in situ SANS with Lithium ion batteries

S. Seidlmayer

2nd internal biennial science meeting of the MLZ
Grainau, 16. Juni 2015

Outline

- Introduction to Li-ion battery systems
- Principles of small-angle (neutron) scattering
- in situ SANS with Li-ion battery cells
- Modelling Li-migration combining in situ SANS and electrochemical data
- Conclusion & Outlook

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- **Introduction to Li-ion battery systems**
- Principles of small-angle (neutron) scattering
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General principle of a Li-ion battery

A battery consists of:

- Cathode (Li source)
- Anode (Li drain)
- Separator
- Electrolyte

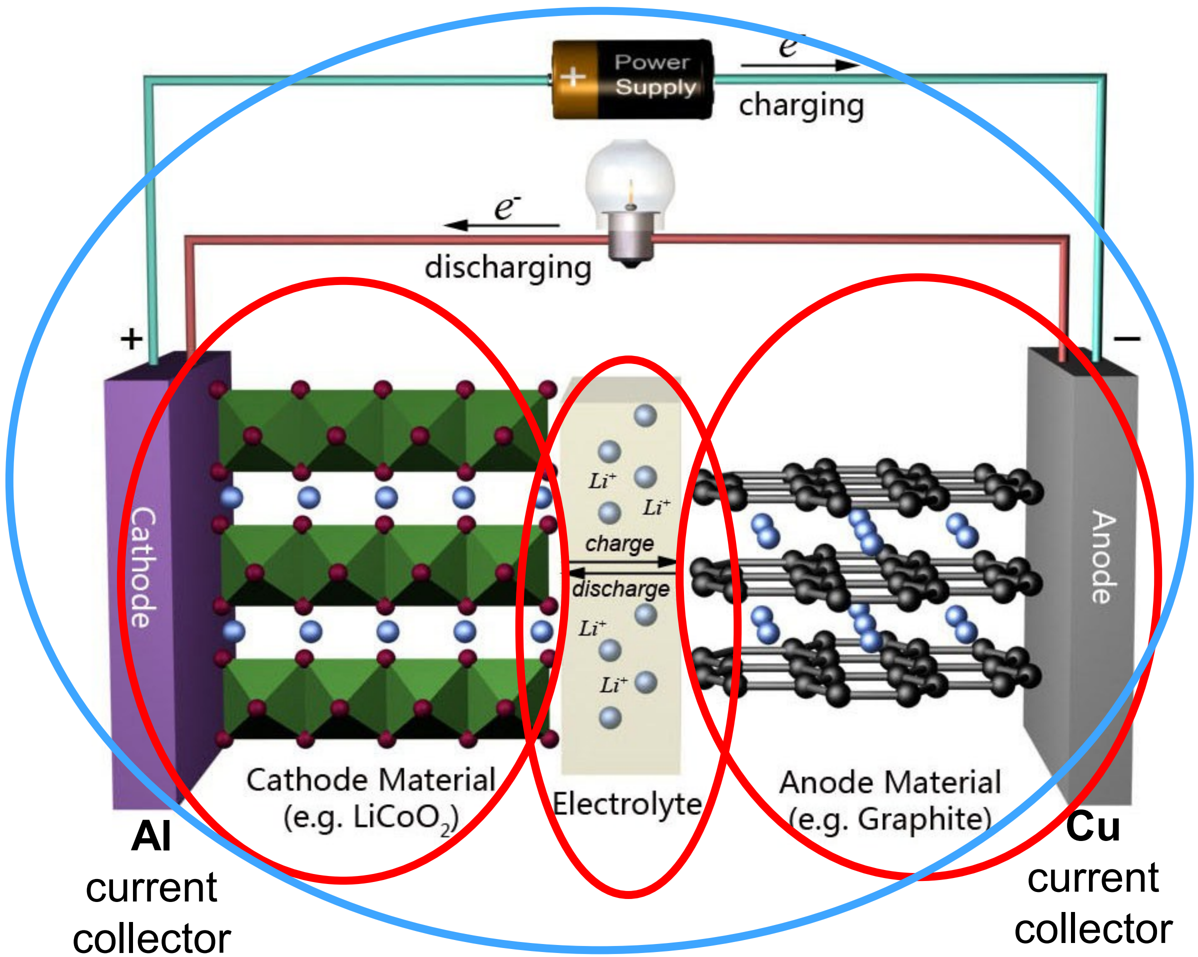

image taken from: http://research.chem.psu.edu/axsgroup/Ran/research/energystorage.html

General principle of a Li-ion battery

A battery consists of:

- Cathode (Li source)
- Anode (Li drain)
- Separator
- Electrolyte
- protective Casing

energy storage through:

- reversible chemical reaction
- difference in electric potential between anode/cathode

image taken from: http://research.chem.psu.edu/axsgroup/Ran/research/energystorage.html

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- **Principles of small-angle (neutron) scattering**
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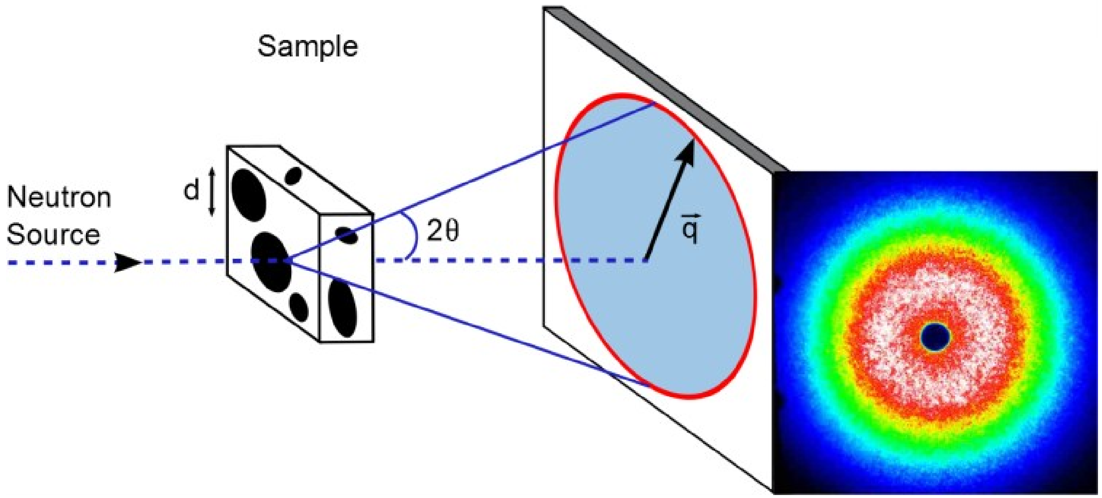
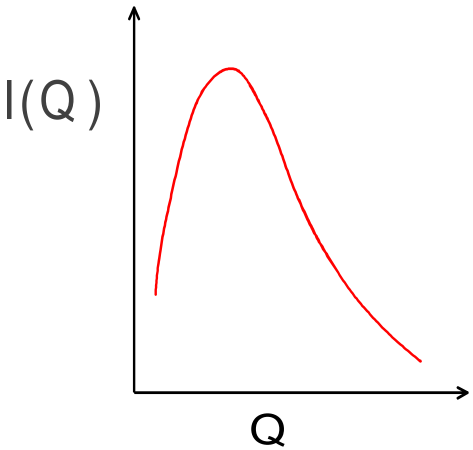
Principles of small-angle scattering

typical experimental setup



radial averaged intensity I (Q)



$Q = \frac{4\pi}{\lambda} \sin(\Theta)$ momentum transfer

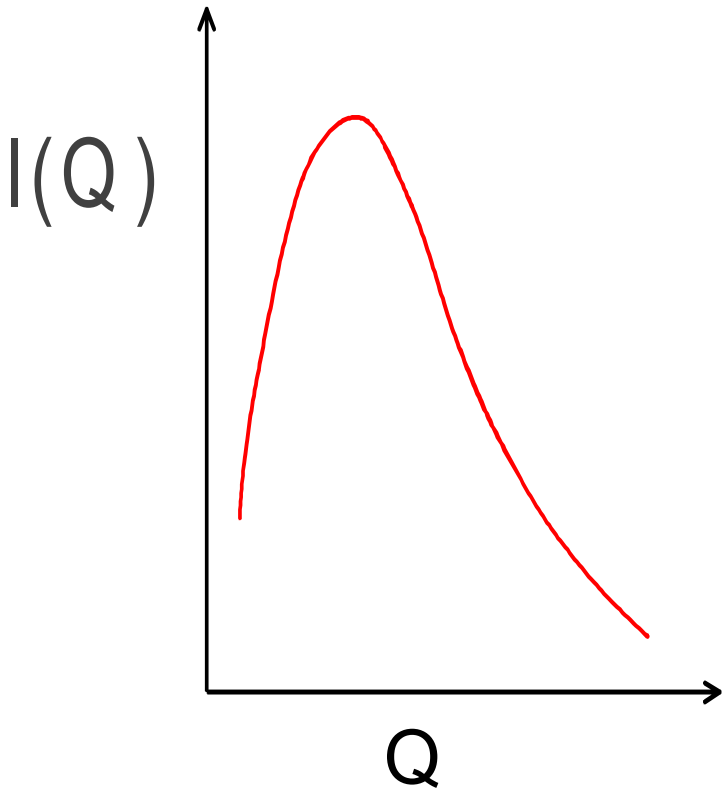
1D-Data modelling
=> physical parameters

transmission geometry, sample directly in the beam or inside a low-background container

Principles of small-angle scattering

$$I(Q) = K\Delta\rho^2 N \times P(Q) \times S(Q)$$

radial averaged intensity I (Q)



Three major factors contribute to intensity:

- P(Q) =
  Form factor or shape factor
  „How do the scattering objects look like (i.e. spheres, ellipsoids, etc.)“

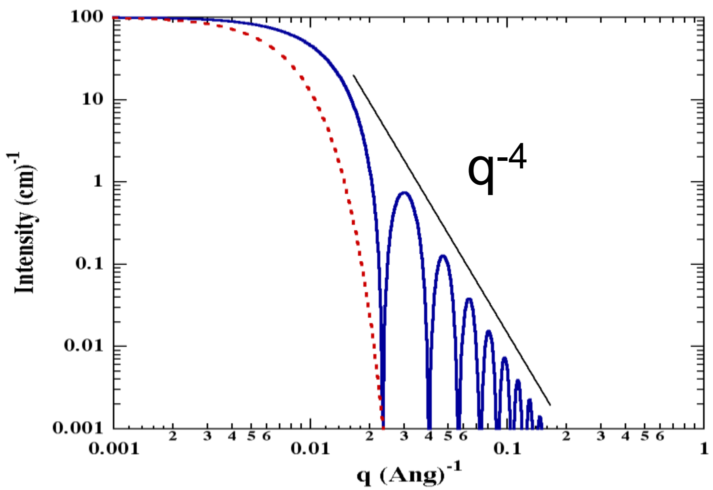
- S(Q) =
  Structure factor
  „How are the objects arranged in space“

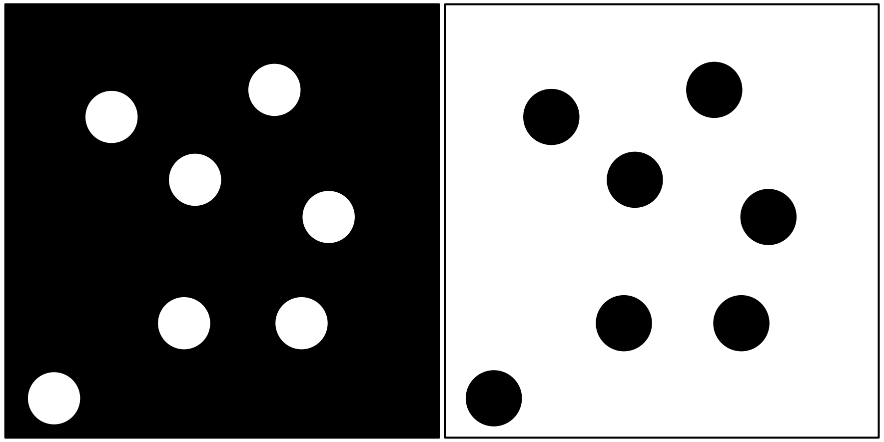
- $\Delta\rho^2$ = scattering contrast factor

  $\Delta\rho^2 = (SLD_1 - SLD_2)^2$

Principles of small-angle scattering

$$I(Q) = K\Delta\rho^2 N \times P(Q) \times S(Q)$$





monodisperse spheres
OR
monodisperse voids
(with smooth interface)

$\Delta\rho^2$ = scattering contrast factor

$\Delta\rho^2 = (SLD_1 - SLD_2)^2$

Image Source: Presentation Winter School for Synchrotron Radiation
Small-angle scattering in materials science by J. Ilavsky,

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- **in situ SANS with Li-ion battery Pouch cells**
- Modelling Li-migration combining in situ SANS and electrochemical data
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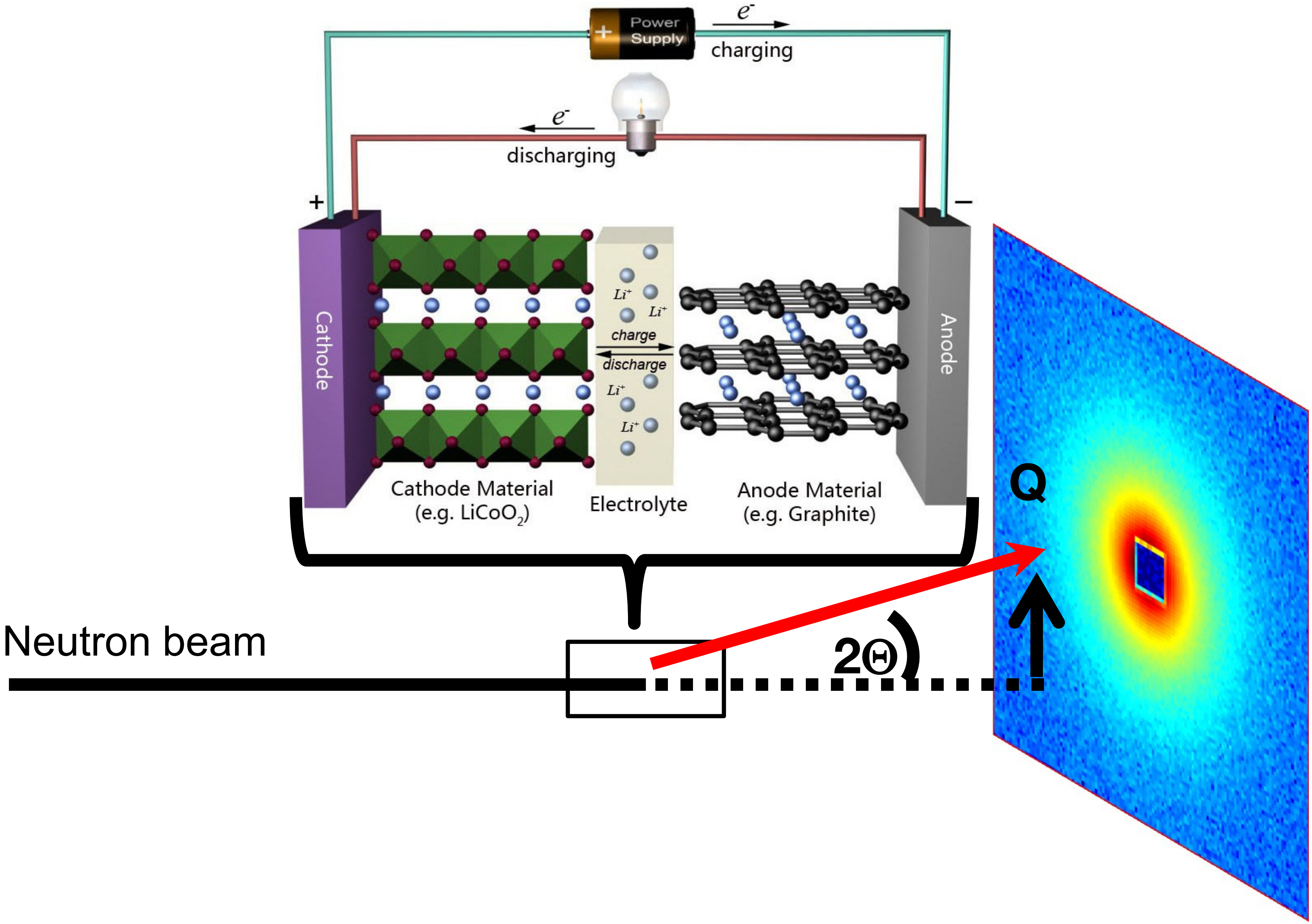
in situ SANS with Li-ion battery cells



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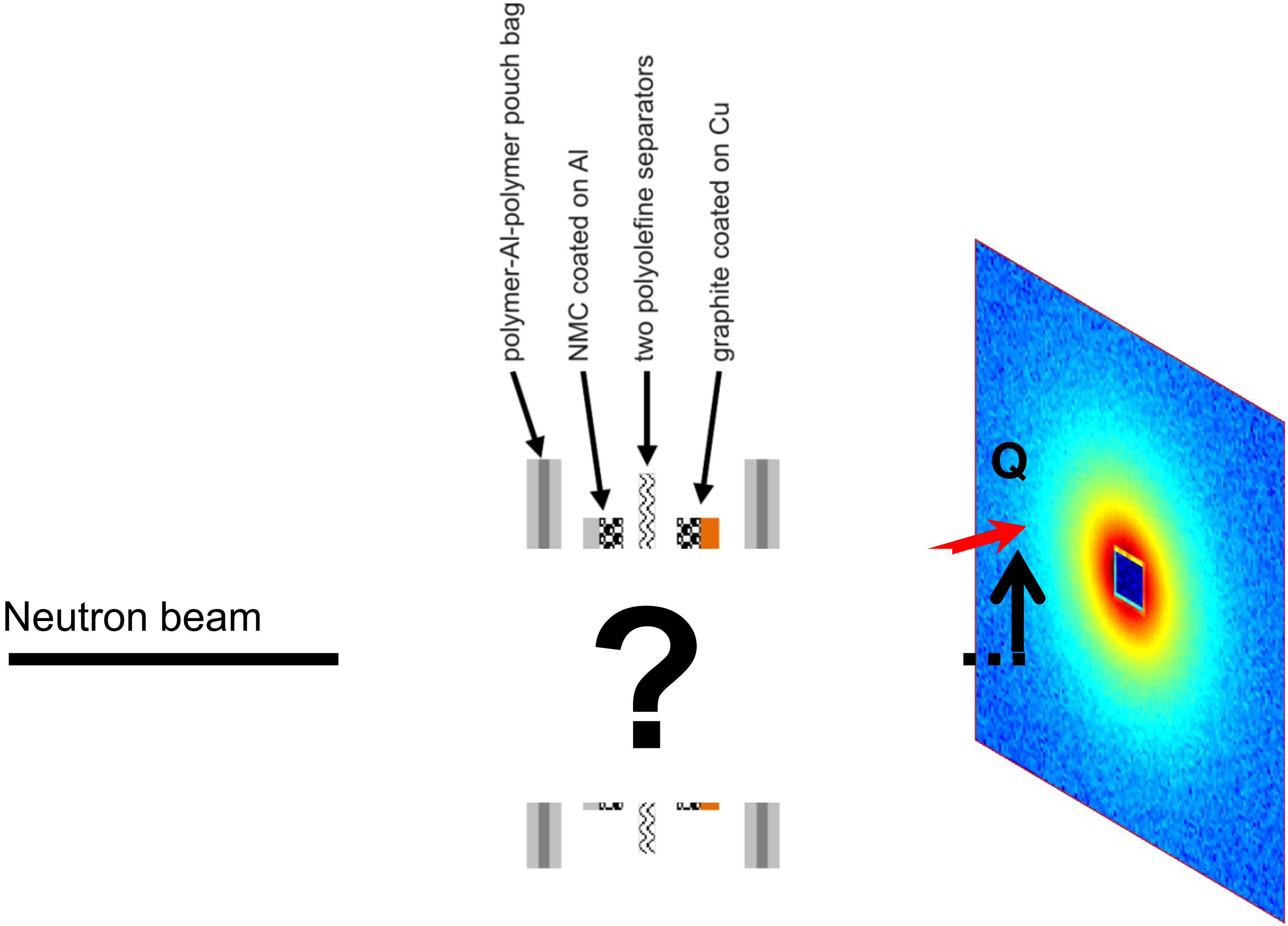
in situ SANS with Li-ion battery cells



S. Seidlmayer, J. Hattendorff, I. Buchberger, L. Karge, H. A. Gasteiger, and R. Gilles, J Electrochem Soc, 162 (2), A3116-A3125 (2015).

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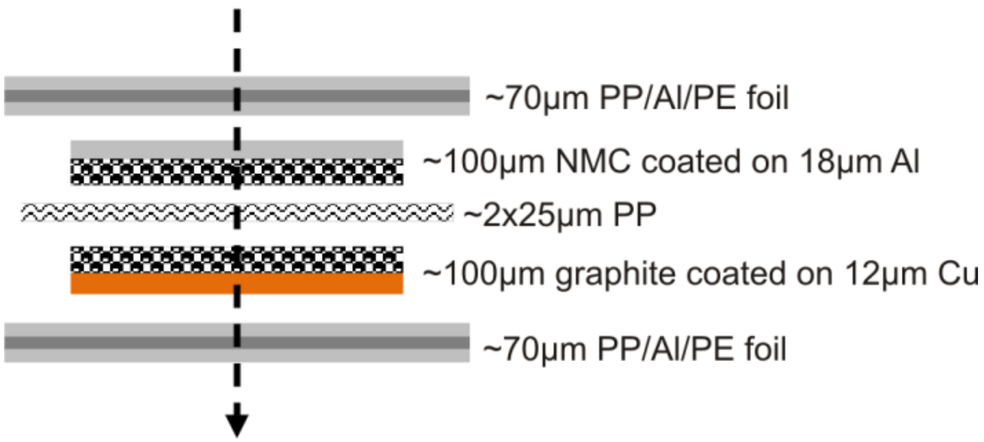

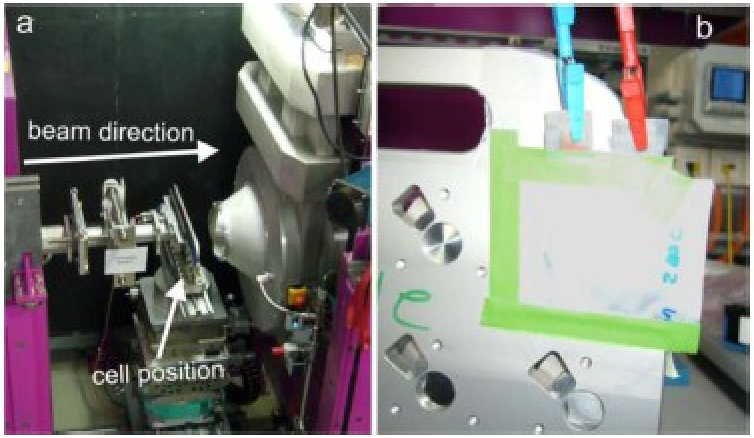

Requirements/Features:

- Thin enough for transmission setup
- total thickness ~0.5mm (transmission ~85%)
- conventional Cell chemistry:
- anode: graphite coated on Cu
- cathode: LiNMC coated on Al
- separator: 2x Celgard 2325
- electrolyte: EC:EMC 3:7|1M $LiPF_6$

in situ easily achieved by direct wiring to a Potentiostat

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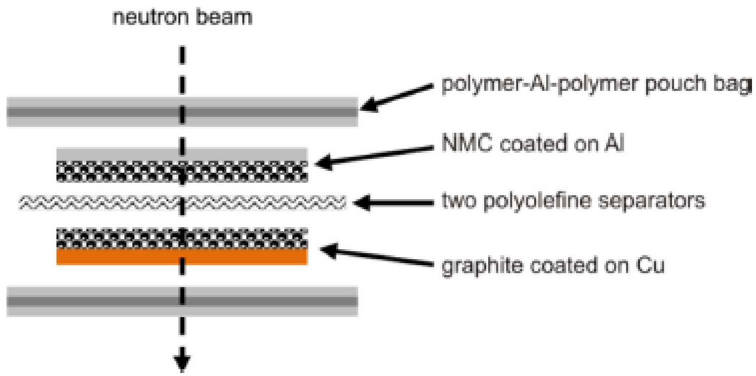

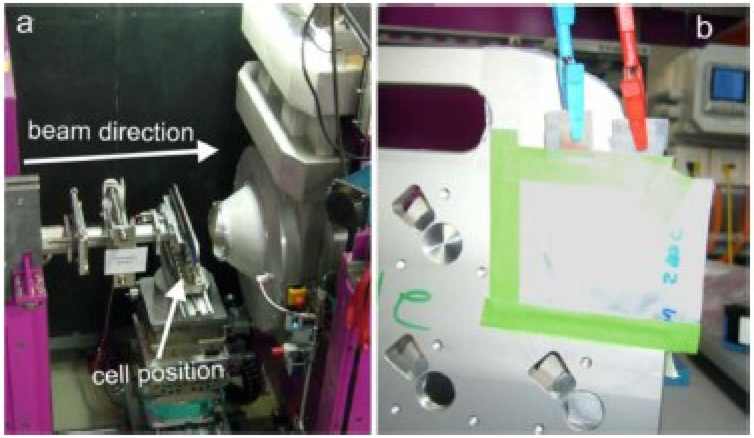

Drawback:

- SANS signal = superposition of all components

ADVANTAGE:

- SANS during in situ cell operation possible

in situ: => compromise limits:

Time resolution and Q-resolution
- fast but probe smaller Q-range vs
- slow but probe larger Q-range

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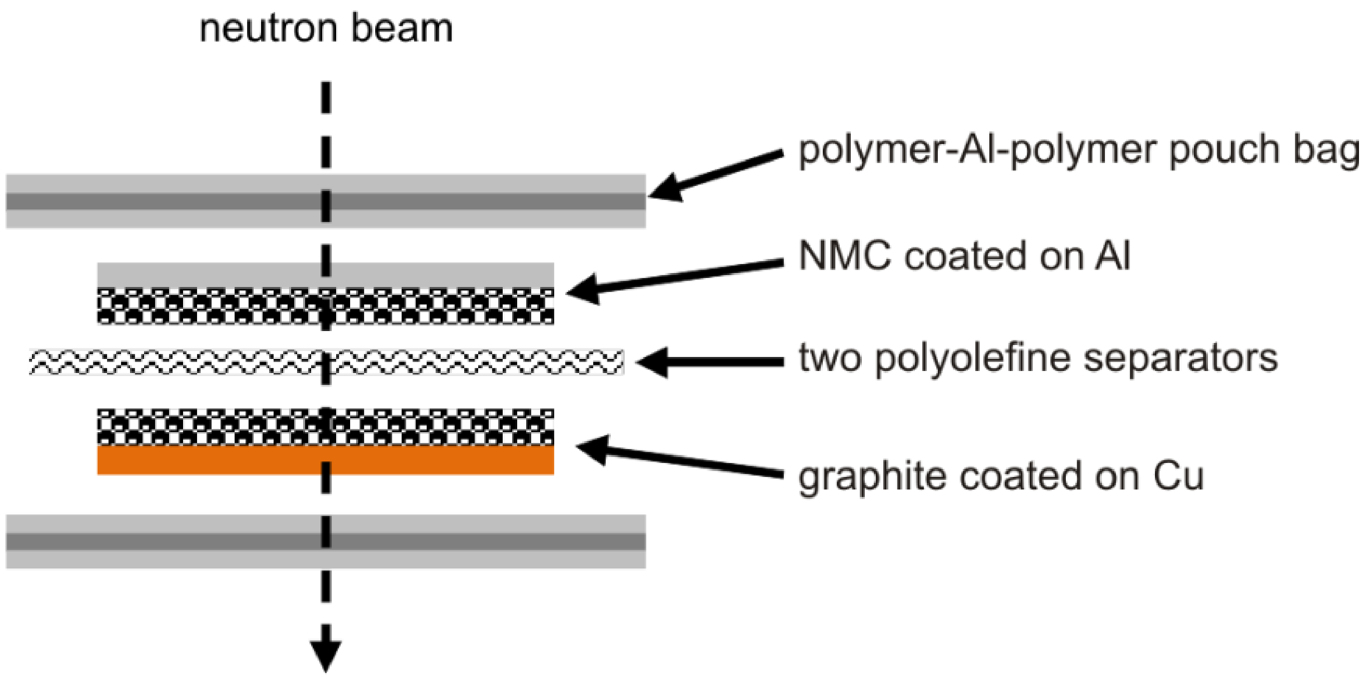
in situ SANS with Li-ion battery cells

$$I(Q) = K\Sigma_i \Delta\rho_i^2 N_i P_i(Q) \times S_i(Q)$$



- Superposition of signals
- measure single parts seperately first

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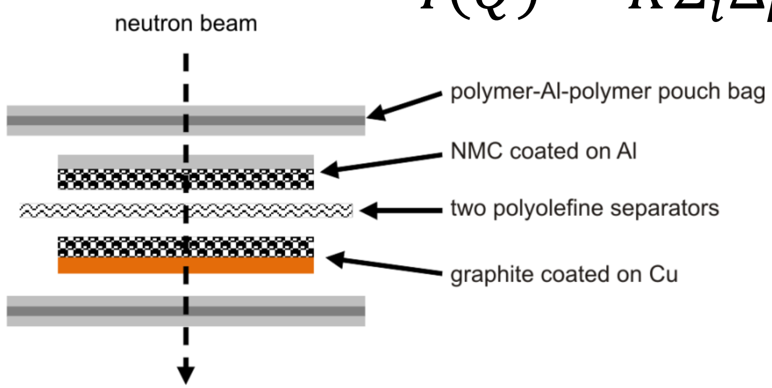
in situ SANS with Li-ion battery cells

Full Cell

$$I(Q) = K\Sigma_i \Delta\rho_i^2 N_i P_i(Q) \times S_i(Q)$$



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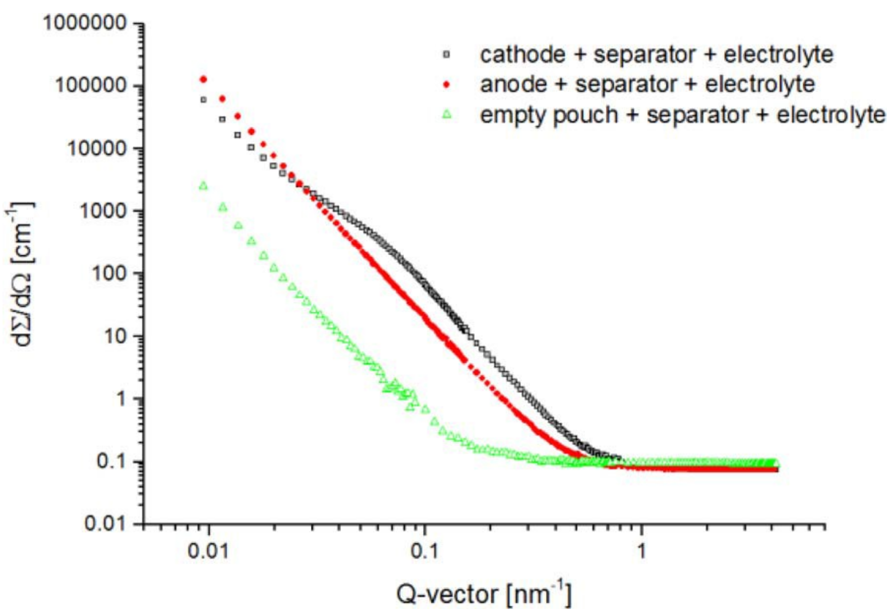

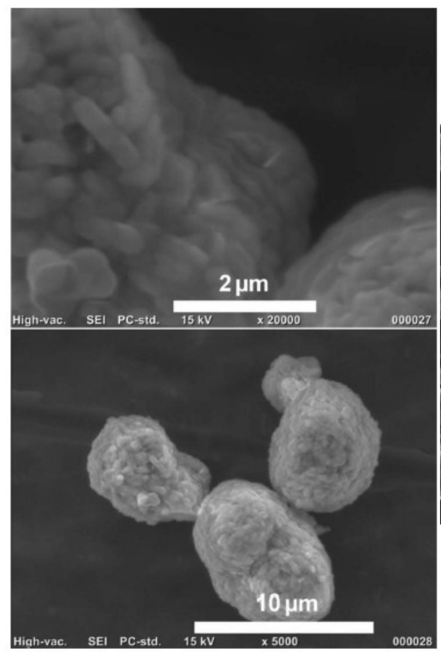

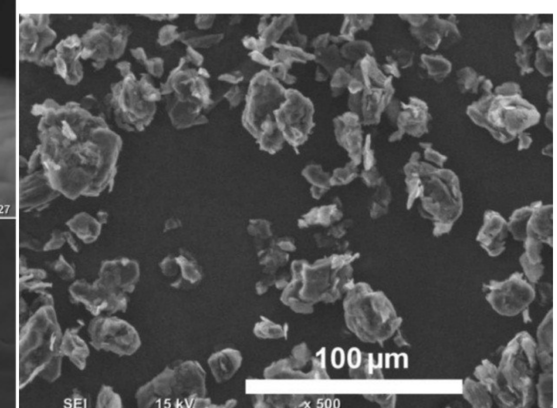

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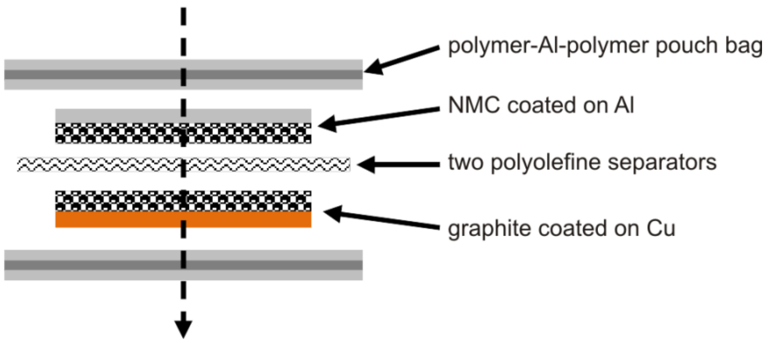
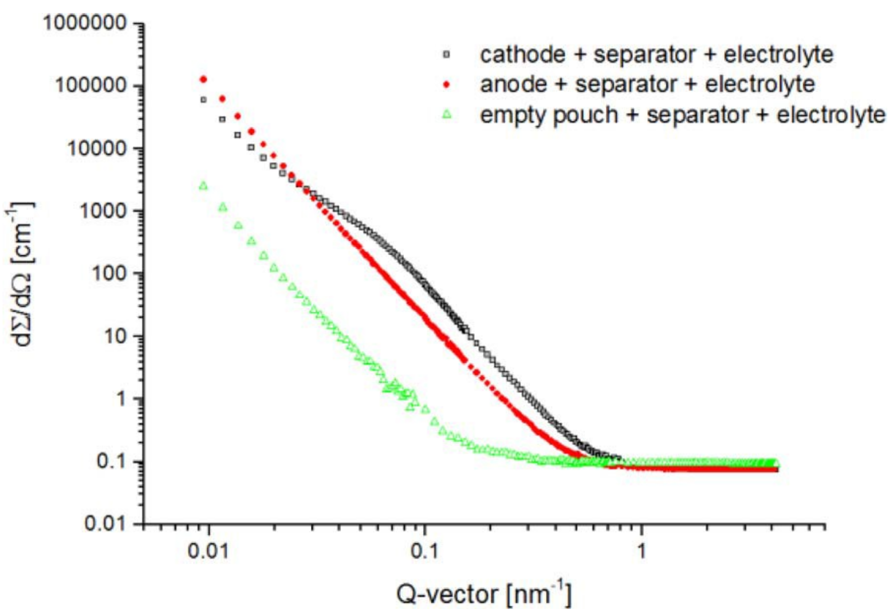
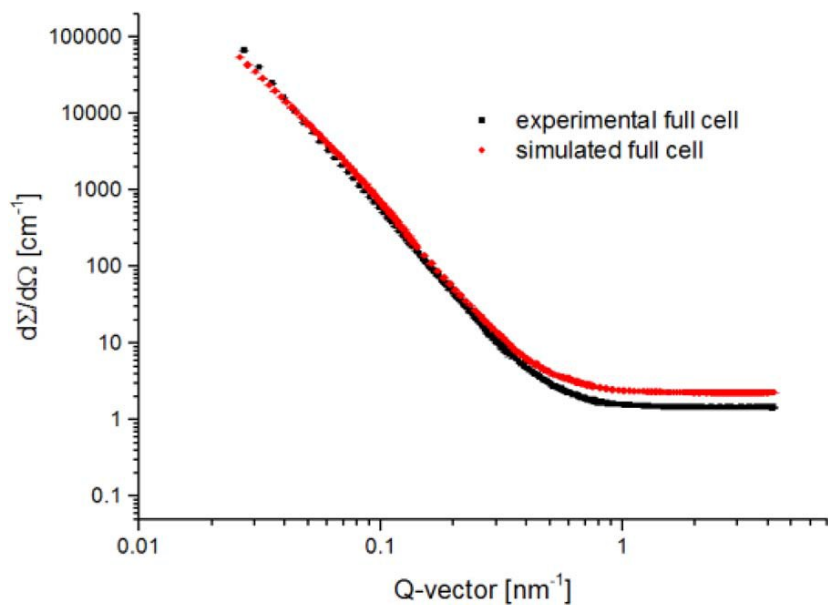


- Superposition of signals
- measure single parts seperately first

Full Cell = 1x Empty cell + 1x Cathode 1x Anode





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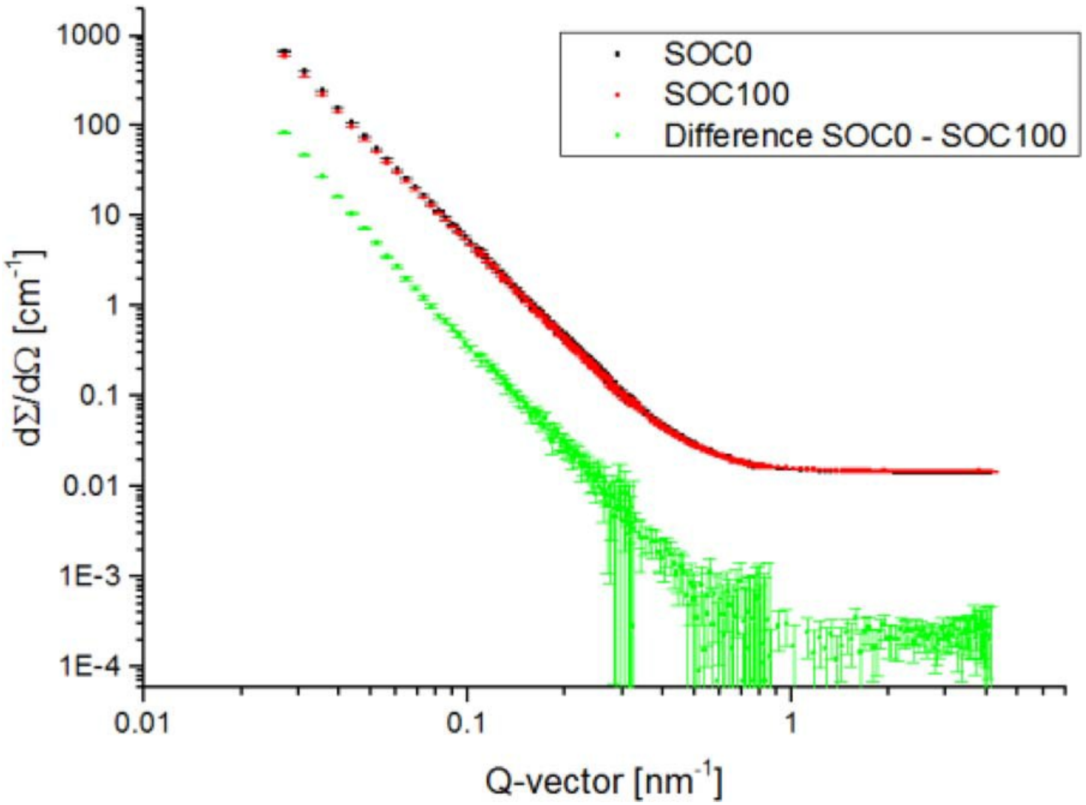

Observations in situ SANS:

- uncharged (SOC0 - **black**)
  charged (SOC100 - **red**)
  Difference plot - green
- No changes to curve shape
- P(Q) and S(Q) ~ constant !
- no change to shape of particles or arrangement of particles in space !

Full Q-Range 0.02 – 4 nm^{-1}
3 SANS-configurations measured
Time required 5min + 10min + 1h

- But small overall intensity shift along y-axis
- overall intensity decrease

$\Rightarrow$ **changes in $\Delta\rho^2$?**

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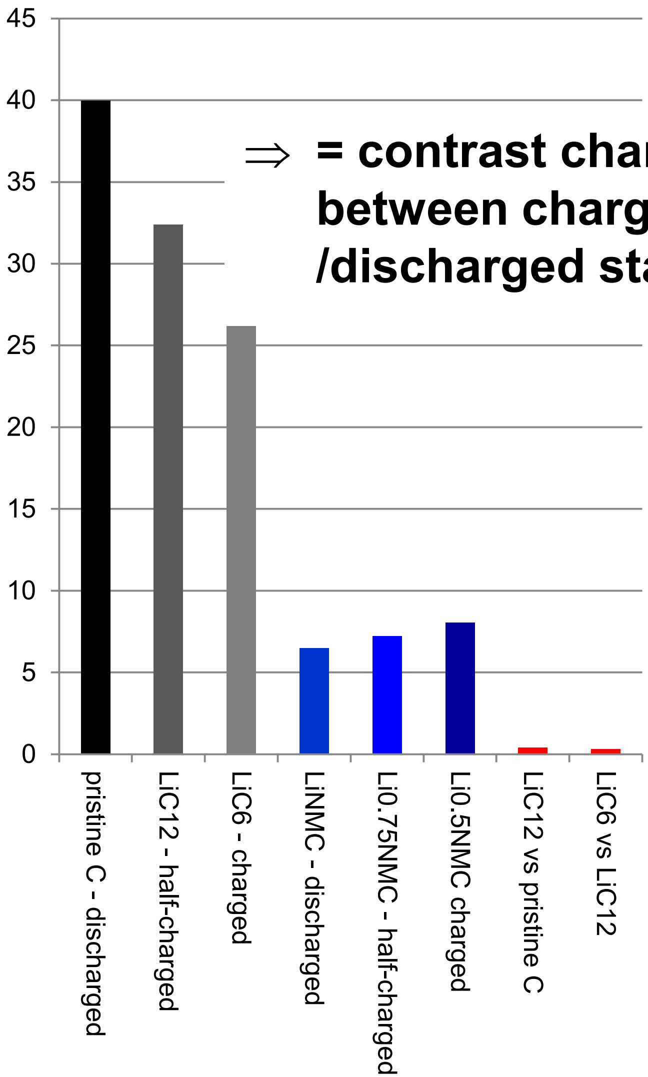
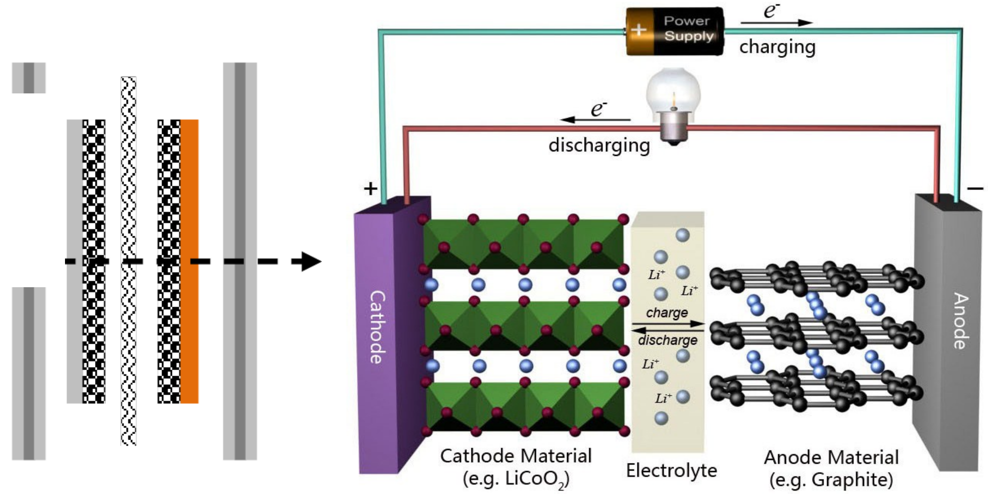
in situ SANS with Li-ion battery cells

$\Delta\rho^2$ vs electrolyte x 10^{10}[cm^{-2}]



⇒ **= contrast change between charged /discharged state**

Contrast changes in side the battery ?

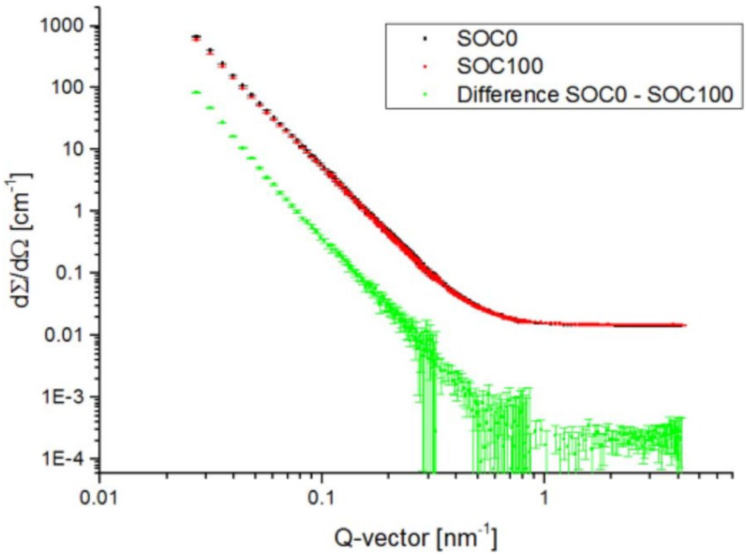


Charging reactions:

anode: C + Li^+ + e^- ⇋ LiC_x (x = 6,12, ...)

cathode: $LiMO_2$ ⇋ $Li_{1-x}MO_2$ + Li^+ + e^-

- Contrast between particles and eletrolyte (electrolyte = constant during reaction)
- SLD decrease when Graphite particles are more and more lithiated



How can we model the contrast change and the resulting intensity variation on a particle size level with in situ experiments ?

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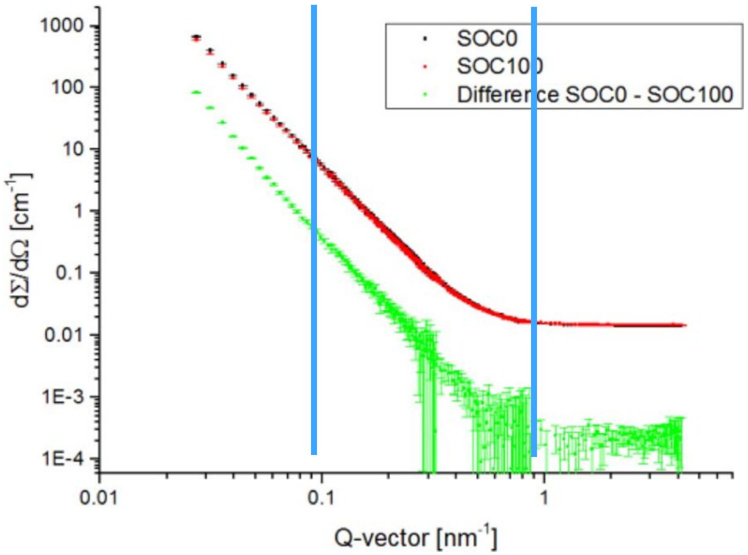
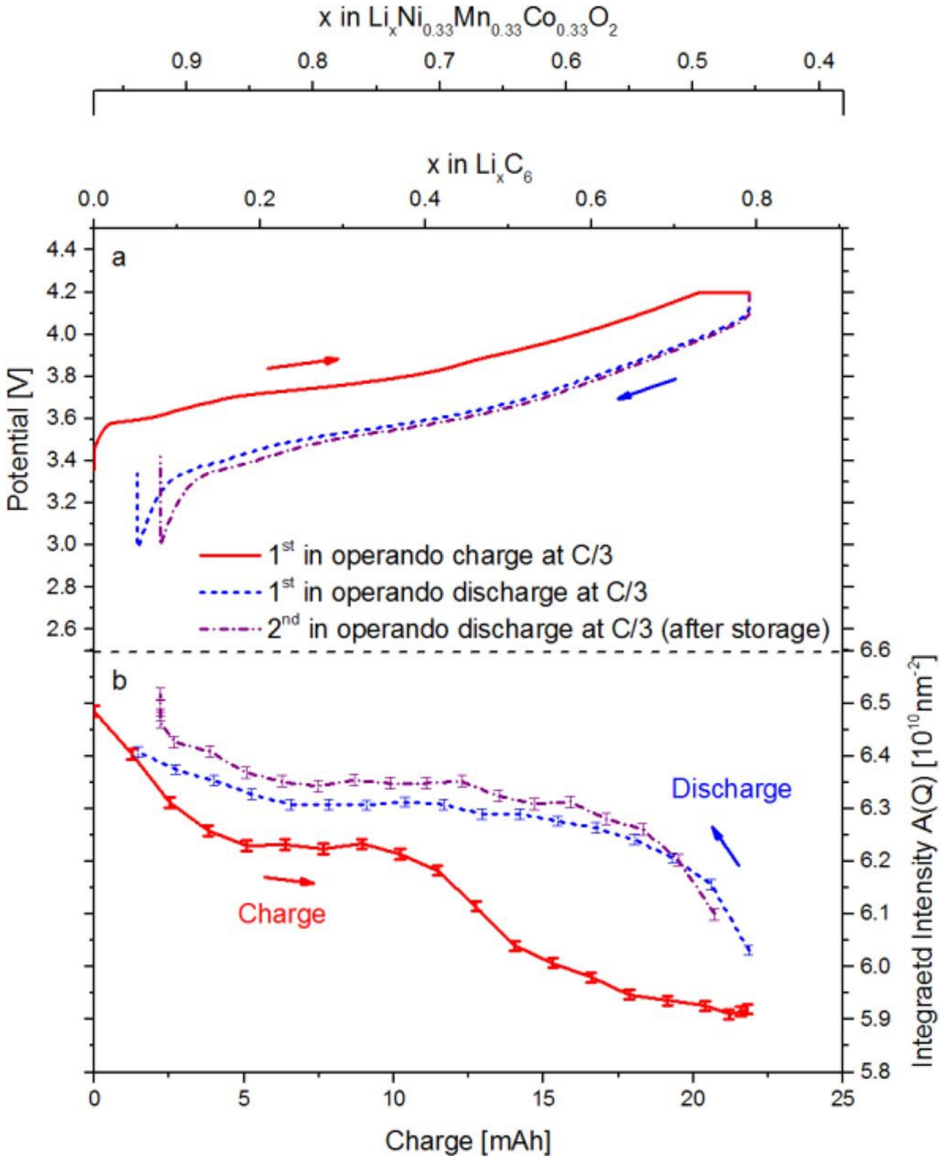


Limit Q-Range for in situ experiment
Q-Range = 0.09 – 0.9 nm^{-1}
SD/Col=8m, λ=6
increase time resolution (10min vs >1h)
Full cell charge in 3h (C/3 Rate)
=> 18 data points

+ simplify the data by integration of whole SANS-curves for each time interval of the in situ measurement



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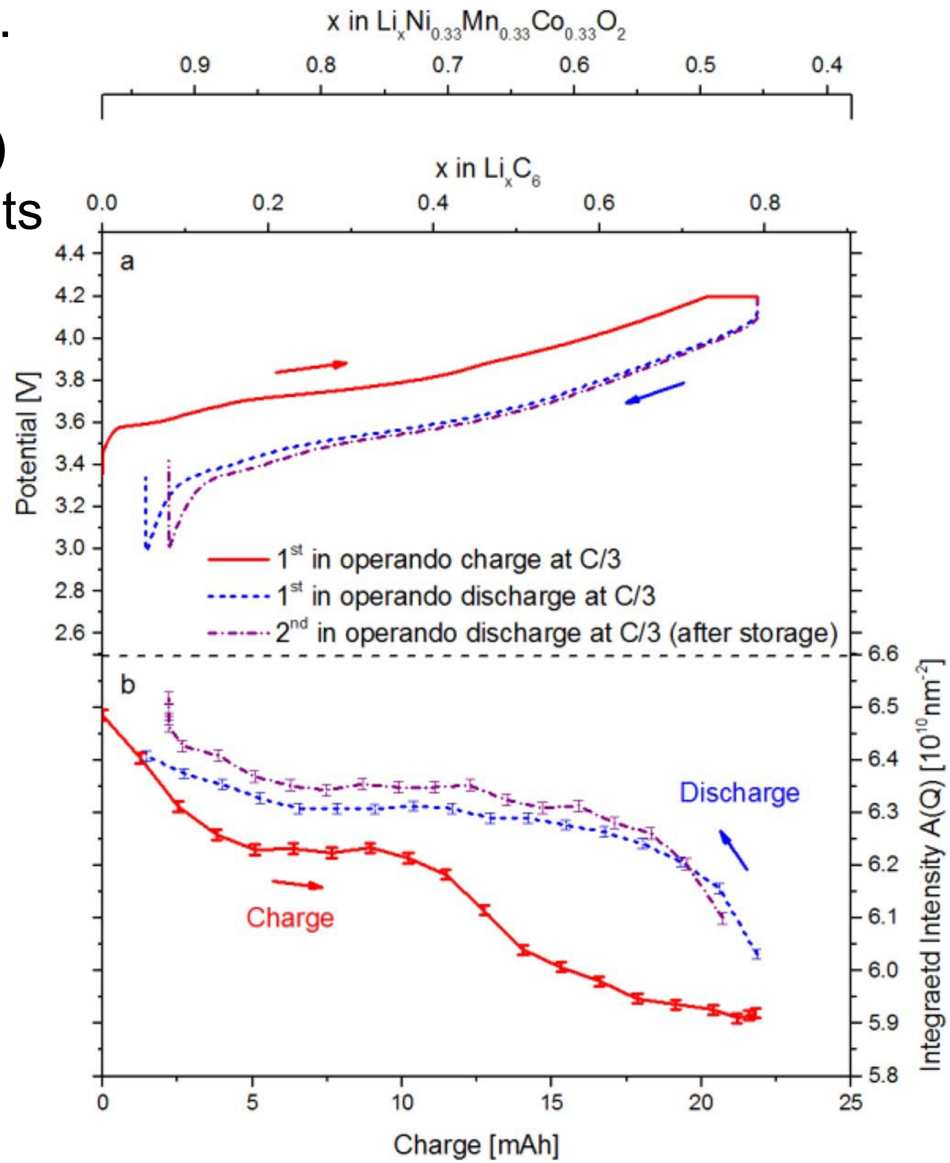
in situ SANS with Li-ion battery cells

Plot integrated scattering intensity vs. charged capacity mAh
=time, respectively = x(Li) in Li_xNMC)
time / step = 10min in first experiments

Observations:

- Charging:
  Gradual intensity decrease
- Step-like feature around 10 mAh
- Discharging
  much longer step visible
- intensity returns back to initial value
- reproducible
  (every cycle)



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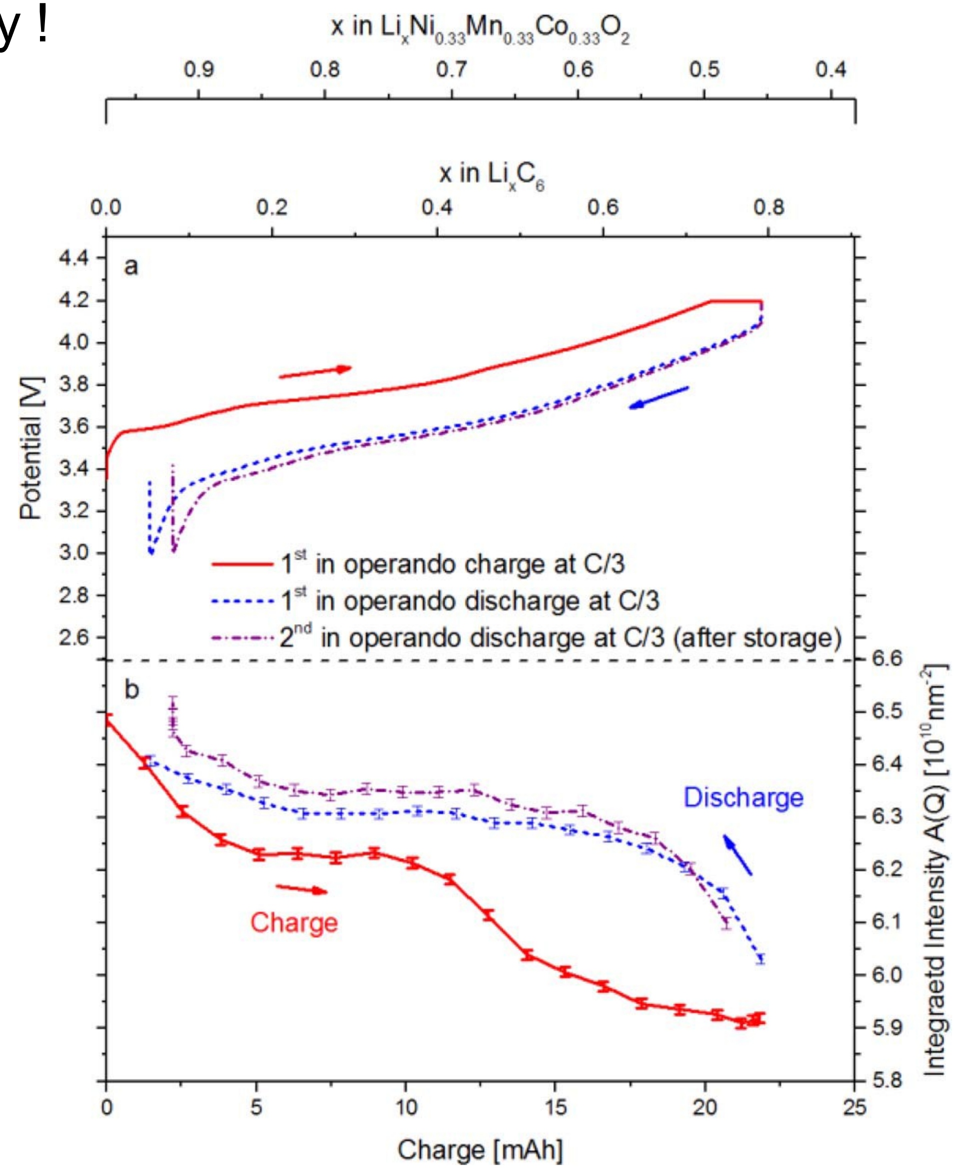
in situ SANS with Li-ion battery cells

Combine SANS and Electrochemistry !

Plot integrated intensity vs dV/dQ



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in situ SANS with Li-ion battery cells

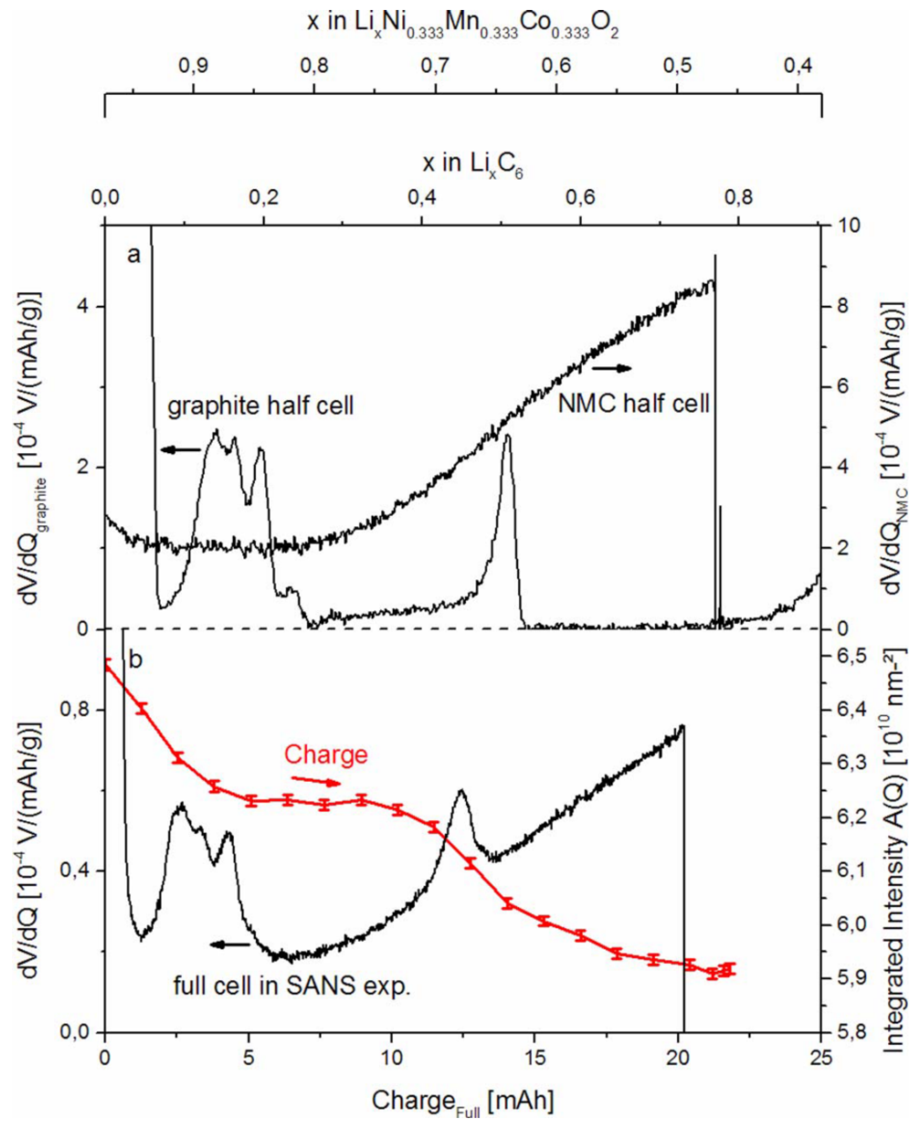
Combine SANS and Electrochemistry !

Plot integrated intensity vs dV/dQ

- Peaks in dV/dQ plot indicate 2-phase transitions

- in graphite/Li system:
  $C_{Graphite}$ => LiC_{24}
  LiC_{24} => LiC_{18}
  LiC_{18} => LiC_{12}
- separated peak between 10-15 mAh:
  LiC_{12} => LiC_6

- for NMC/Li system:
  Solid-Solution
  => no Peaks



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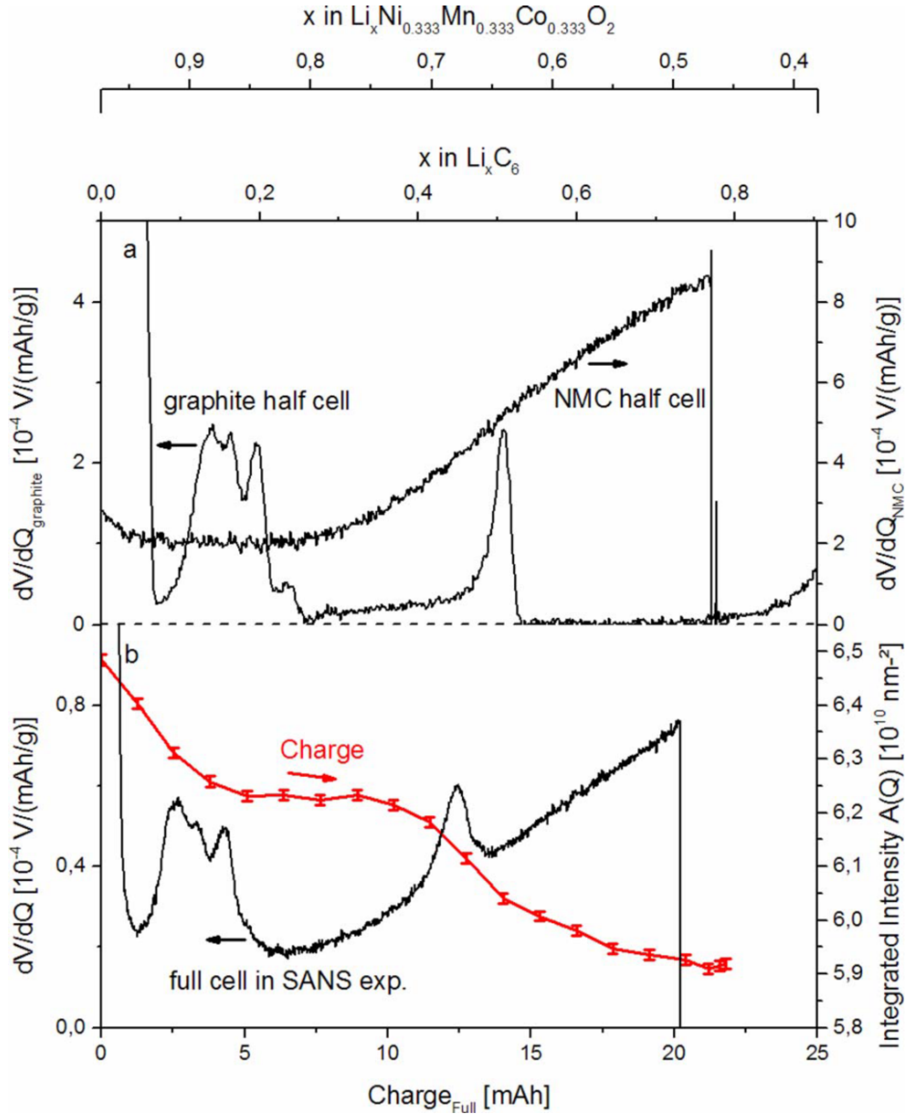
Combine SANS and Electrochemistry:

Plot integrated intensity vs dV/dQ

Observations:

- Intensity drops in SANS coincide with peaks in 1st derivative dV/dQ plot
- We can model Li-migration with SANS !



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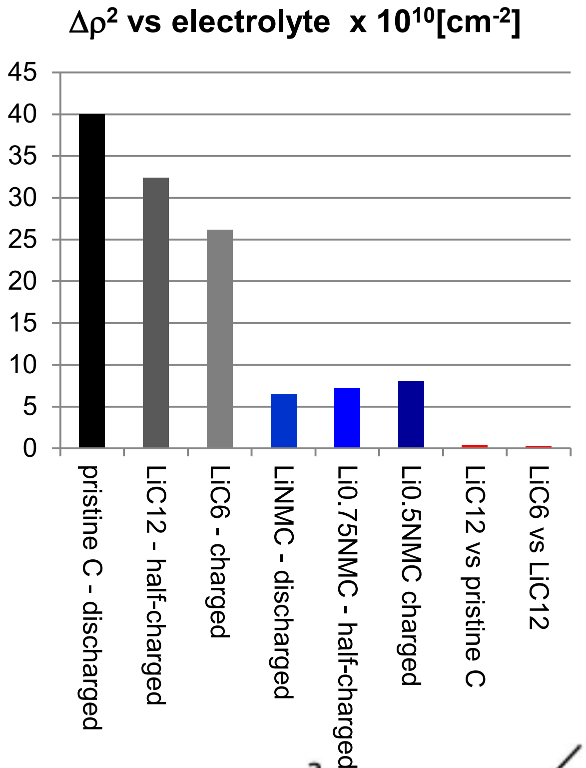
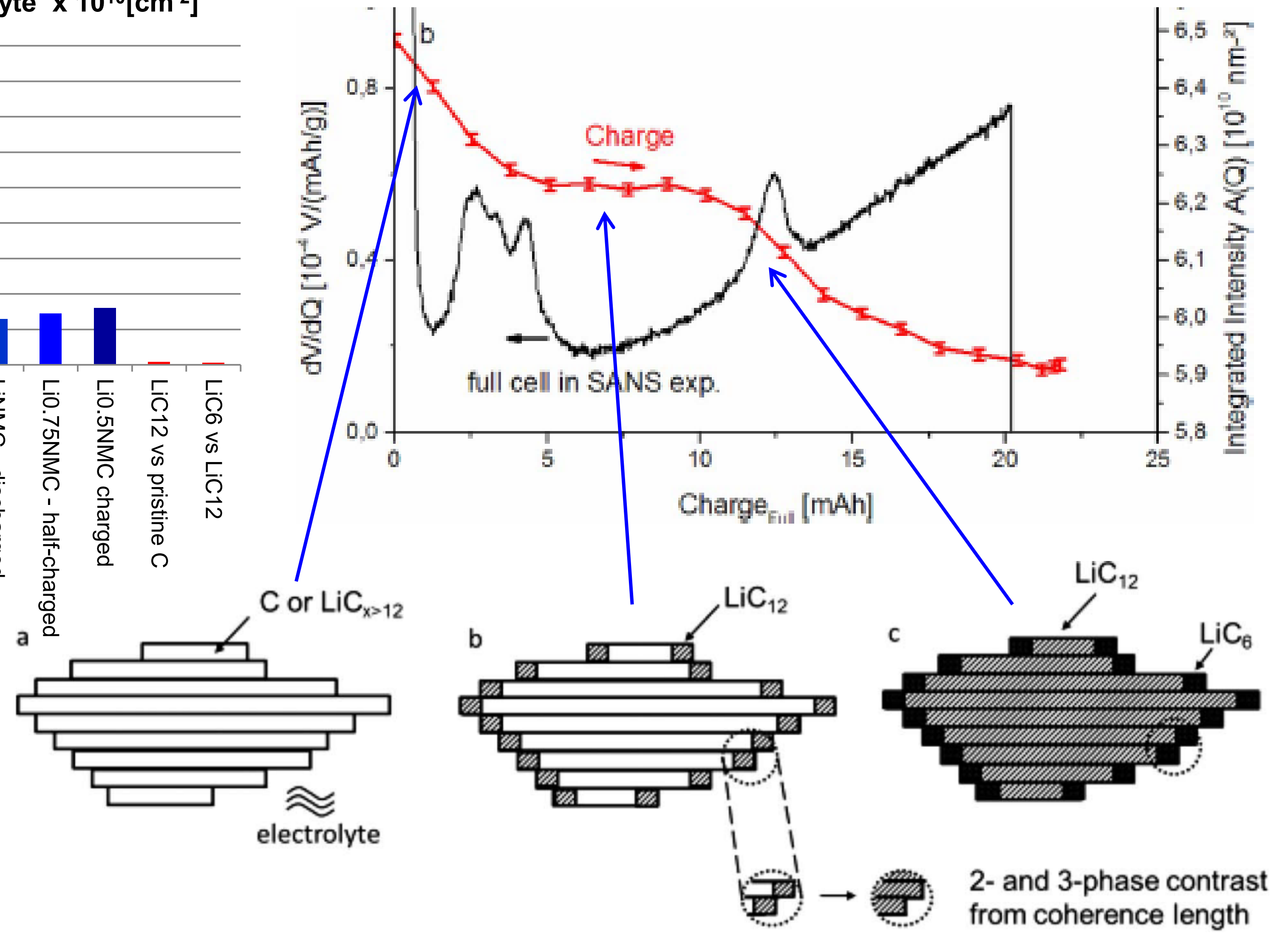
Modelling Li-migration

Interpretation of in situ SANS:





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Conclusion & Outlook

Conclusion

- In situ SANS allows monitoring the lithiation reactions on a particle level due to contrast changes
- under realistic conditions (full cell data, conventional chemistry)

Outlook

- Creation of kinetical and dynamical models correlating contrast & intensity changes with chemical reactions

⇒ alternative method for extraction of diffusion & transport parameters for graphite (particles) lithiation process

- Induce Li-plating on graphite particles (i. e. by cooling or using high C-Rate) and monitor with SANS
- Improving the time resolution to ~2-3 minutes/step should be possible

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- Dr. habil. R. Gilles[1]
- **J. Hattendorff[2]**
- I. Buchberger[2]
- Prof. Dr. H. Gasteiger[2]

[1] Heinz Maier-Leibnitz Zentrum (MLZ), Lichtenbergstr. 1 85748 Garching
[2] Lehrstuhl für Technische Elektrochemie, Lichtenbergstr. 4, 85748 Garching

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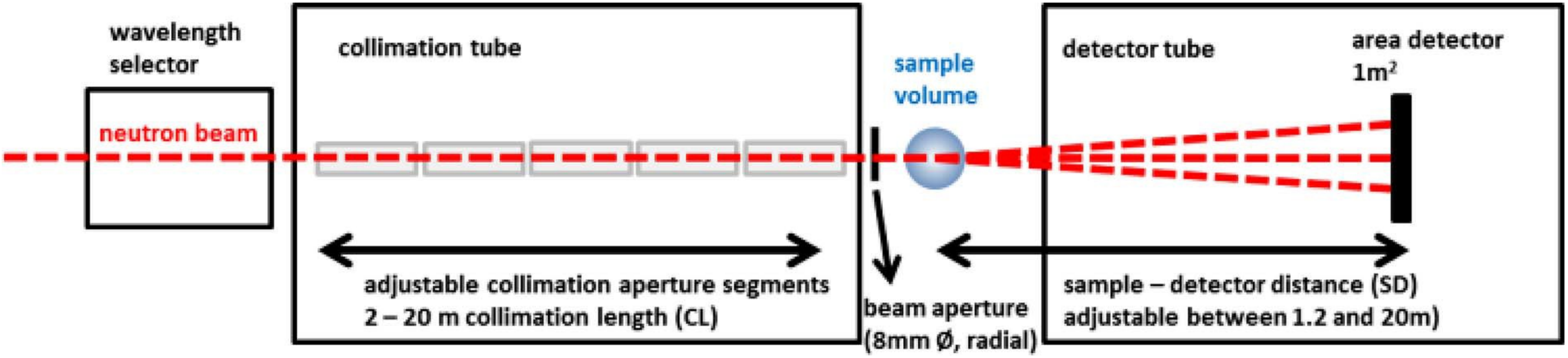
Bundesministerium für Bildung und Forschung

Thank you

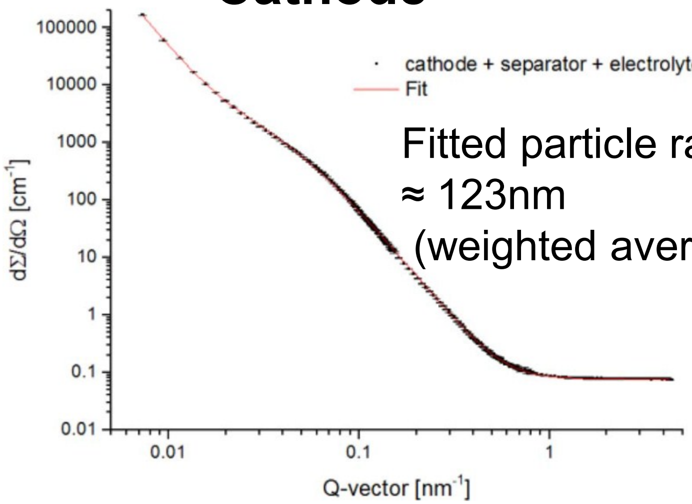
for your attention !

SANS-1 instrument setup

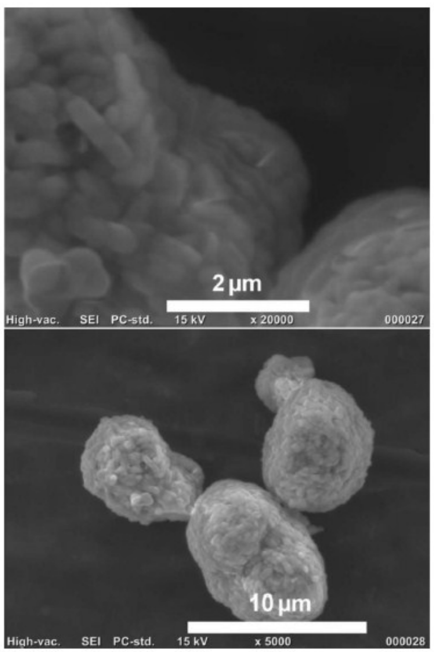


single component measurements
ex situ
3 configurations
full instrument Q-Range

Cathode



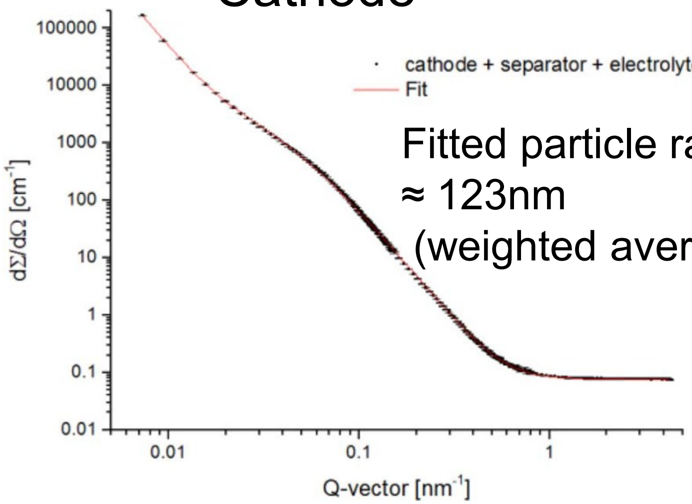
Fitted particle radius
≈ 123nm
(weighted average)



$$\underbrace{\frac{I_0 \times \sin((D-1)\arctan(Q \times x_i))}{(D-1) \times Q \times x_i (1 + Q^2 x_i^2)^{((D-1)/2)}}}_{\text{mass fractal}} + \underbrace{c_0 + c_1 \times Q^{-a}}_{\text{Porod-Background}}$$

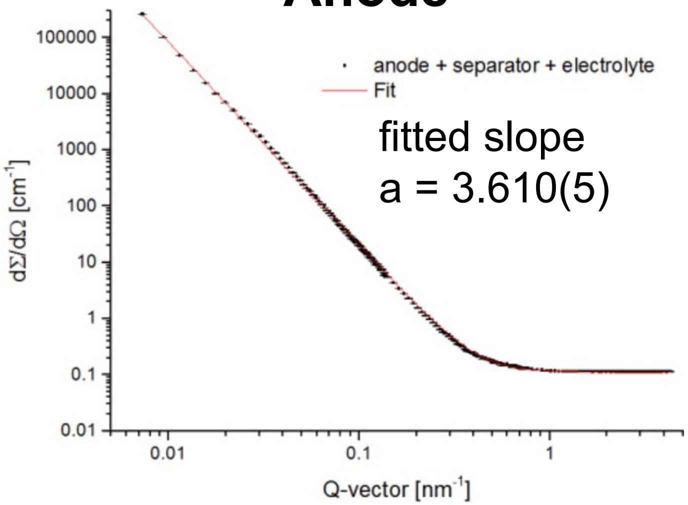
in situ SANS with Li-ion battery cells

Cathode



Fitted particle radius
≈ 123nm
(weighted average)

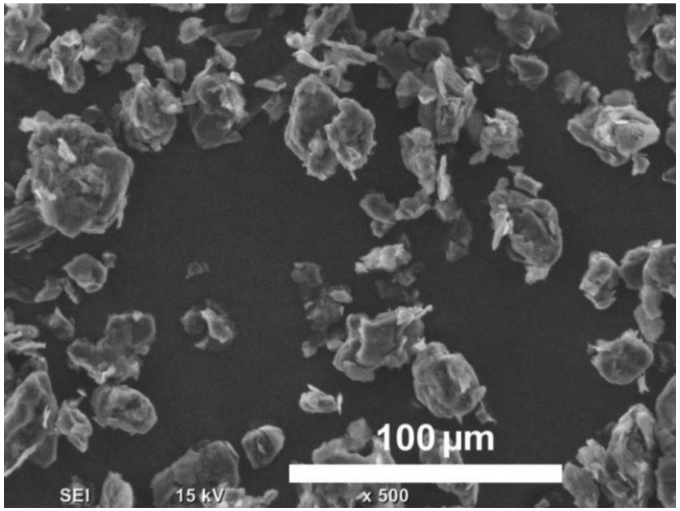
Anode



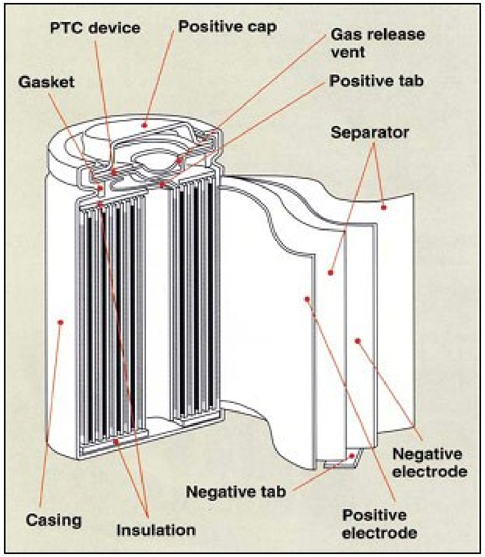
fitted slope
a = 3.610(5)

$$c_0 + c_1 * Q^{-a}$$

very large particles (>10µm)
⇒ only surface scattering
⇒ Fit as Porod or surface fractal



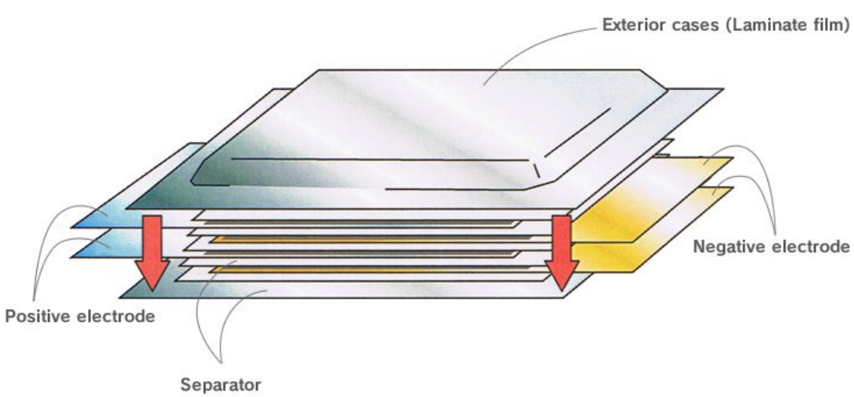
Introduction to Li-ion battery systems



Rolled electrode layers

Different Cell types can be assembled

18650 type – i. e. Sony



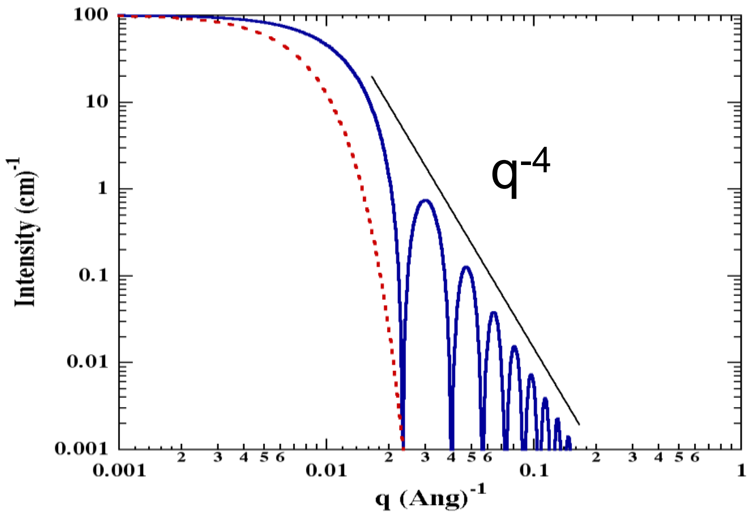
stacked electrode layers

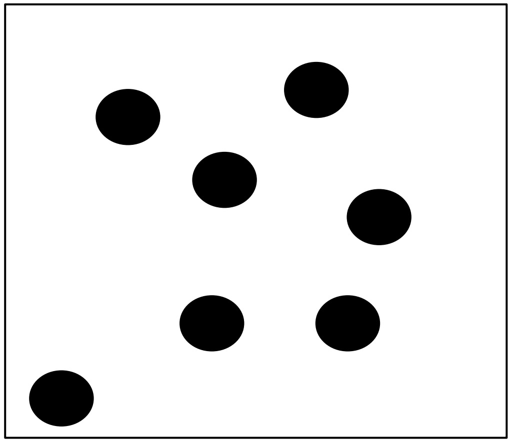
prismatic cell
(hard case)

Pouchbag
(soft case)

Principles of small-angle scattering

$$I(Q) = K\Delta\rho^2 N \times P(Q) \times S(Q)$$





monodisperse spheres
(with smooth interface)

P(Q) =
Form factor or shape factor
„How do the scattering objects look like (i.e. spheres, ellipsoids, etc.)“

Image Source: Presentation Winter School for Synchrotron Radiation
Small-angle scattering in materials science by J. Ilavsky,

Principles of small-angle scattering

$$I(Q) = K\Delta\rho^2 N \times P(Q) \times S(Q)$$

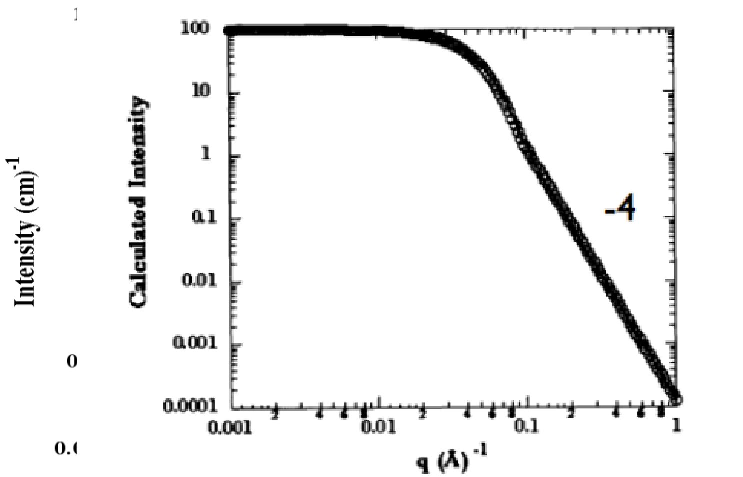
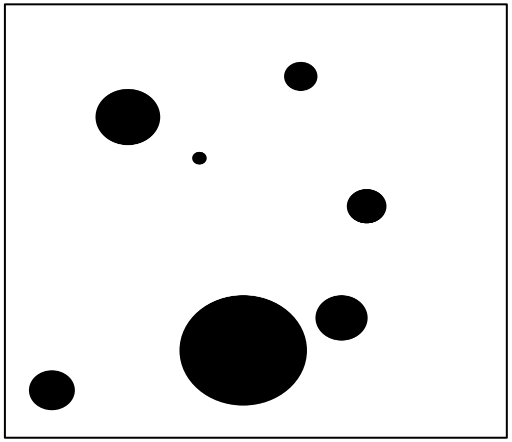


Fig. 11. Calculated scattering (○) from polydisperse spheres with Porod surfaces (power law −4). The solid line follows equation (24) with $R_g = 39.495$ Å as calculated and $P = 4$, $G = 100$ cm^{-1} (fixed in the sphere calculation) and $B = 0.000\,127\,52$ from Porod's law.

monodisperse spheres (with smooth interface)

polydisperse Spheres



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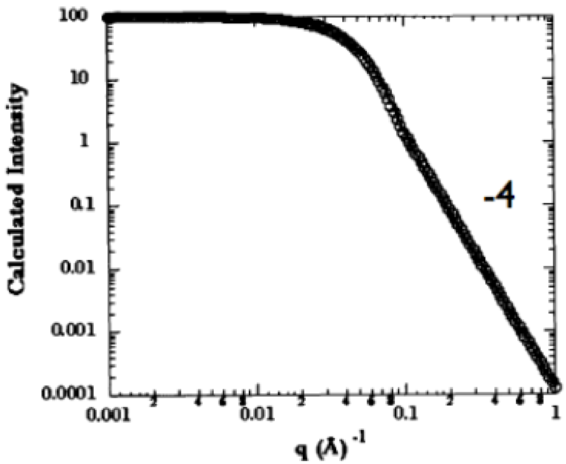


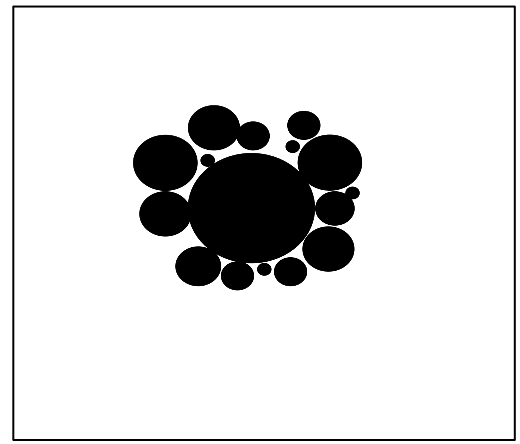
Fig. 11. Calculated scattering (○) from polydisperse spheres with Porod surfaces (power law −4). The solid line follows equation (24) with $R_g = 39.495$ Å as calculated and $P = 4$, $G = 100\ \mathrm{cm}^{-1}$ (fixed in the sphere calculation) and $B = 0.000\,127\,52$ from Porod's law.

with $d_f = 2$) and $B = 0.08 = 2G/R_g^2$ from equation (30).

polydisperse Spheres

polydisperse spheres

mass fractal aggregate

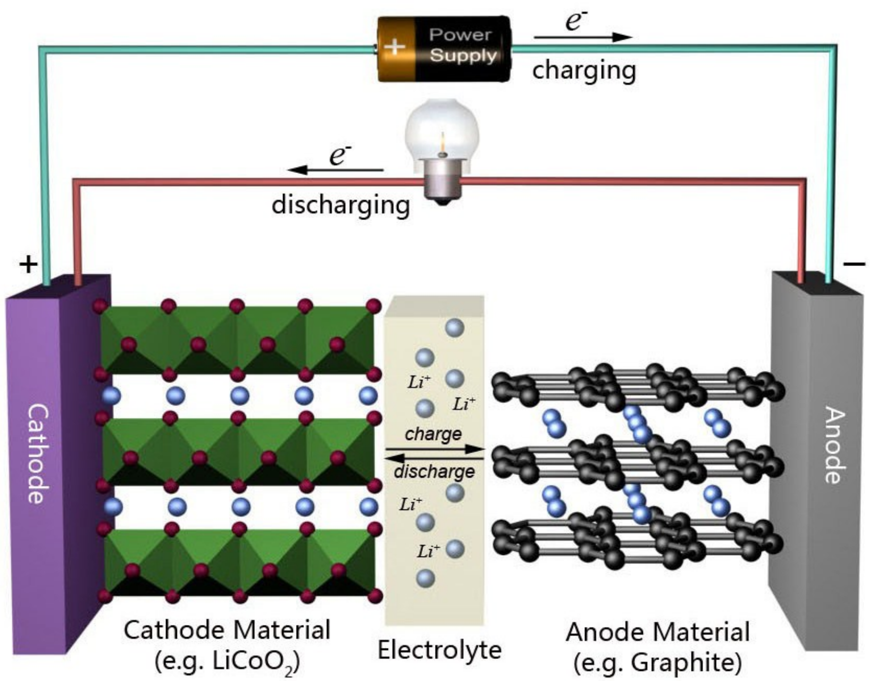


S(Q) =
Structure factor
„How are the objects arranged in space“

Image Source: Presentation Winter School for Synchrotron Radiation
Small-angle scattering in materials science by J. Ilavsky,

NMC-Graphite-system

- established in commercial batteries
- state of the art:
- Graphite-anode
- layered oxide NMC-cathode ($LiNi_{1/3}Mn_{1/3}Co_{1/3}O_2$)
- electrolyte: EC:EMC 3:7 / 1M $LiPF_6$



Charging reactions:

anode: $C + Li^+ + e^- \leftrightharpoons LiC_x$ (x = 6,12,...)

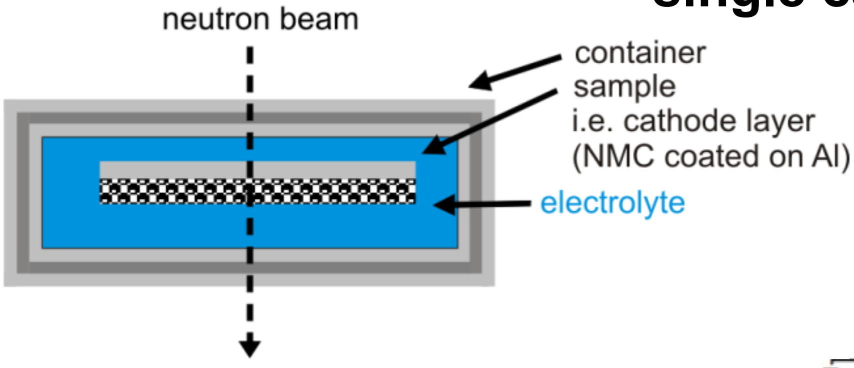
cathode: $LiMO_2 \leftrightharpoons Li_{1-x}MO_2 + Li^+ + e^-$

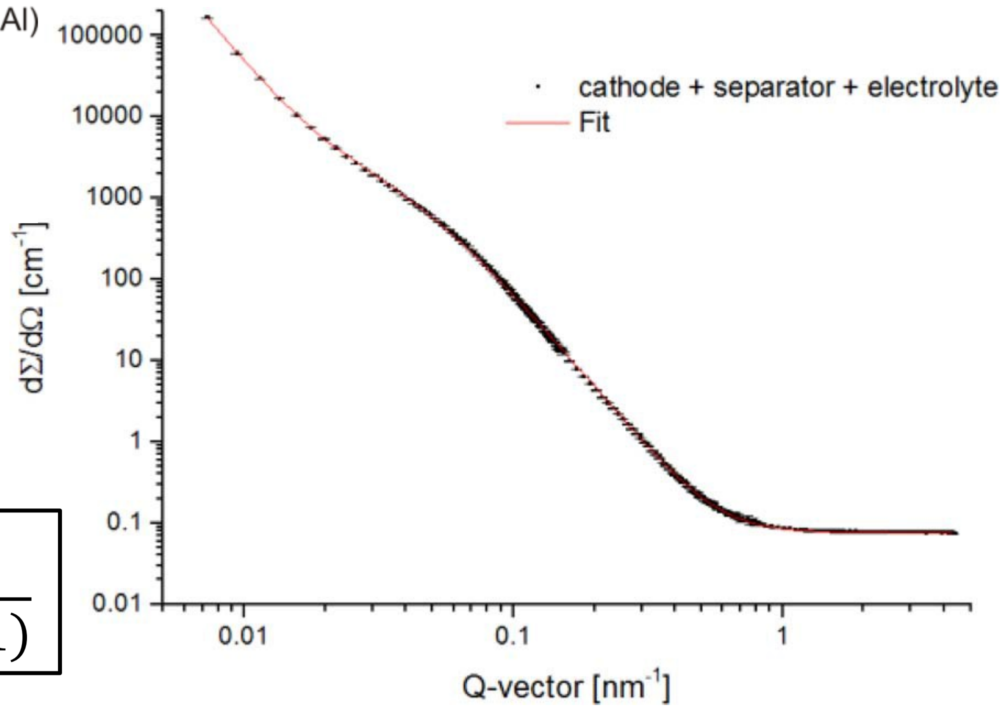
intercalation type reactions
solid-solution on cathode
mix of solid-solution / multiple step transition on anode

image taken from: http://research.chem.psu.edu/axsgroup/Ran/research/energystorage.html

classical approach

single cathode layer



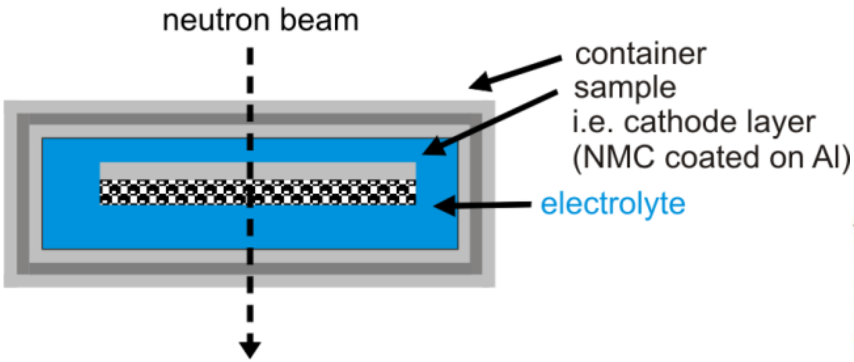


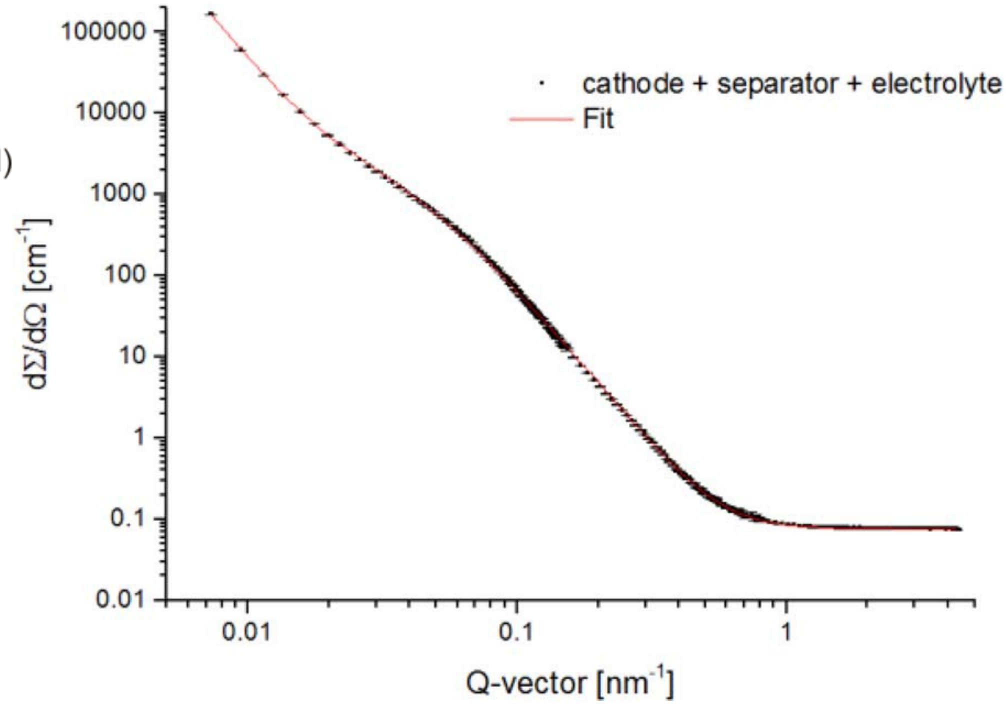
cathode layer only
superposition of Porod-like-background and mass fractal particle distribution:

$$x_i^2 = \frac{2R_g^2}{D(D+1)}$$

Parameters:
c_0 = 0.11145(3)
c_1 = 0.000250(7)
slope a = 4 (fixed)
I_0 = 7070(22)
D = 2.9544(3)
R_g = 86.9(1) nm.

S. Seidlmayer, J. Hattendorff, I. Buchberger, L. Karge, H. A. Gasteiger, and R. Gilles, J Electrochem Soc, 162 (2), A3116-A3125 (2015).





cathode layer only
superposition of Porod-like-background and mass fractal particle distribution:

Parameters:
c_0 = 0.11145(3)
c_1 = 0.000250(7)
a = 4 (fixed)
I_0 = 7070(22)
D = 2.9544(3)
R_g = 86.9(1) nm.

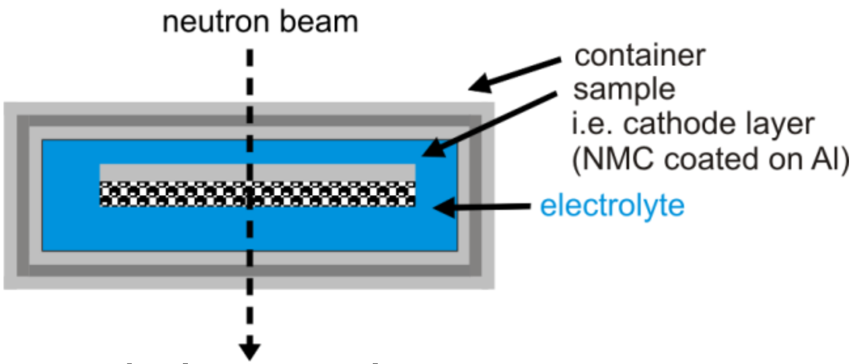
$$R_{disc} = \sqrt{\frac{1}{2}} R_g \approx 123nm$$

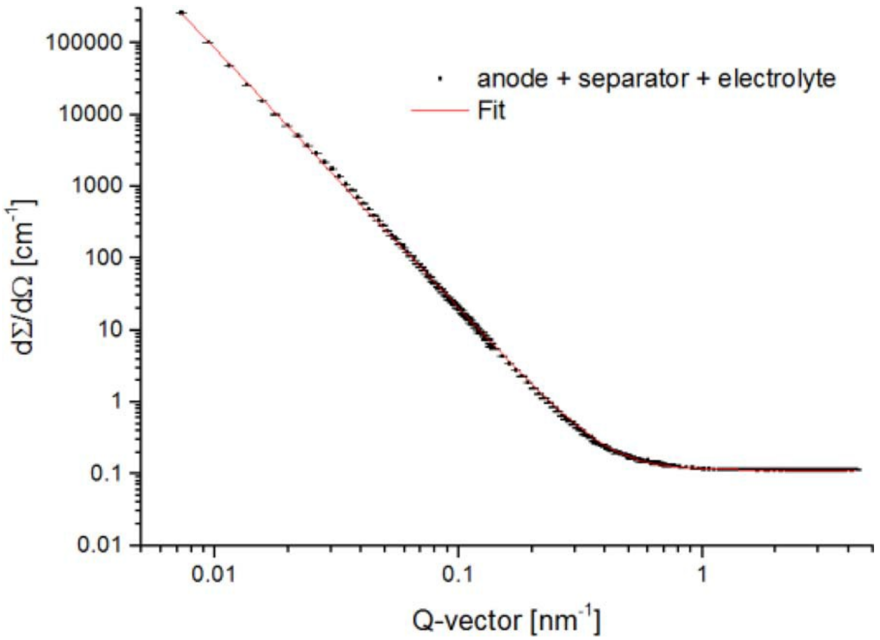
SEM-Images of dry electrode material consistent with SANS

S. Seidlmayer, J. Hattendorff, I. Buchberger, L. Karge, H. A. Gasteiger, and R. Gilles, J Electrochem Soc, 162 (2), A3116-A3125 (2015).

in situ SANS with Li-ion battery cells

single anode layer





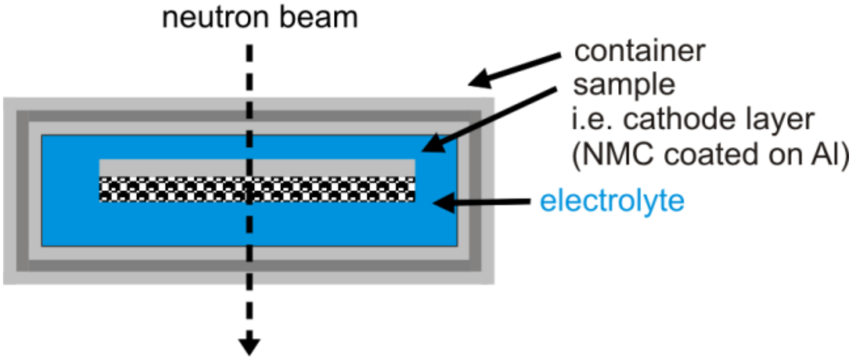
anode layer only
Porod-like-background

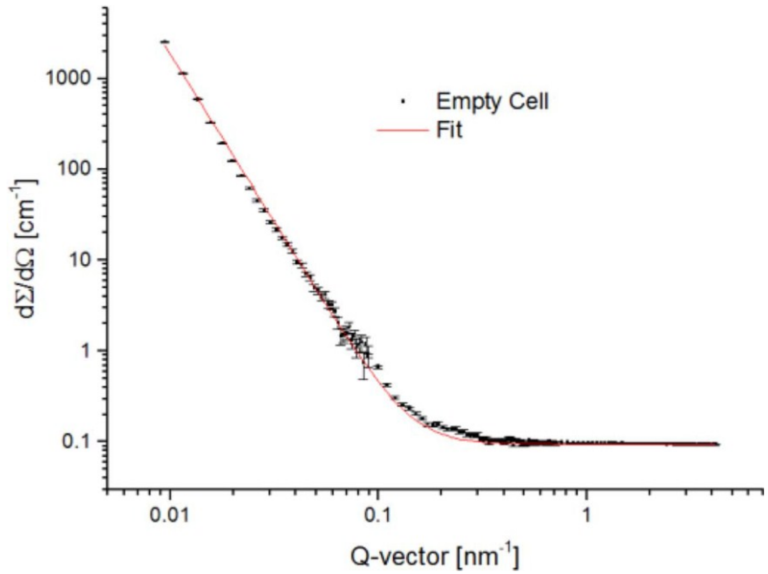
c_0 = 0.1129(3)
c_1 = 0.0050(1)
a = 3.610(5)

SEM-Image of dry electrode material
Particles are very large > 10µm
consistent with SANS (Porod-like)

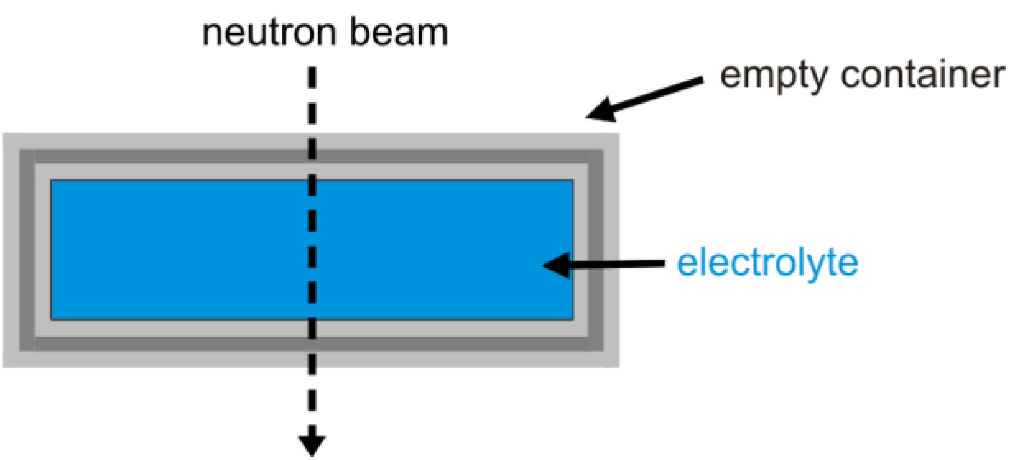
S. Seidlmayer, J. Hattendorff, I. Buchberger, L. Karge, H. A. Gasteiger, and R. Gilles, J Electrochem Soc, 162 (2), A3116-A3125 (2015).

Measure sample in a container





Start with empty container



empty cell modeled with a Porod-Background function:
slope a = 3.70(1)
c0 = 0.0947(3)
c1 = 7.1(2) x10−5.

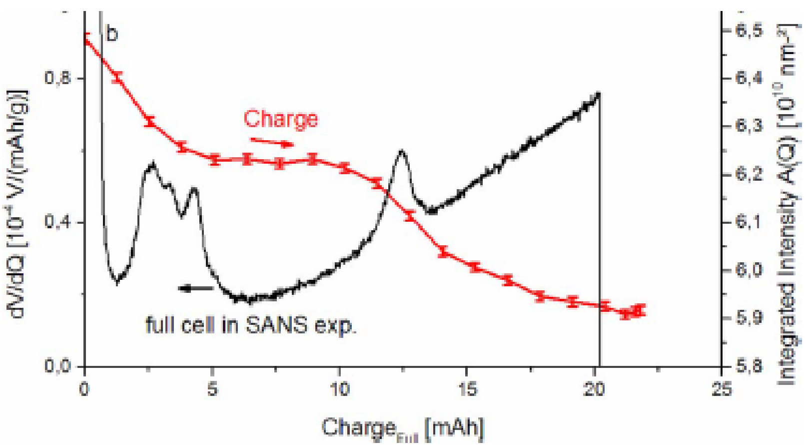
$$c_0 + c_1 * Q^{-a}$$

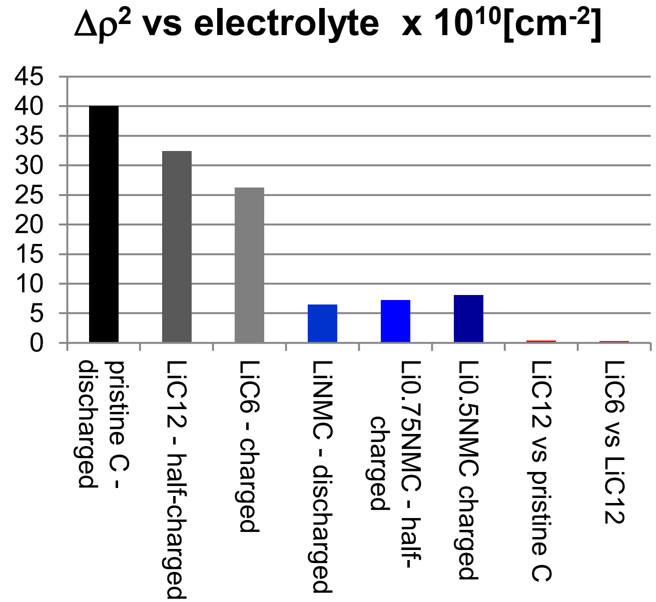
S. Seidlmayer, J. Hattendorff, I. Buchberger, L. Karge, H. A. Gasteiger, and R. Gilles, J Electrochem Soc, 162 (2), A3116-A3125 (2015).

Modelling Li-migration

Interpretation of in situ SANS:

- Intensity Plateau equals a shell of lithiated carbon on the outer particle
- Model of the lithiation process:
  Carbon particles are lithiated from surface to core
- drop of SANS intensity due to change in contrast between electrolyte and particles
- contrast between lithiated surface and pristine graphite core is nearly ~0
- after surface is transformed into LiC_{12} no more contrast change (plateau region)
- when transformation of surface from LiC_{12} to LiC_6 starts further decrease in SANS intensity





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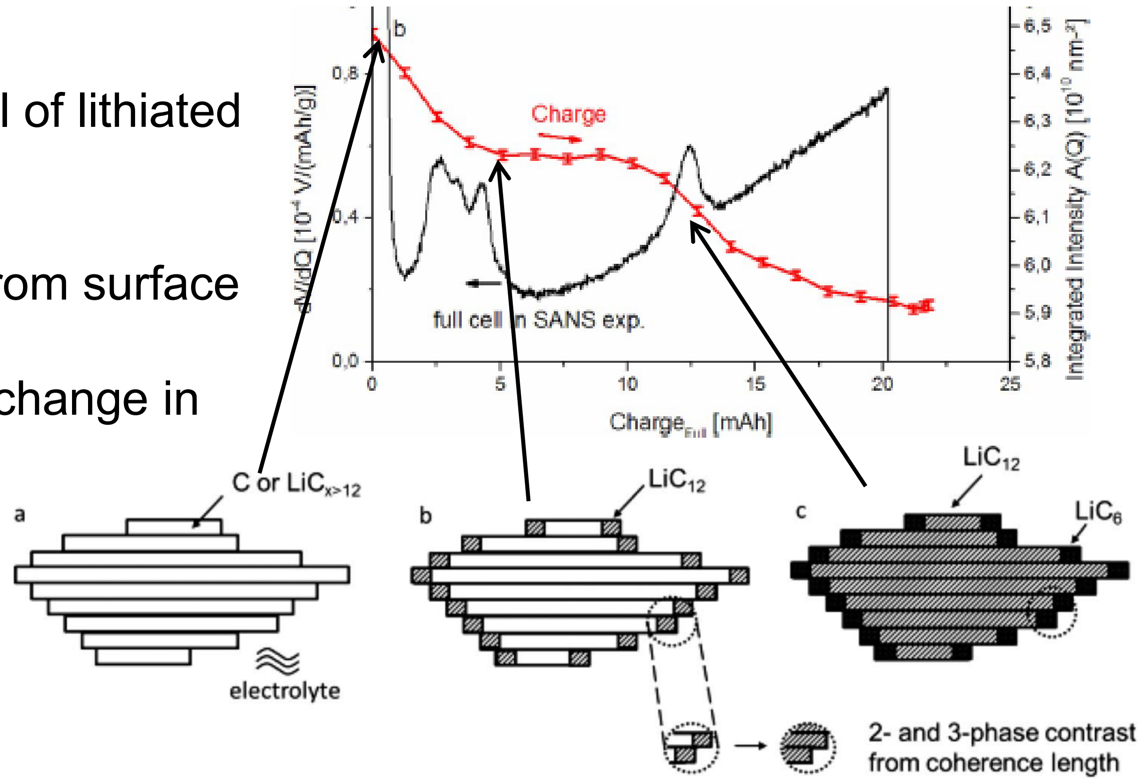
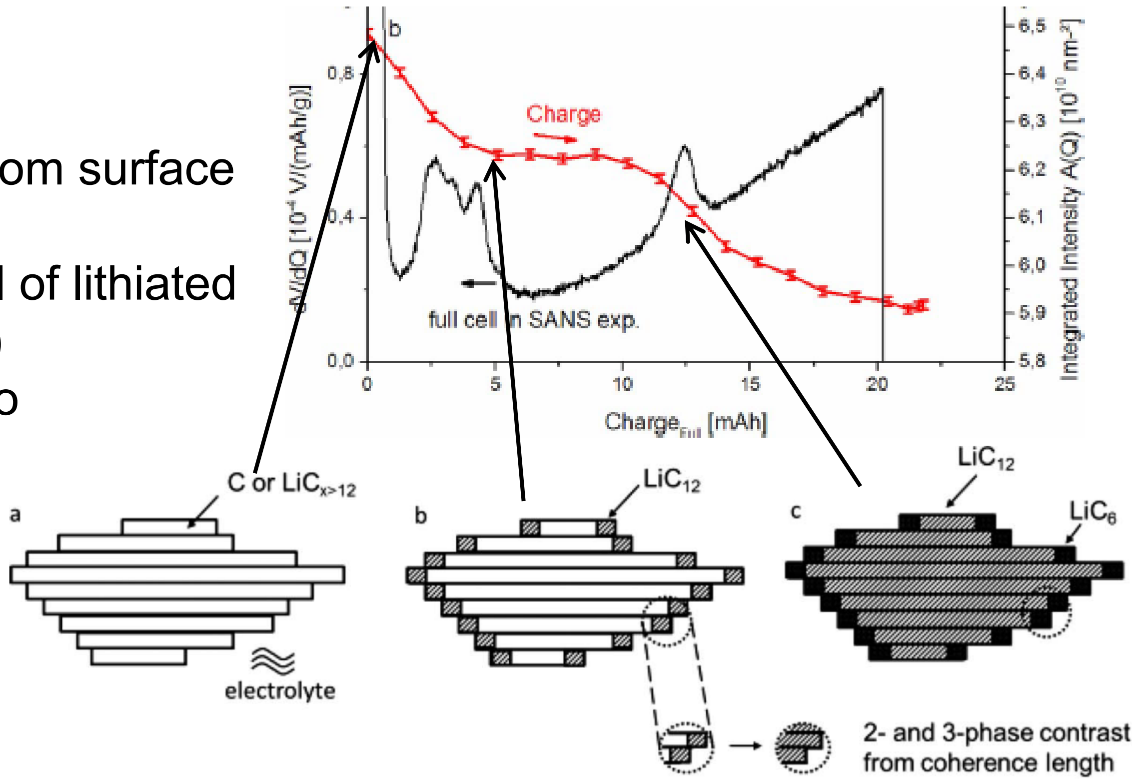


S. Seidlmayer, J. Hattendorff, I. Buchberger, L. Karge, H. A. Gasteiger, and R. Gilles, J Electrochem Soc, 162 (2), A3116-A3125 (2015).

Modelling Li-migration

Interpretation of in situ SANS:

- Model of the lithiation process: Carbon particles are lithiated from surface to core **(a => b)**
- Intensity Plateau equals a shell of lithiated carbon on the outer particle **(b)**
- after surface is transformed into LiC_{12} no more contrast change (plateau region) **(b => c)**
- when transformation of surface from LiC_{12} to LiC_6 starts further decrease in SANS intensity **(c)**



cell has 27.6 mAh total anode capacity

~13.8 mAh = all graphite must have completely changed to LiC_{12}

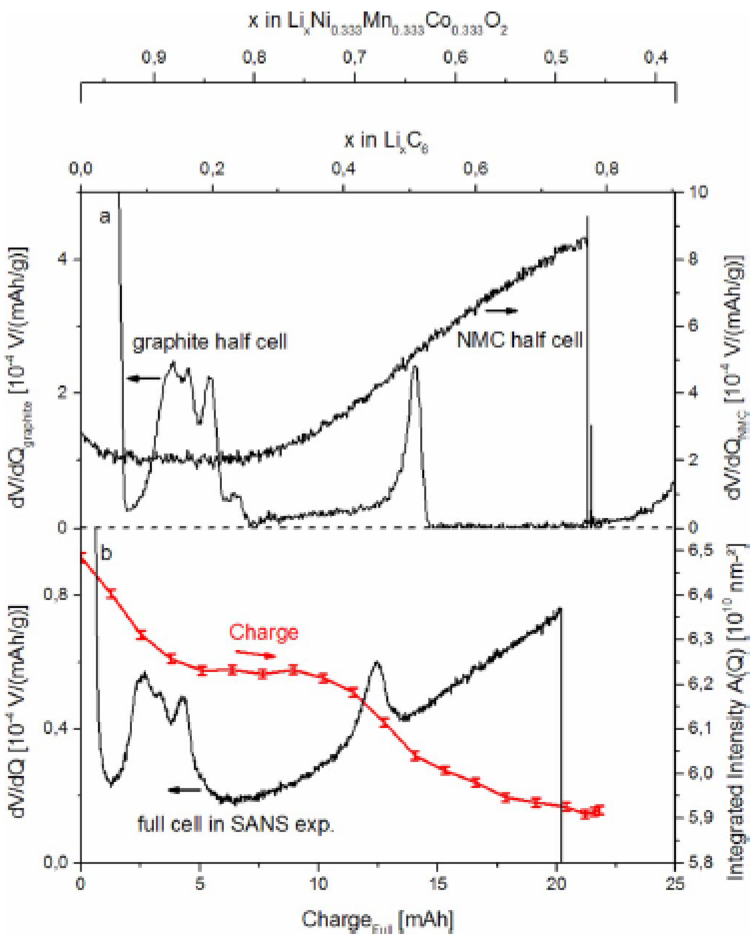
S. Seidlmayer, J. Hattendorff, I. Buchberger, L. Karge, H. A. Gasteiger, and R. Gilles, J Electrochem Soc, 162 (2), A3116-A3125 (2015).

Modelling Li-migration

Interpretation of in situ SANS:

=> Plot integrated scattering curves vs. 1st derivative dV/dQ

- Gradual SANS intensity decrease due to change to scattering contrast factor caused by the phase transitions:
- decrease up to first „plateau“ (region between 5-10 mAh)
  $C_{Graphite}$ => LiC_{24} => LiC_{18} => LiC_{12}
- 2nd decrease:
  LiC_{12} => LiC_6



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