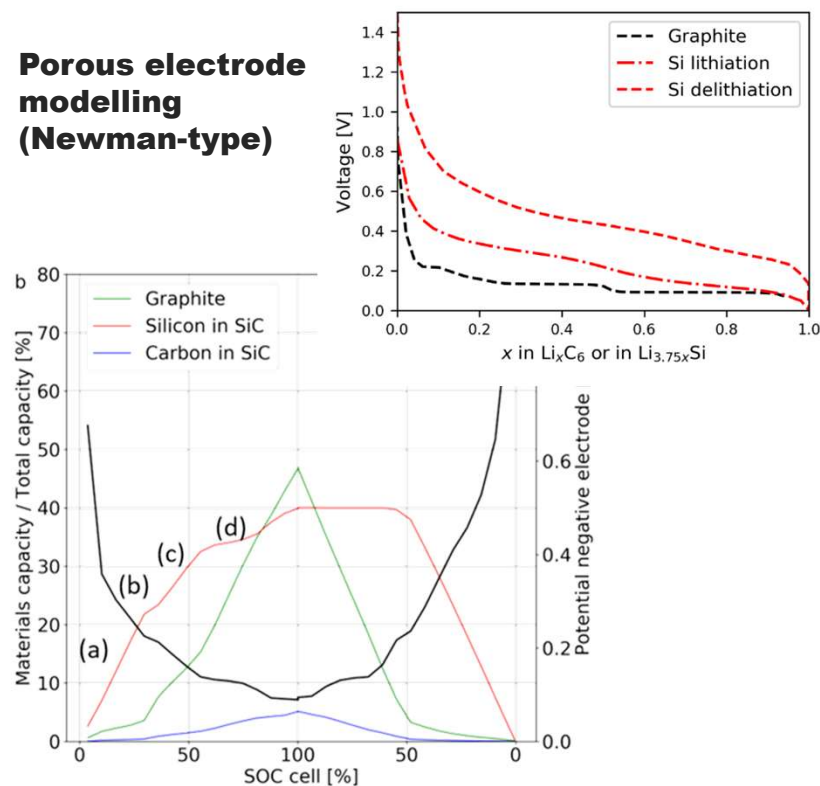
SAXS



#2 Operando investigation of silicon-based anodes for batteries

Reaction & degradation mechanisms in pouch cells

Porous electrode modelling (Newman-type)



P-F Lory *et al* 2020 *J. Electrochem. Soc.* **167** 120506

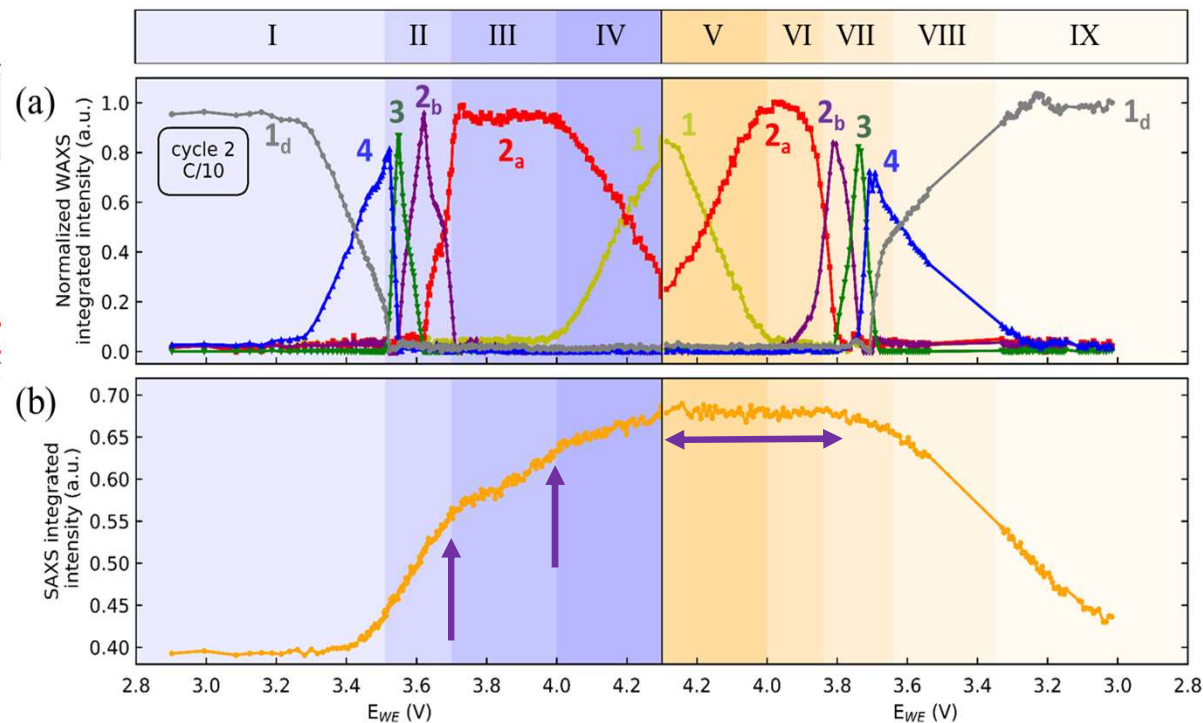
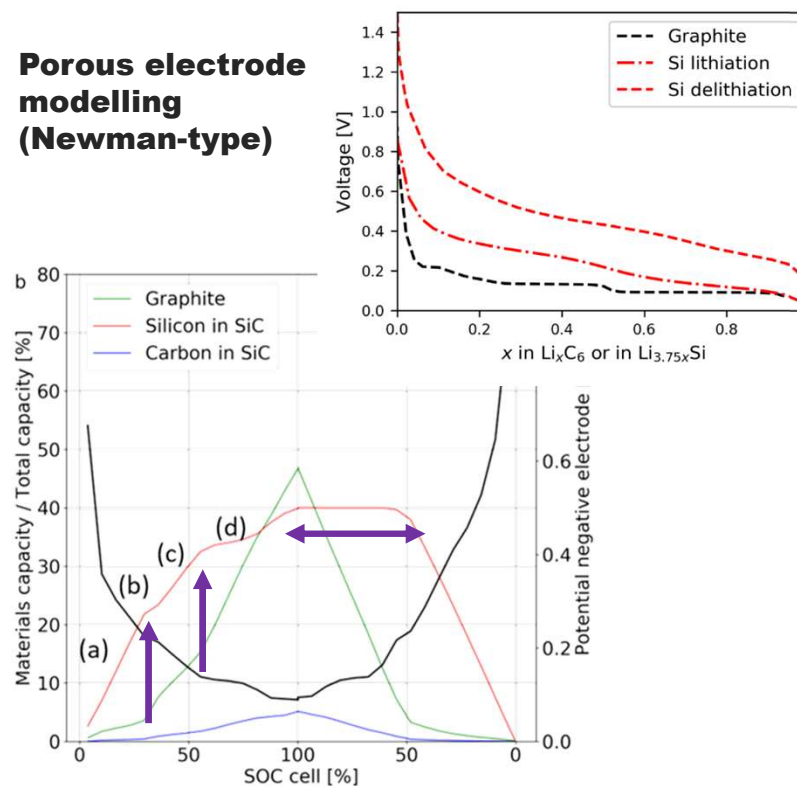


C. Berhaut *et al*, ACS Nano (2019), 13, 10, 11538-11551

#2 Operando investigation of silicon-based anodes for batteries

Reaction & degradation mechanisms in pouch cells

Porous electrode modelling (Newman-type)



SAXS and WAXS data evolutions nicely correlate across the 9 identified regions of sequential (de)lithiation

SAXS data captures the main features of silicon behavior in the composite

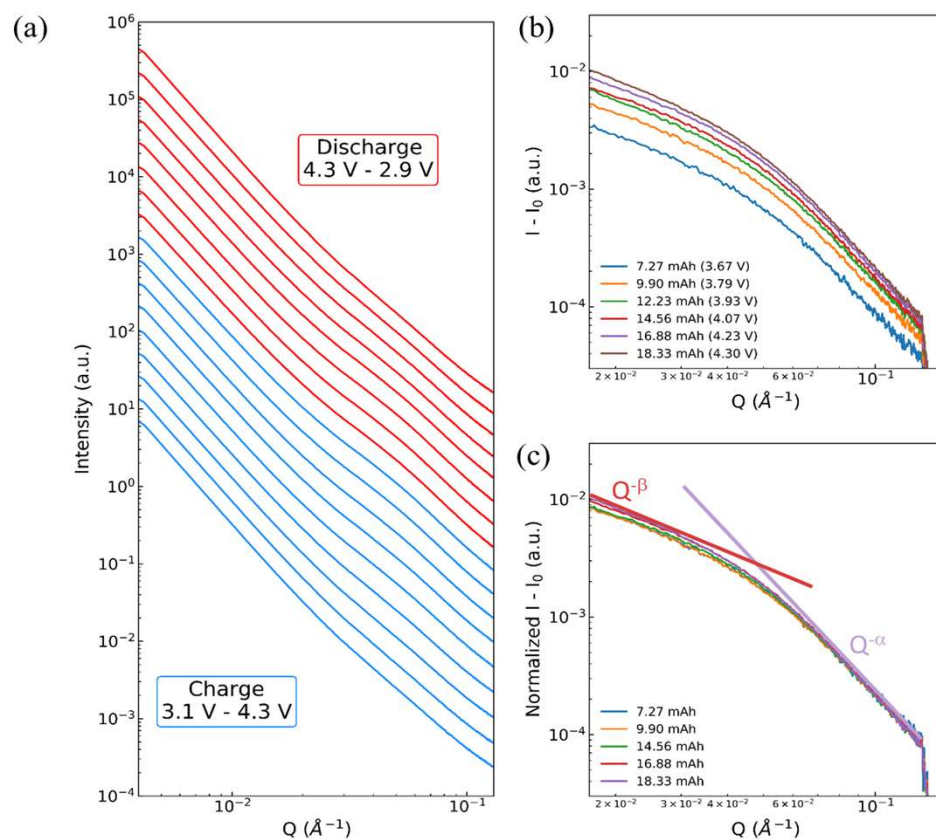
P-F Lory *et al* 2020 *J. Electrochem. Soc.* **167** 120506



C. Berhaut *et al*, *ACS Nano* (2019), 13, 10, 11538-11551

#2 Operando investigation of silicon-based anodes for batteries

Reaction & degradation mechanisms in pouch cells



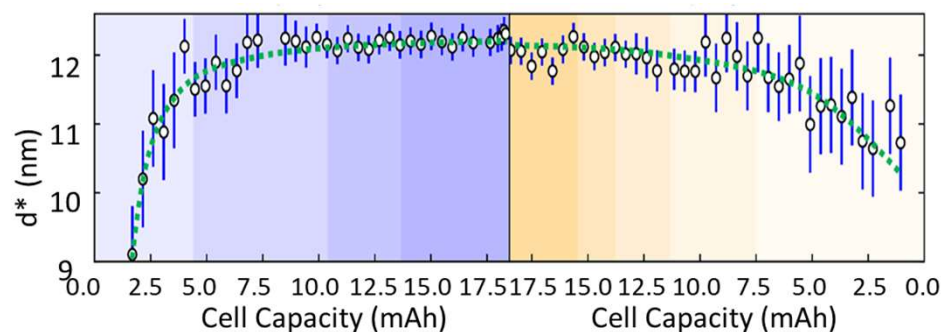
$$I(Q) \propto (\Delta\rho)^2 \times P(Q) \times S(Q)$$

$(\Delta\rho) = (\rho_{\text{LiSi}} - \rho_{\text{medium}})$ Contrast, highly sensitive to Li

$P(Q)$ form factor (size/shape Si domains)

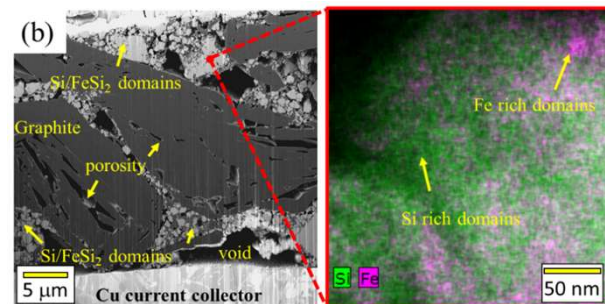
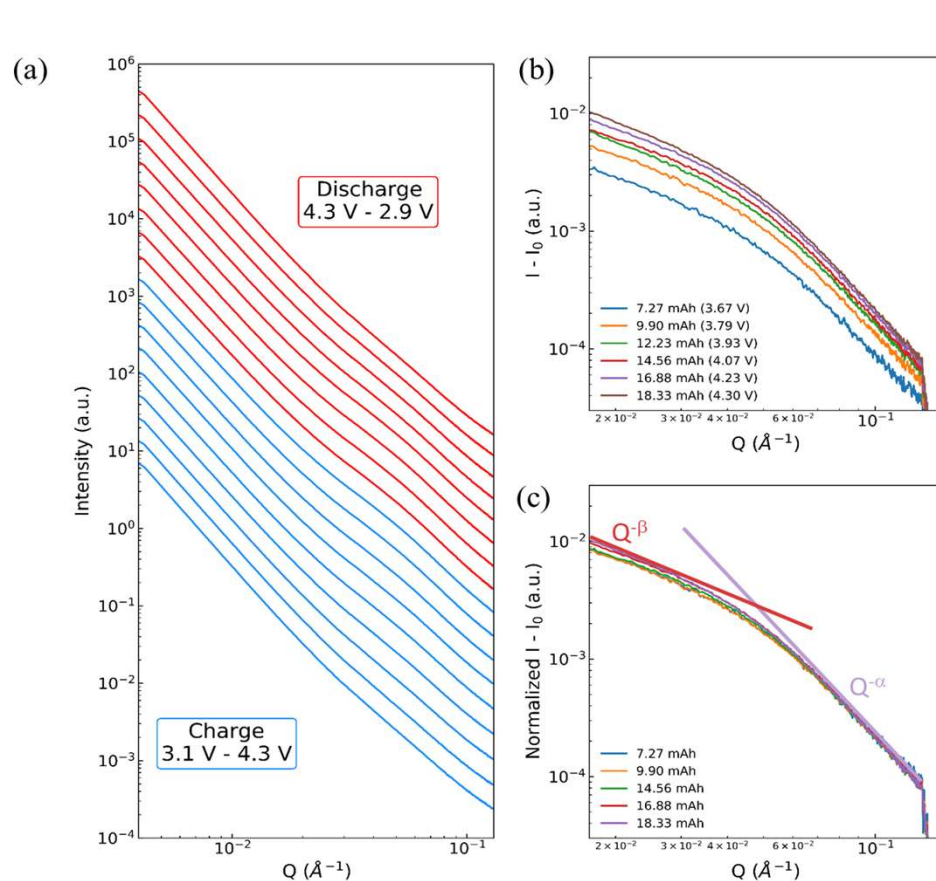
$S(Q)$ structure factor (organization)

$d^* = 2\pi/Q^*$ is a model-free characteristic structural fingerprint of the materials nanoscale organization

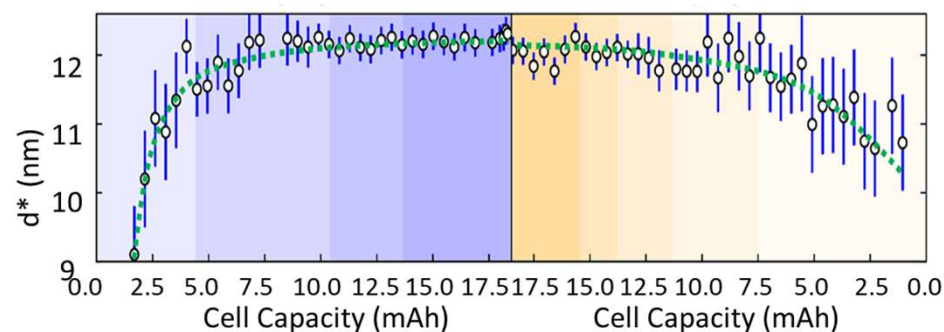


#2 Operando investigation of silicon-based anodes for batteries

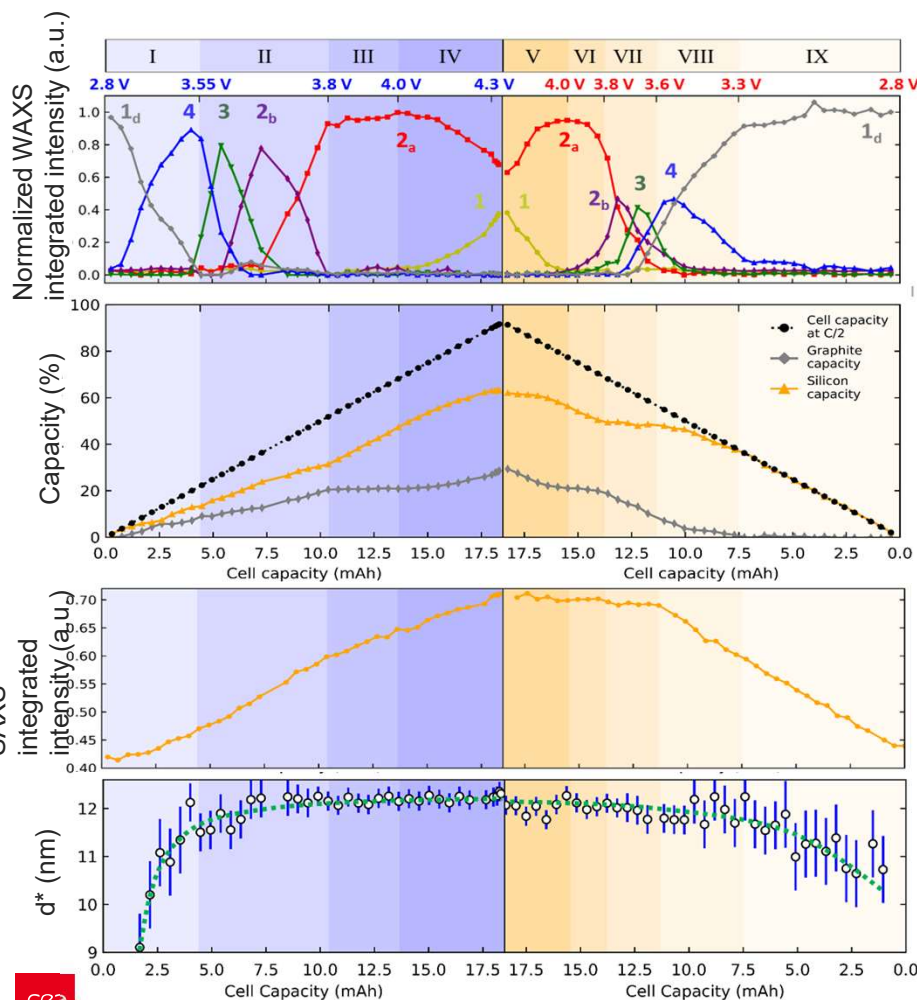
Reaction & degradation mechanisms in pouch cells



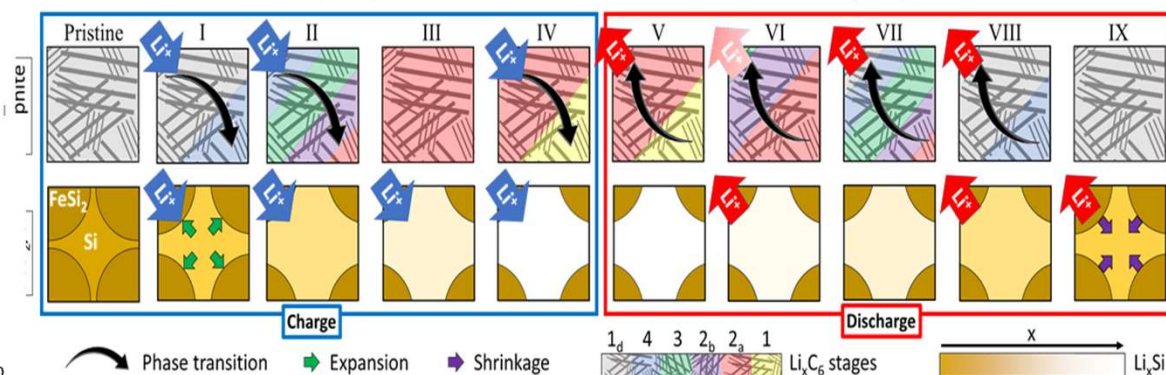
$d^* = 2\pi/Q^*$ is a model-free characteristic structural fingerprint of the materials nanoscale organization



#2 Operando investigation of silicon-based anodes for batteries



**Sequential lithiation of Si-Gr blended anodes
-> the silicon contribution is deduced from Gr**



Silicon phase

1. Intensity variations proportional to the amount of Li incorporated
2. Mean size of Si nanodomains (volume expansion)

#2 Operando investigation of silicon-based anodes for batteries

Can we probe potential 2D / 3D heterogeneities in the electrode ?

Depth-resolved charge dynamics by scanning μ SAXS and SAXS-CT

#2 Operando investigation of silicon-based anodes for batteries

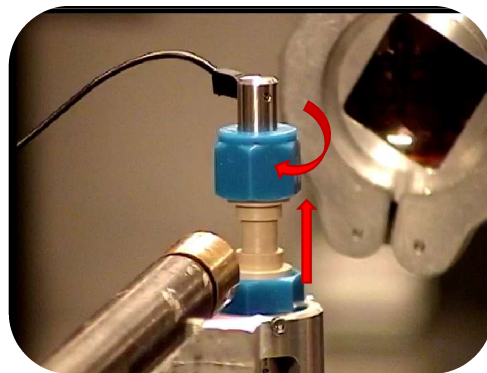
Can we probe potential 2D / 3D heterogeneities in the electrode ?

Depth-resolved charge dynamics by scanning μ SAXS and SAXS-CT

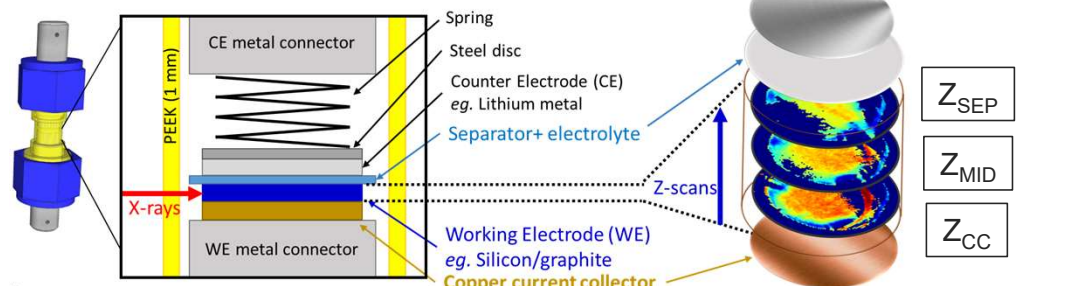


Marta Mirolo
Jakub Drnec
ID31-ESRF

ID31 high energy 70 keV – SAXS/WAXS-CT



Electrode diameter 7 mm
Half-cell configuration



#2 Operando investigation of silicon-based anodes for batteries

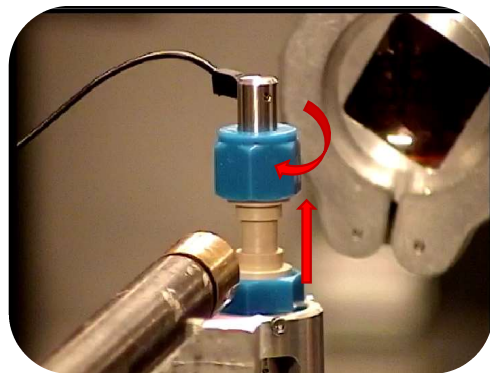
Can we probe potential 2D / 3D heterogeneities in the electrode ?

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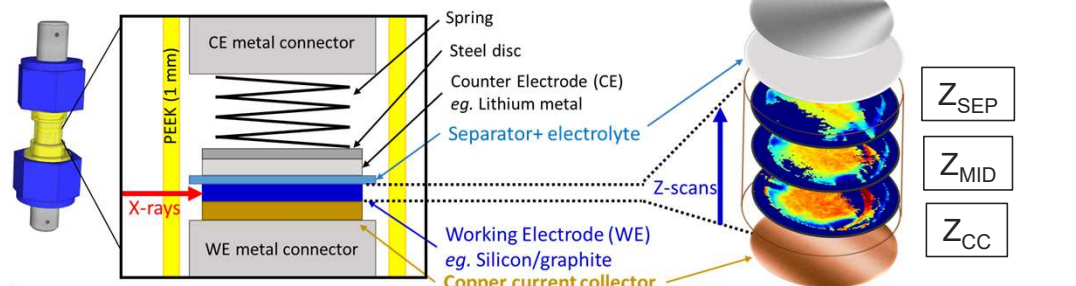
Marta Mirolo
Jakub Drnec
ID31-ESRF

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Electrode diameter 7 mm

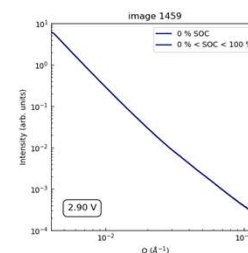
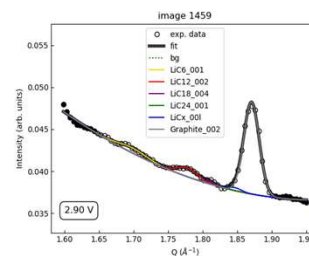
Half-cell configuration



In each pixel :

graphite

WAXS



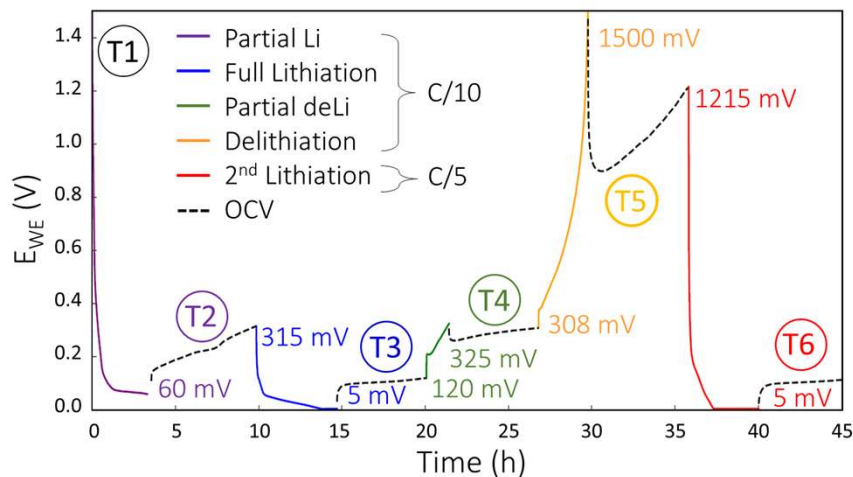
silicon

SAXS

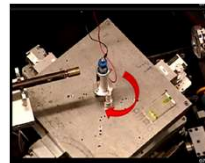
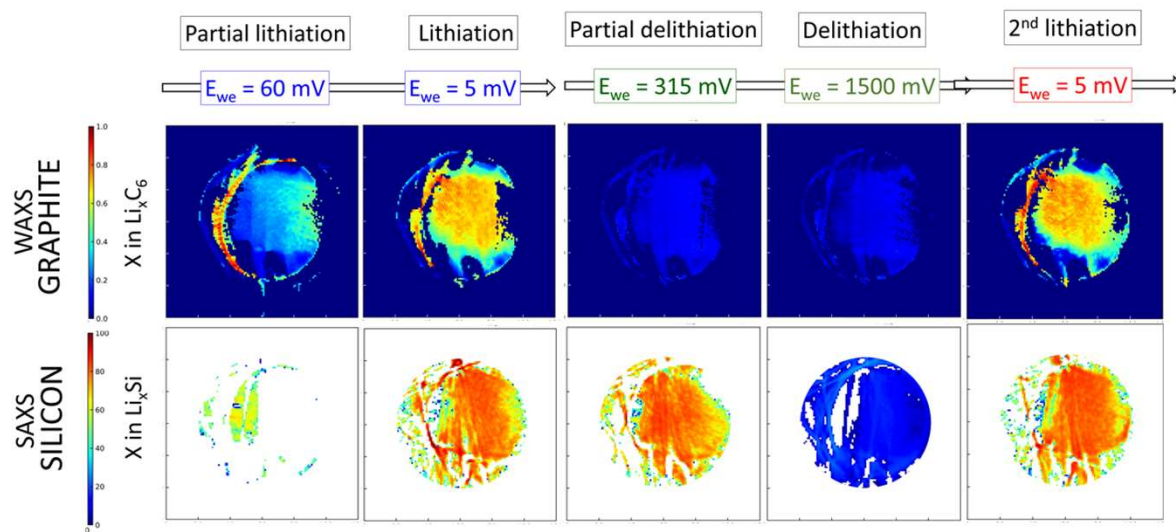
#2 Operando investigation of silicon-based anodes for batteries

Depth-resolved charge dynamics by scanning μ SAXS and SAXS-CT

Cell cycling (C/10, C/5) –silicon-graphite anode



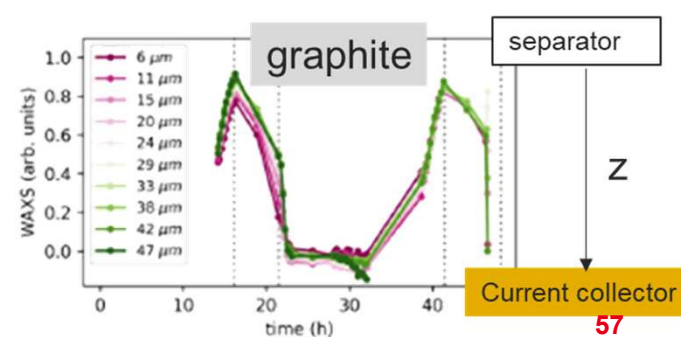
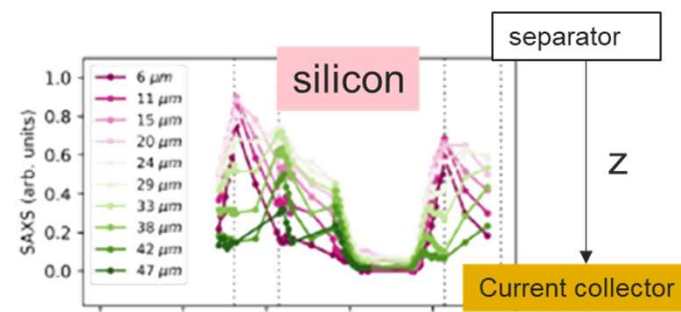
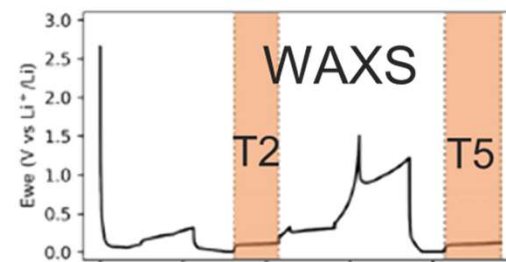
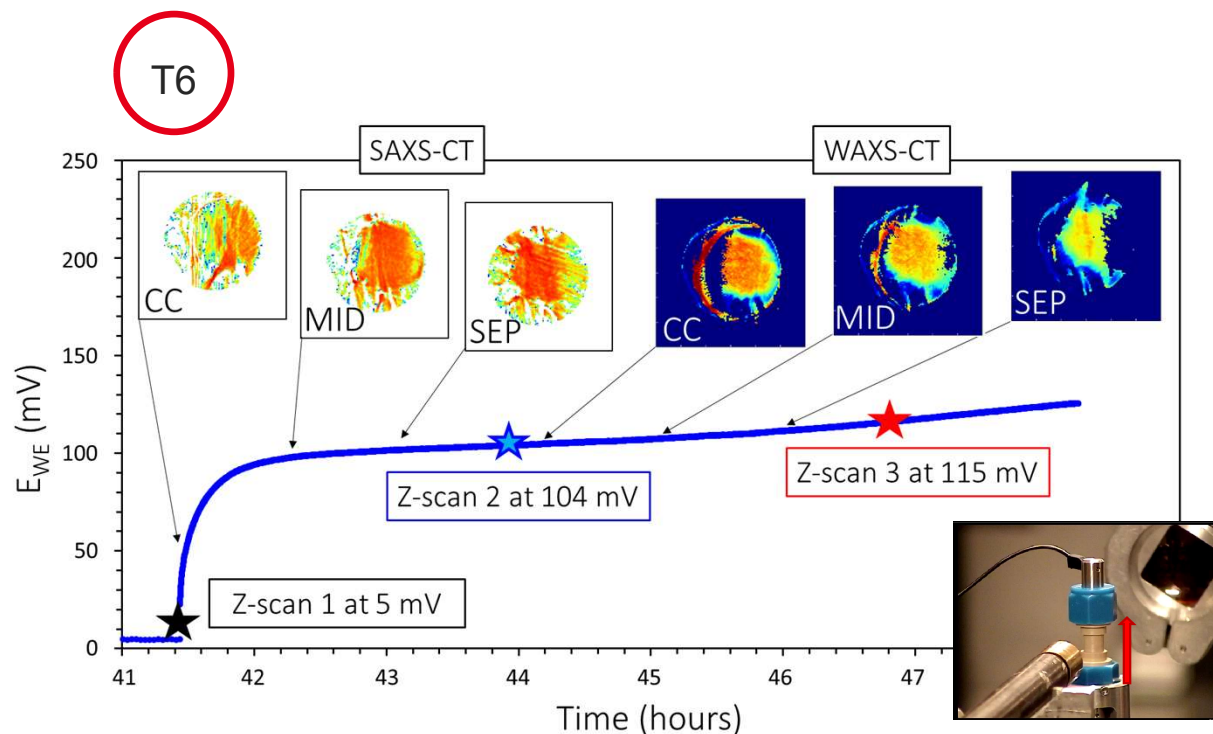
Middle slice (middle of the electrode)



Christopher L. Berhaut, Marta Mirolo, Diana Zapata Dominguez, Isaac Martens, Stéphanie Pouget, Nathalie Herlin-Boime, Marion Chandesris, Samuel Tardif, Jakub Drnec*, Sandrine Lyonnard*. Charge Dynamics Induced by Lithiation Heterogeneity in Silicon-Graphite Composite Anodes. Adv. Energy Mater. 2023, 13, 2301874. DOI:10.1002/aenm.202301874

#2 Operando investigation of silicon-based anodes for batteries

Depth-resolved charge dynamics by scanning μ SAXS and SAXS-CT



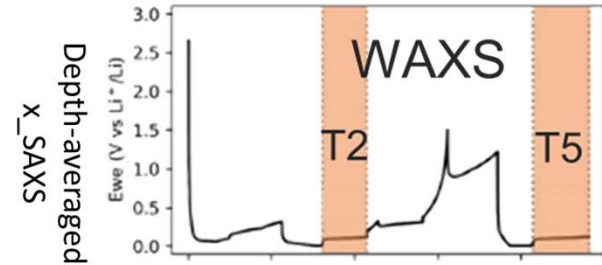
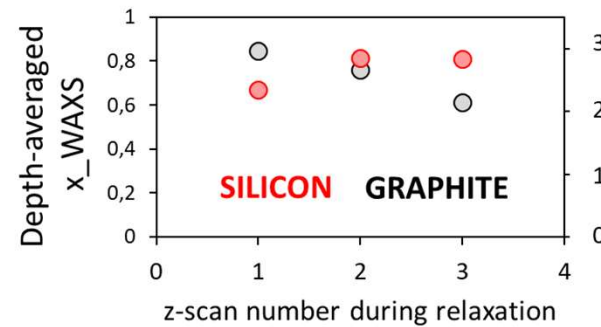
Christopher L. Berhaut, Marta Mirolo, Diana Zapata Dominguez, Isaac Martens, Stéphanie Pouget, Nathalie H. Tardif, Jakub Drnec*, Sandrine Lyonnard*. Charge Dynamics Induced by Lithiation Heterogeneity in Silicon-Graphite. *Nature Energy* 2023, 13, 2301874. DOI:10.1002/aenm.202301874

#2 Operando investigation of silicon-based anodes for batteries

Depth-resolved charge dynamics by scanning μ SAXS and SAXS-CT

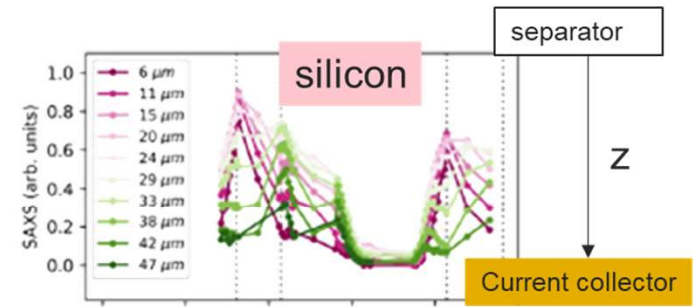
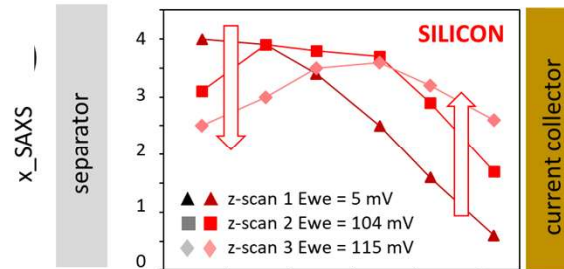


Depth-averaged lithium content
Graphite loosing, Silicon gaining

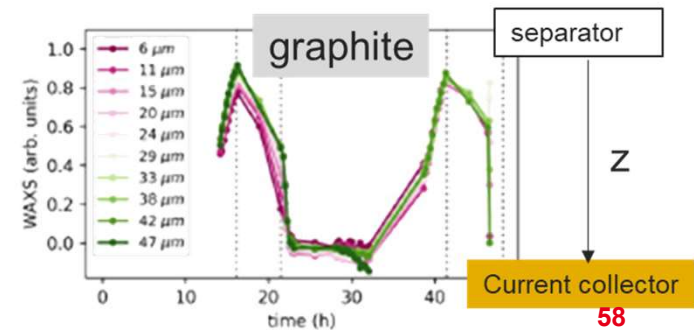
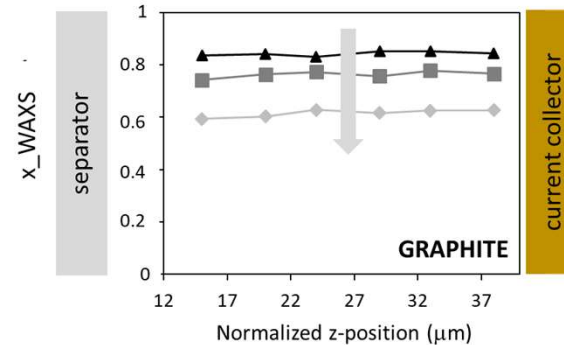


Depth-resolved lithium content

z-gradients in silicon
Different dynamics depending on location (CC or SEP)



No- z-gradients in graphite
Continuous loss of lithium

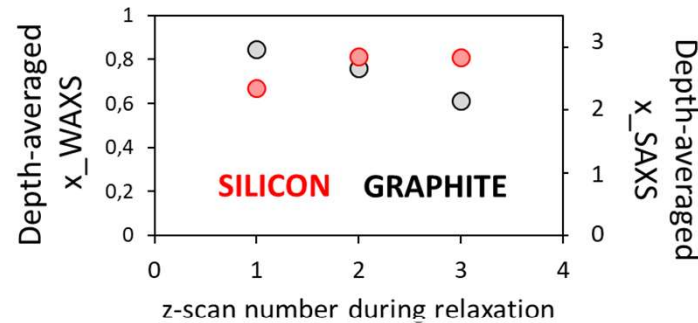


#2 Operando investigation of silicon-based anodes for batteries

Depth-resolved charge dynamics by scanning μ SAXS and SAXS-CT

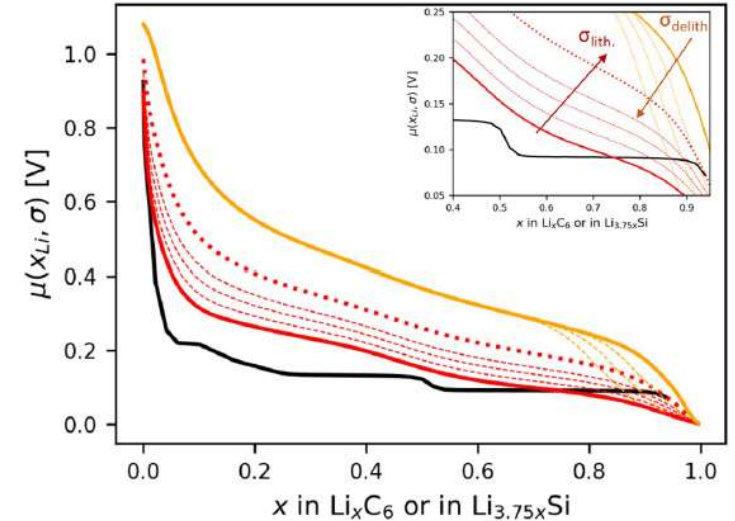
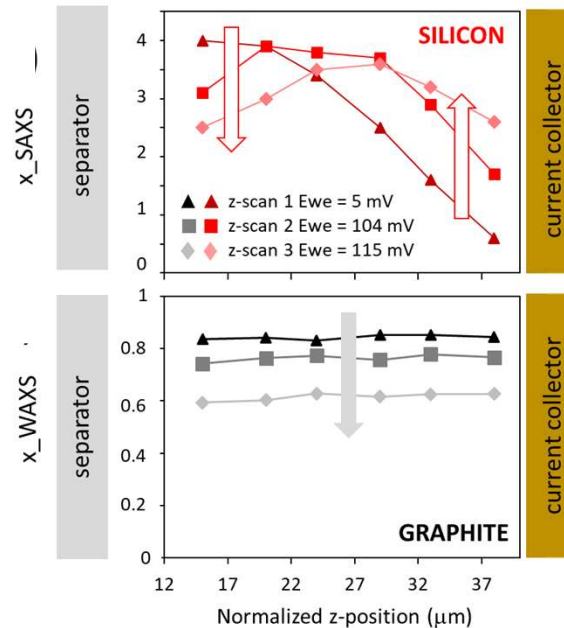


Depth-averaged lithium content
Graphite loosing, Silicon gaining



Depth-resolved lithium content

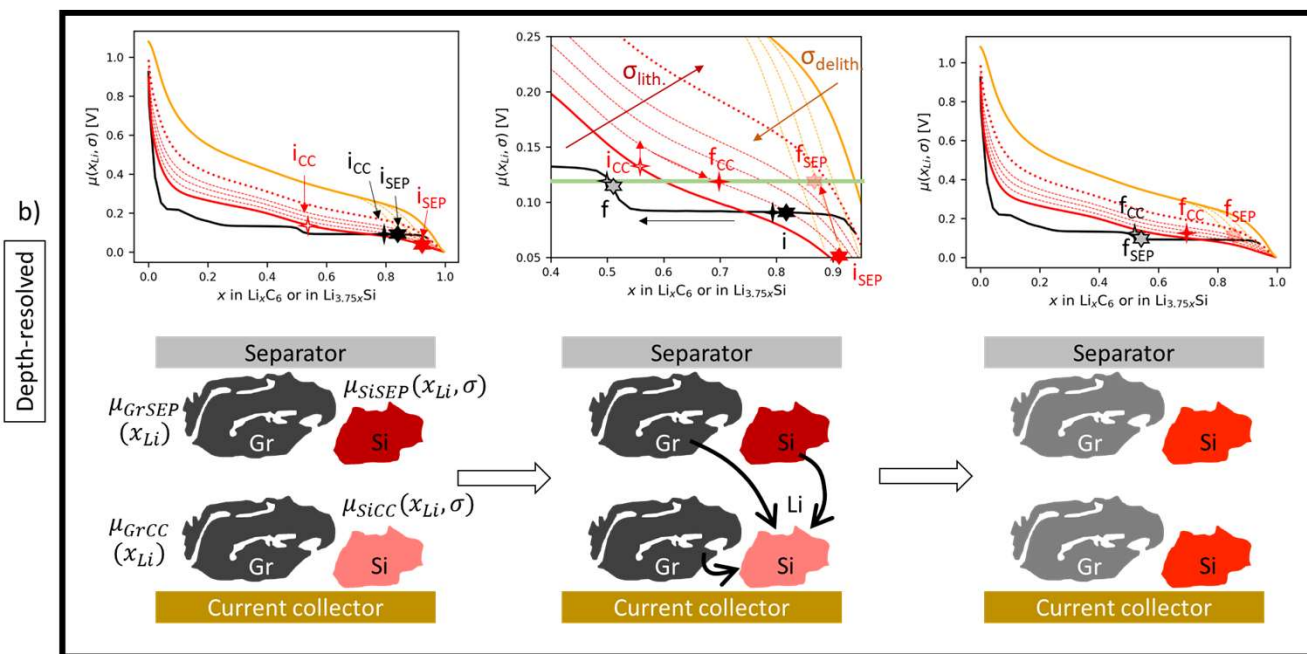
z-gradients in silicon
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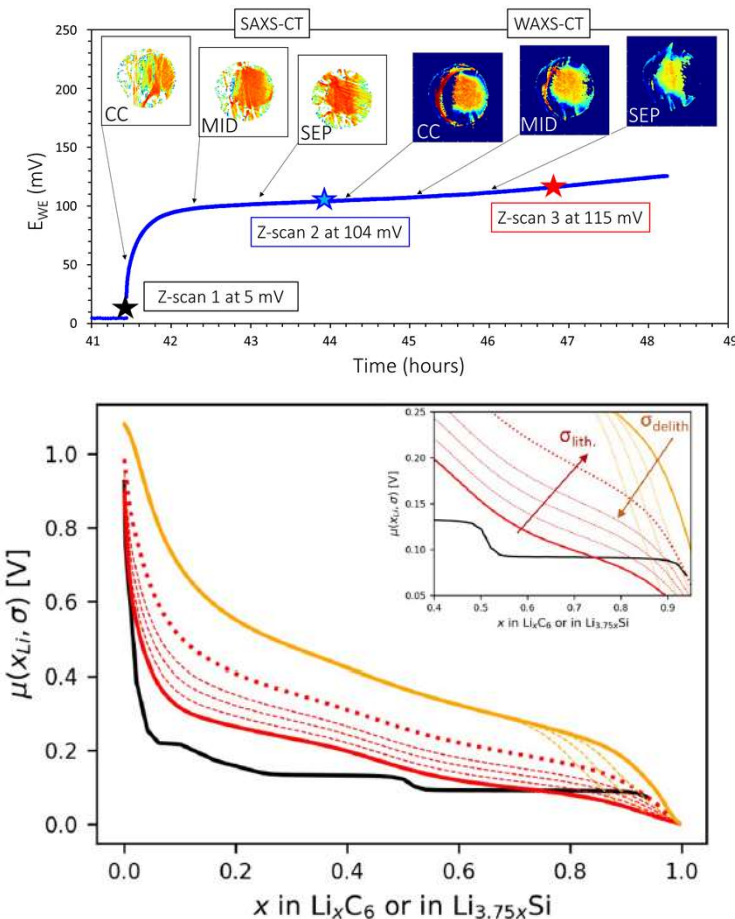
#2 Operando investigation of silicon-based anodes for batteries

Depth-resolved charge dynamics by scanning μ SAXS and SAXS-CT

Modelling



At OCV, highly lithiated silicon particles can start the delithiation process at a lower potential compared to the pseudo-equilibrium potential

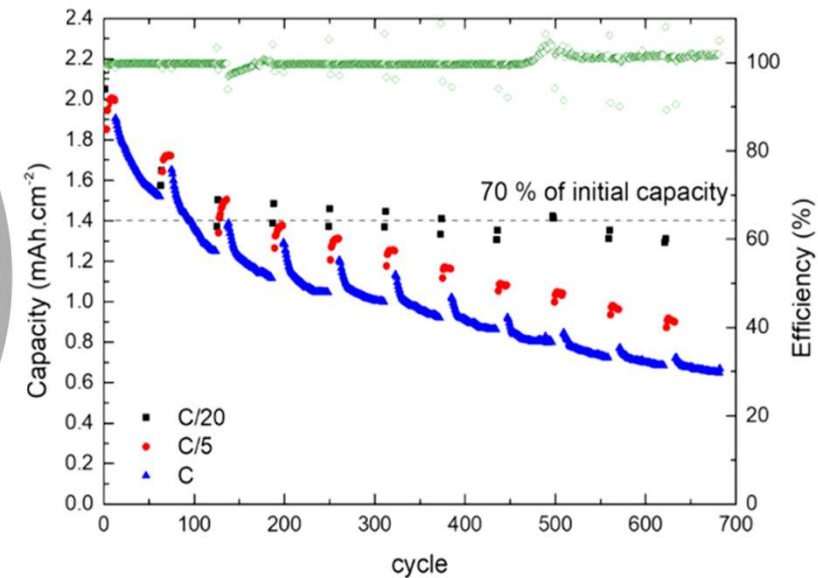
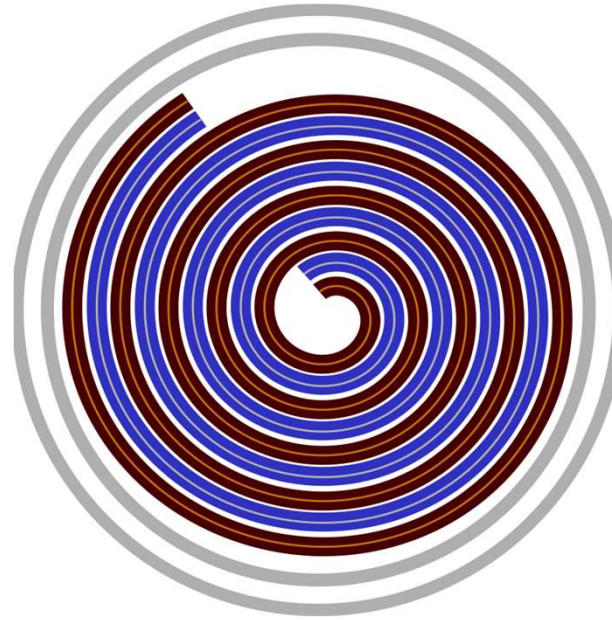


#2 Operando investigation of silicon-based anodes for batteries

3D heterogeneities and defects in cylindrical cells by SWAXS-CT

Industry-grade cylindrical Li-ion cell

Silicon-Graphite anode ; NMC622 cathode

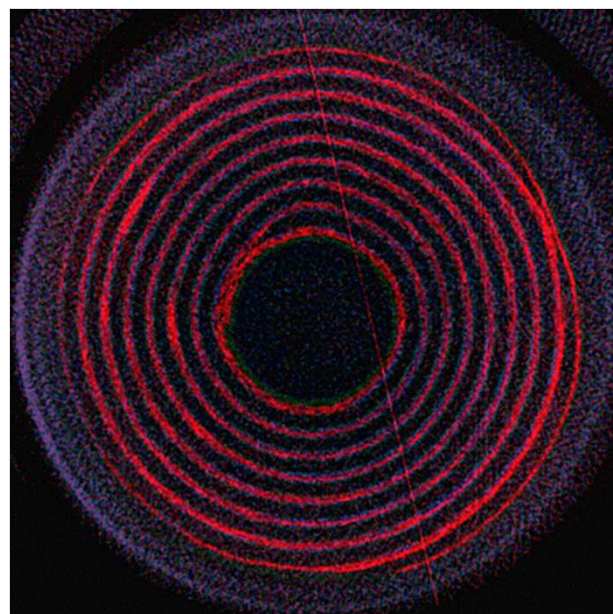


30 mAh

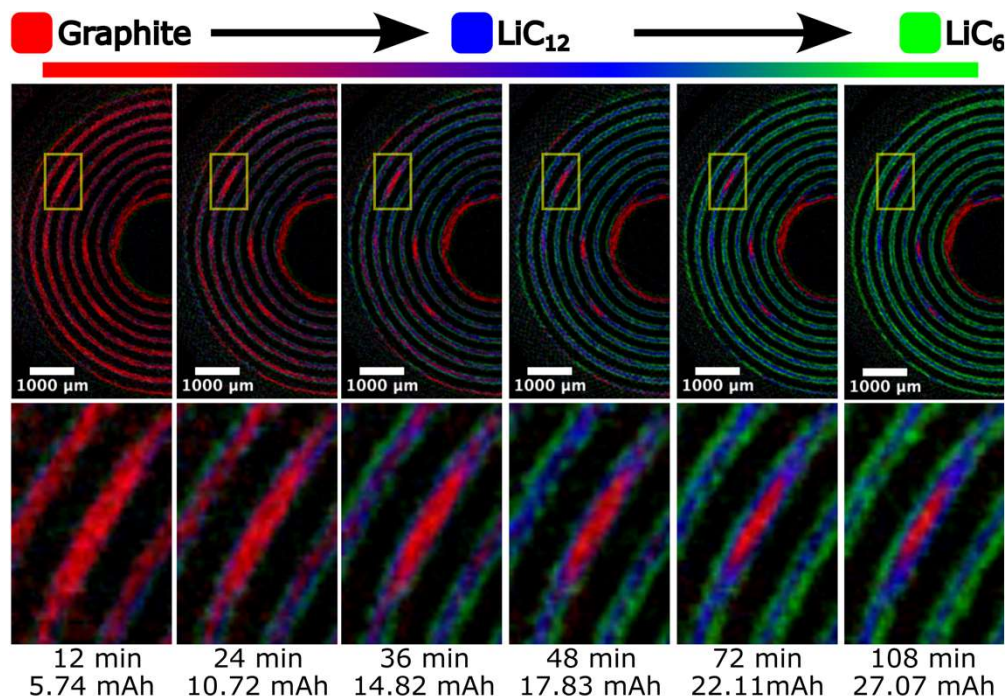
#2 Operando investigation of silicon-based anodes for batteries

3D heterogeneities and defects in cylindrical cells by SWAXS-CT

Operando WAXS-CT ID31@ESRF



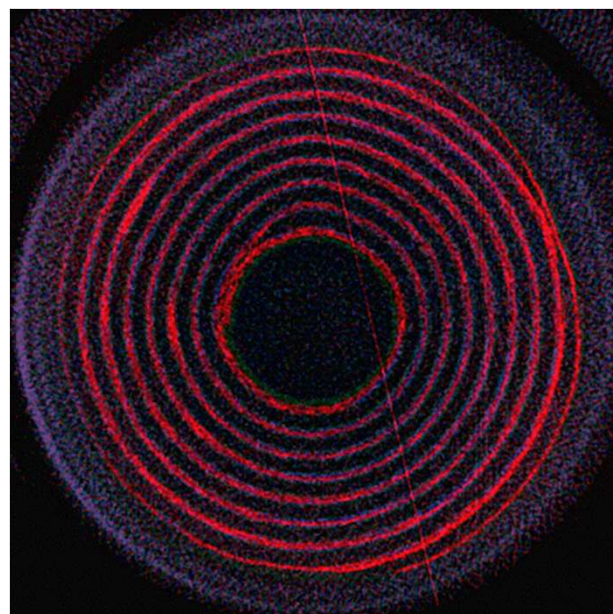
70 keV
Beam 5*10 μm
1 slice-CT
in 5 minutes



#2 Operando investigation of silicon-based anodes for batteries

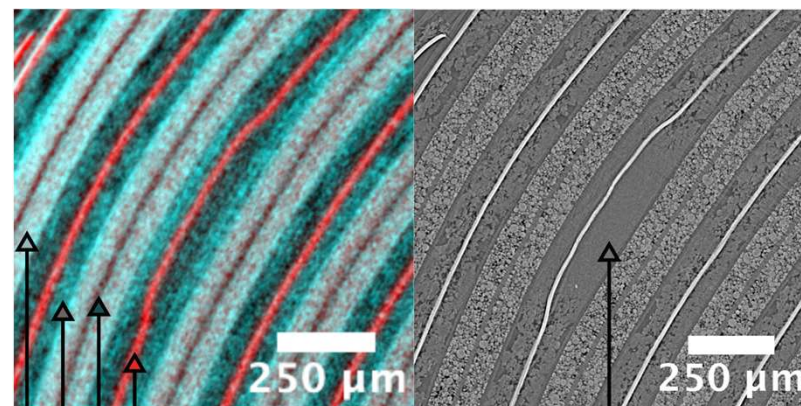
3D heterogeneities and defects in cylindrical cells by SWAXS-CT

Operando WAXS-CT ID31@ESRF



70 keV
Beam 5*10 μm
1 slice-CT
in 5 minutes

« dead » graphite areas correspond to
locally bent current collector and compacted
anode microstructure



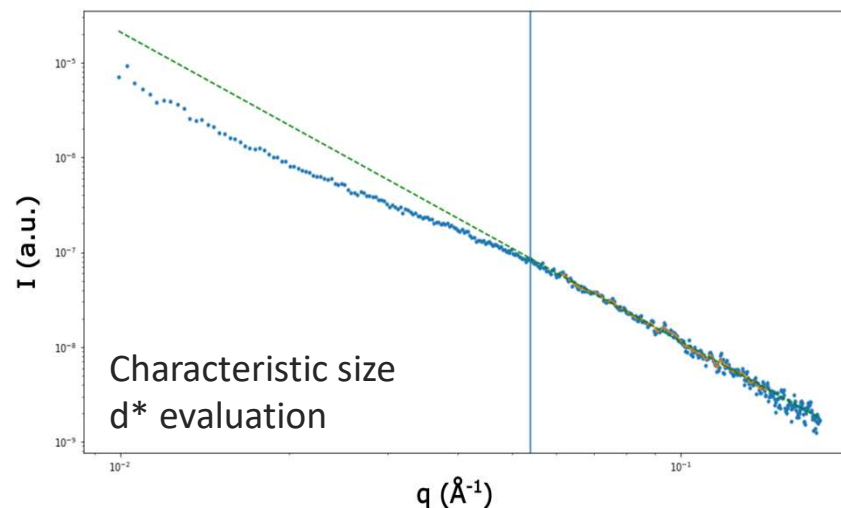
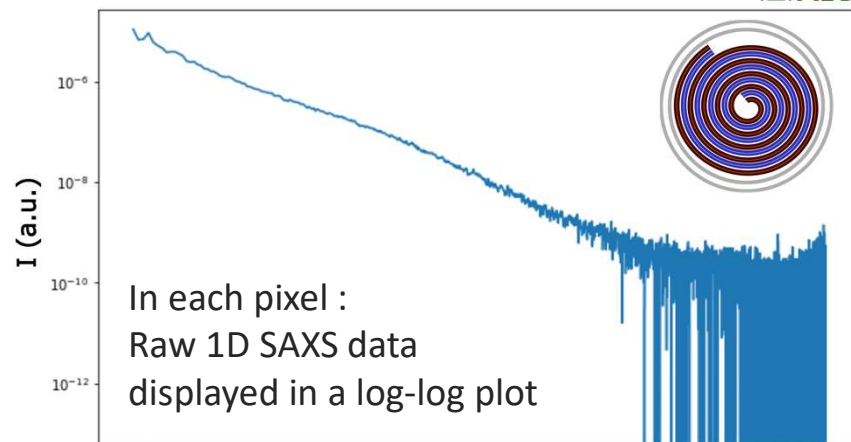
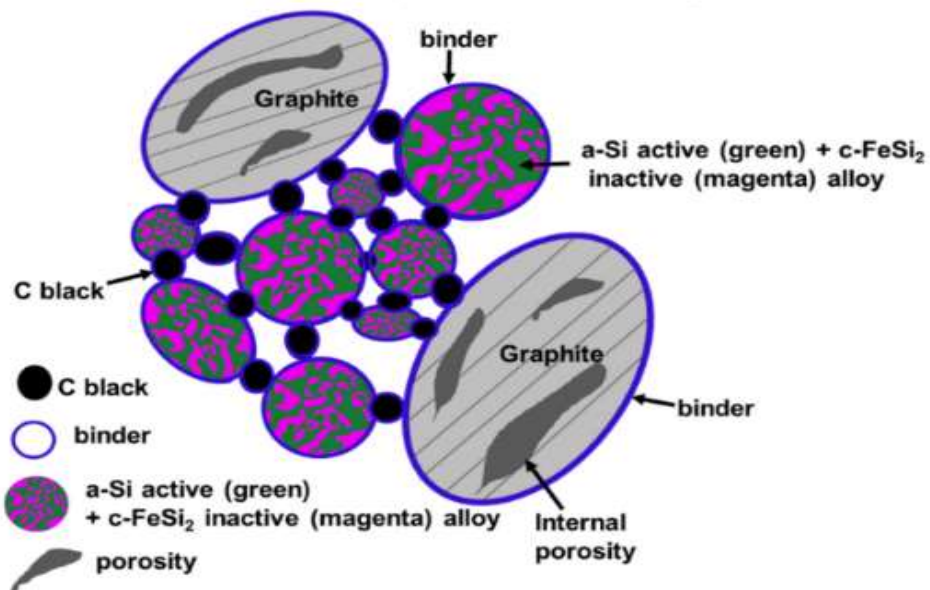
Cu c.c.
Al c.c.
Anode
Cathode

Compressed
Structure

#2 Operando investigation of silicon-based anodes for batteries

3D heterogeneities and defects in cylindrical cells by SWAXS-CT

Silicon is nanostructured : SAXS informs on both the amount of Li_xSi and characteristic “swelling” state (d^*)

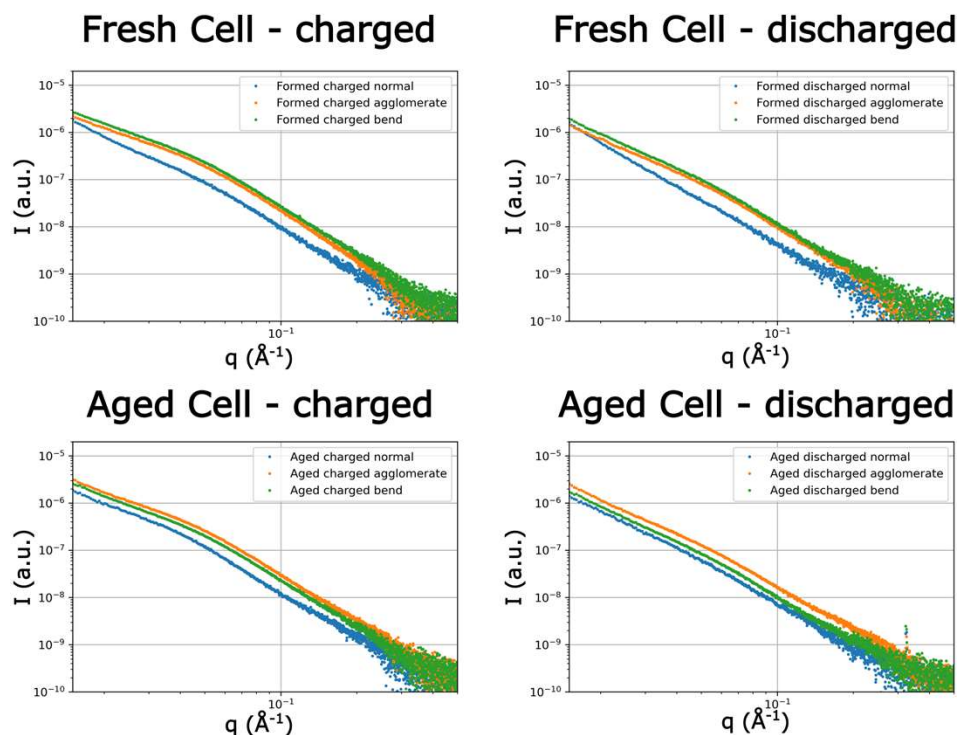


#2 Operando investigation of silicon-based anodes for batteries

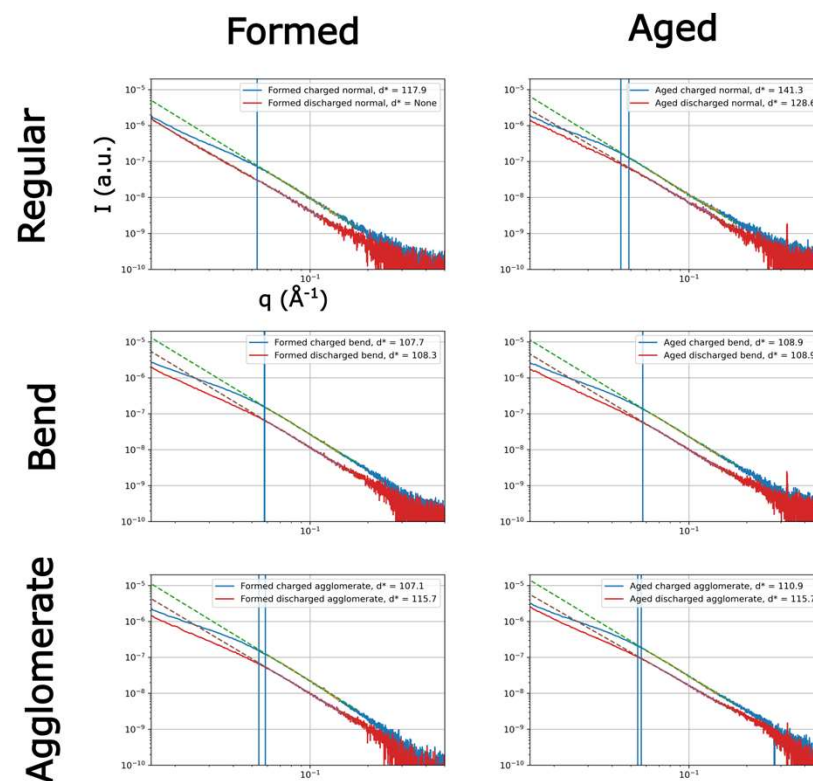
3D heterogeneities and defects in cylindrical cells by SWAXS-CT



E. Lübke



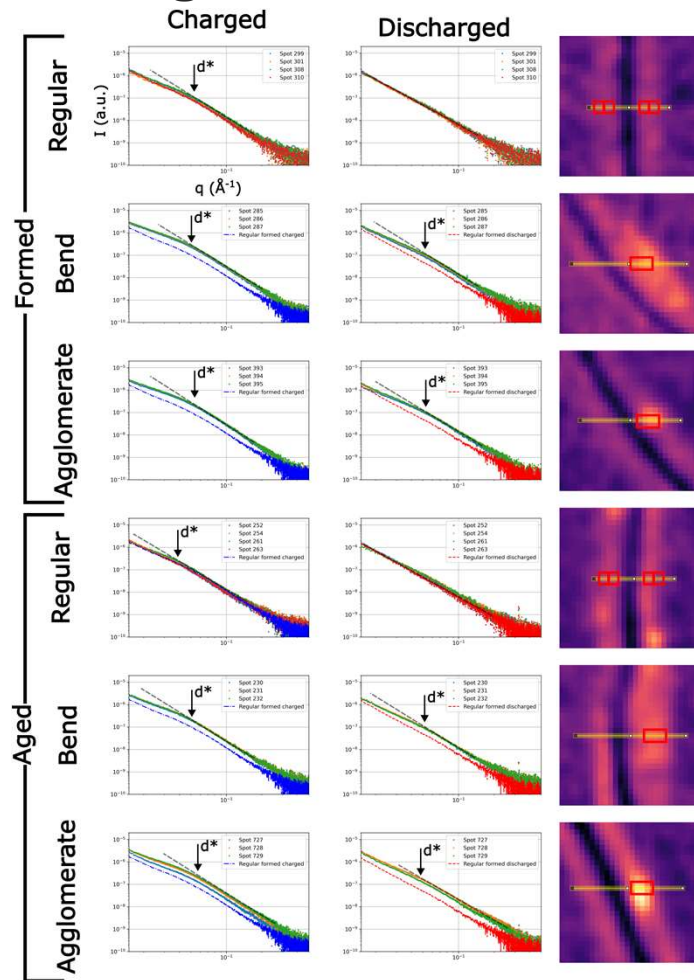
Averaged raw SAXS profiles extracted in regular, bent and agglomerate areas for both the formed and aged cell plotted against each other to highlight the differences between the defect within a certain state of health/charge.



Averaged raw SAXS profiles extracted in regular, bent and agglomerate areas for both the formed and aged cell plotted against each other to highlight the differences between the discharged and charged state for the different types. The output d^* is in Å.

#2 Operando investigation of silicon-based anodes for batteries

3D heterogeneities and defects in cylindrical cells by SWAXS-CT

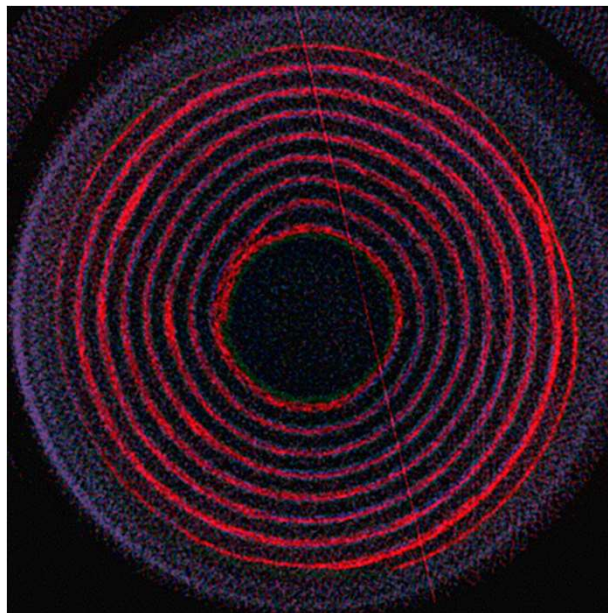


		Normal	Bend	Agglomerate
Fresh - charged		11.8 nm	10.8 nm	10.9 nm
Fresh - discharged		None	10.8 nm	11.6 nm
Aged - charged		14.1 nm	10.9 nm	11.1 nm
Aged - discharged		12.9 nm	10.9 nm	11.6nm

#2 Operando investigation of silicon-based anodes for batteries

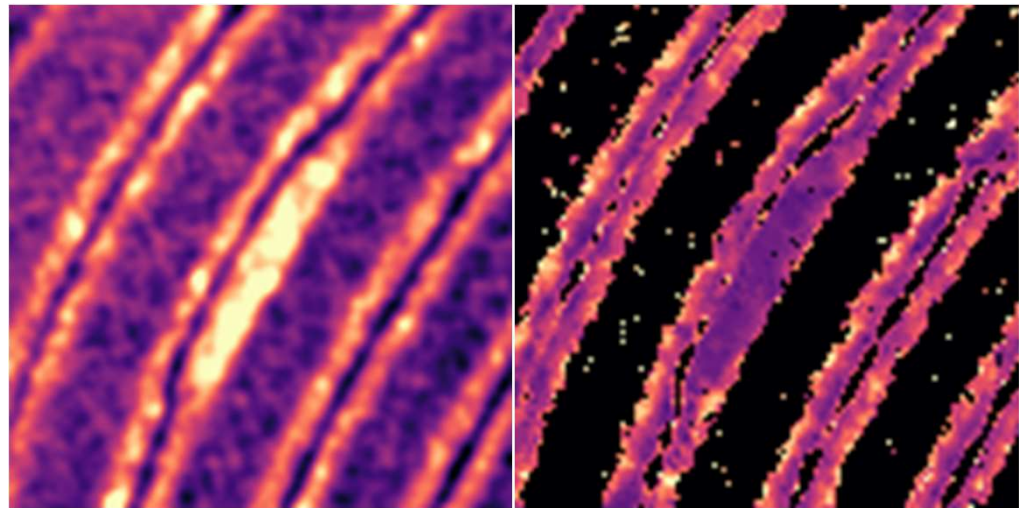
3D heterogeneities and defects in cylindrical cells by SWAXS-CT

Operando WAXS-CT ID31@ESRF




70 keV
Beam 5*10 μm
1 slice-CT
in 5 minutes

SAXS-CT ID31@ESRF



Si-content (Intensity)

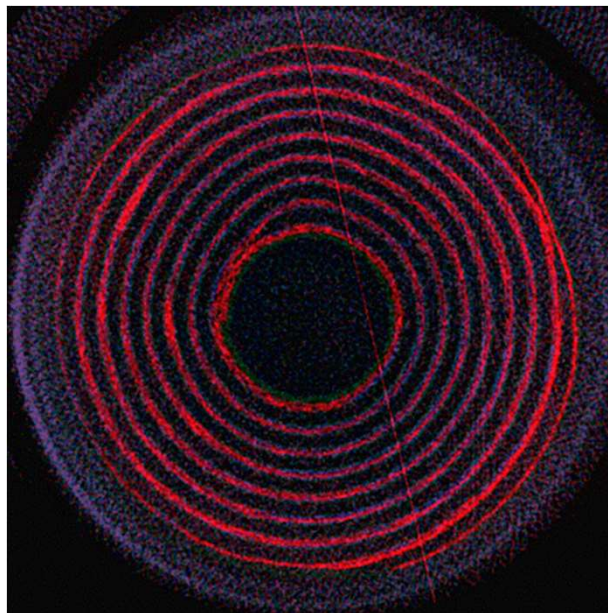
Si expansion (d*)

The defects are due to localized Silicon agglomeration

#2 Operando investigation of silicon-based anodes for batteries

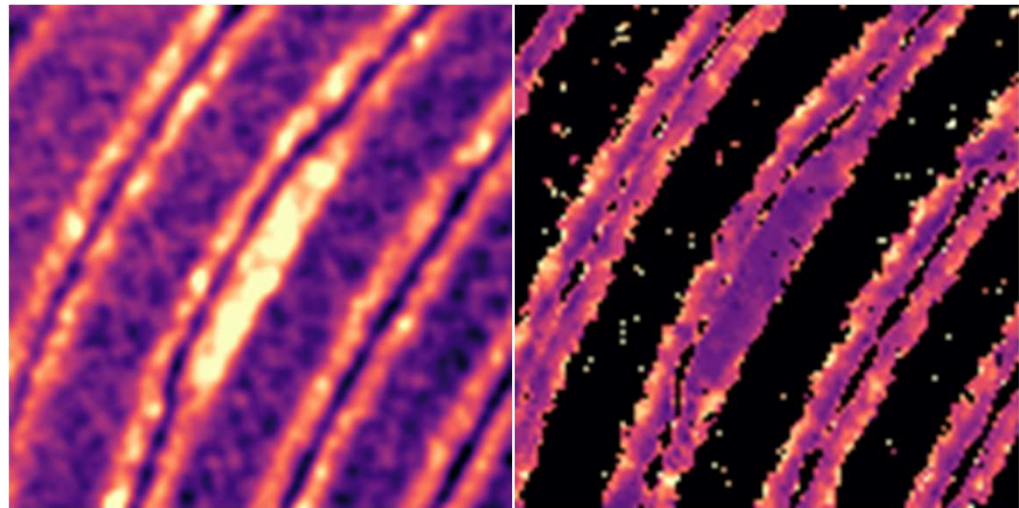
3D heterogeneities and defects in cylindrical cells by SWAXS-CT

Operando WAXS-CT ID31@ESRF




70 keV
Beam 5*10 μm
1 slice-CT
in 5 minutes

SAXS-CT ID31@ESRF



Si-content (Intensity)

Si expansion (d*)

The defects are due to localized Silicon agglomeration

#2 Operando investigation of silicon-based anodes for batteries

3D heterogeneities and defects in cylindrical cells by SWAXS-CT

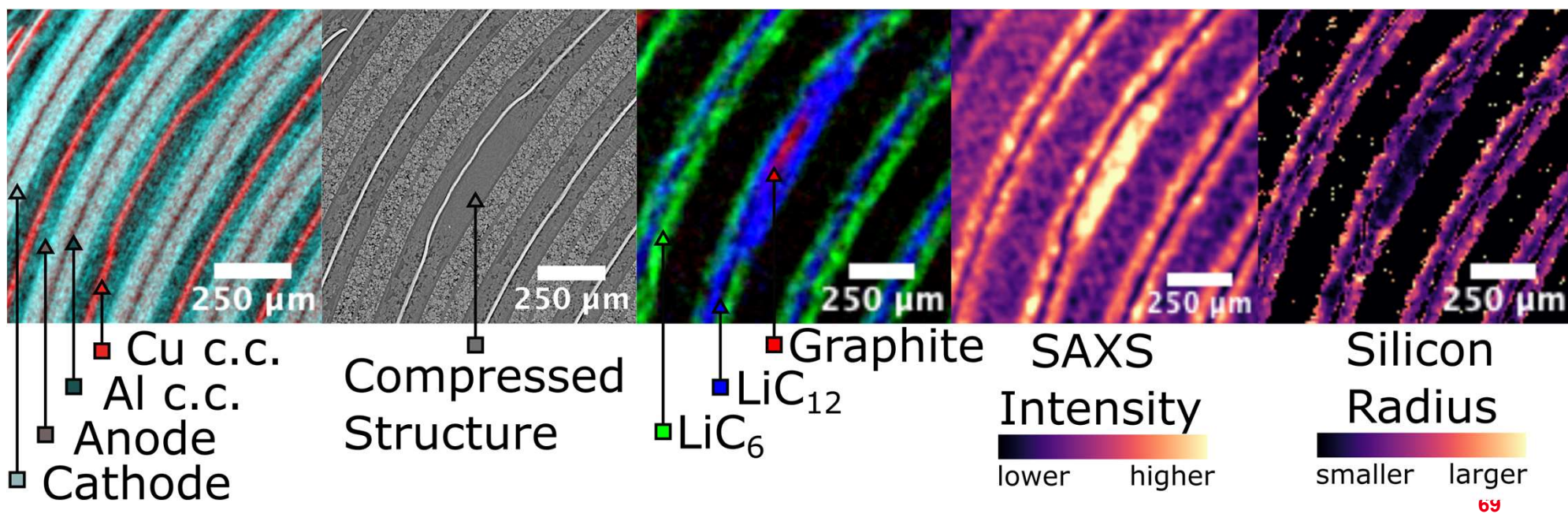
Correlative analysis unravels the origin of local defects

NeXT:
Deformed
Different Li-distribution

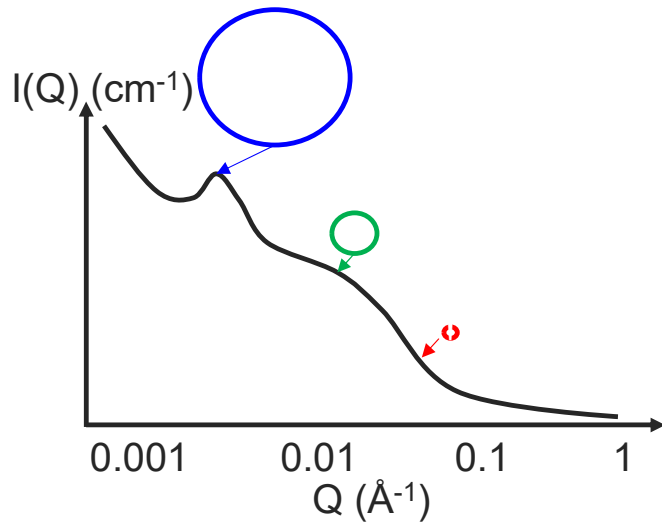
High-Res XCT:
Compressed microstructure

WAXS-CT:
Lower graphite lithiation
Slower kinetics

SAXS-CT:
Silicon material accumulation
Lower Si-expansion



Conclusions and take-home message



SAXS/SANS is very powerful to look at:
Soft matter / organic species
Sizes and shapes of objects / Nanoscale
Organizations / Porous materials/ Interfaces

Energy storage and conversion : structural evolution of a nanostructured material

Suitable to nanosized particles-based electrodes and composites

Suitable to see nanopores and/or interfacial evolutions (Graphite, Cathodes)

Suitable to look at nanosized intermediates (Li-S)

Suitable to investigate polymer/hybrid electrolytes

It is not always easy to be quantitative.....

Small is good !

Do not hesitate to go to small angles !



Characterization of materials and devices using Neutron & Synchrotron techniques



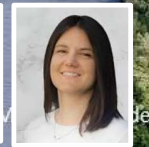
Our lab



NEXT- L. Helfen



BM02 – N. Blanc, G. Chahine
 BM32 – S. Tardif, J-S. Micha
 ID31 – J. Drnec, M. Mirolo, V. Vinci, J. Ruellou
 BM05 – P. Cook, J. Vijayakumar
 ID13 – M. Burghammer, J. Liu, A. Medjahed
 ID16a – F. Monaco, P. Cloetens, D. Karpov
 ID16b – J. Villanova, O. Stamat



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