Ion charge storage in supercapacitor nanopores quantified by modeling and *in situ* SAXS

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Ion electrosorption in nanoporous carbons

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Tracking the structural arrangement of ions in carbon supercapacitor nanopores using *in situ* small-angle X-ray scattering†

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A carbon nanopore model to quantify structure and kinetics of ion electrosorption with *in situ* small-angle X-ray scattering†

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Quantification of ion confinement and desolvation in nanoporous carbon supercapacitors with modelling and *in situ* X-ray scattering

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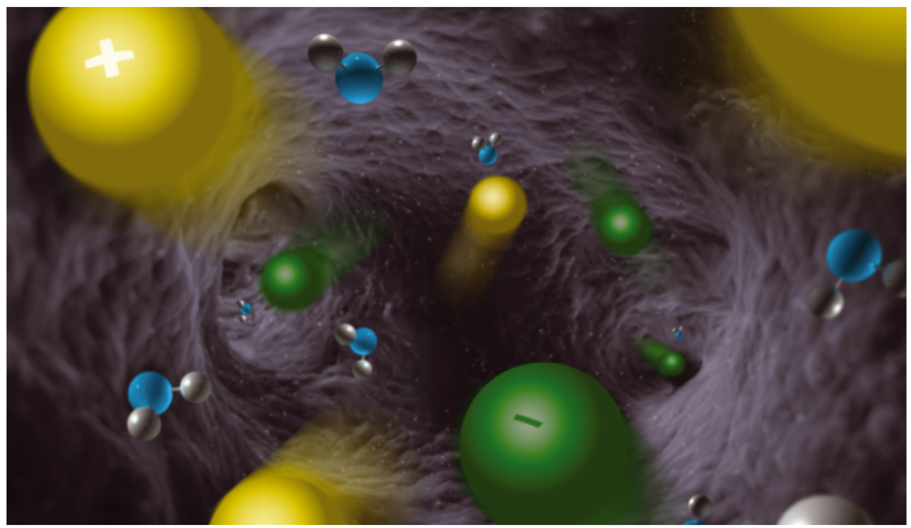
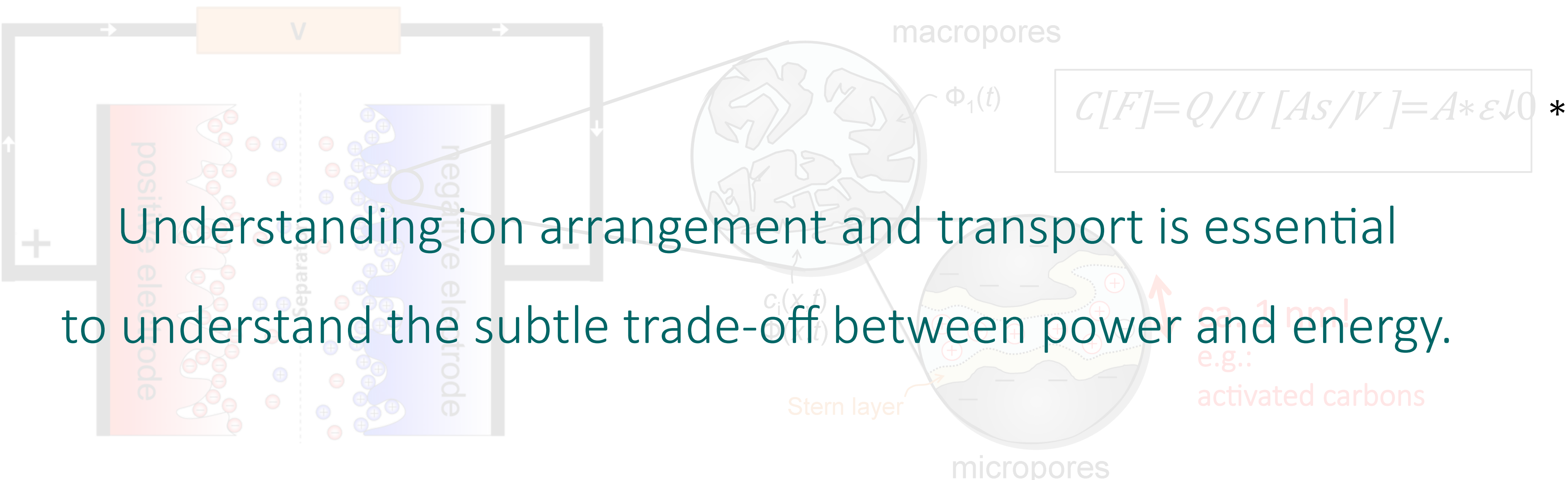


- Effective energy storage devices with high power densities.
- We study **activated and carbide derived carbons** with **aqueous 1M CsCl**
- Making pores smaller: energy density ↑ but power density ↓



Understanding ion arrangement and transport is essential to understand the subtle trade-off between power and energy.

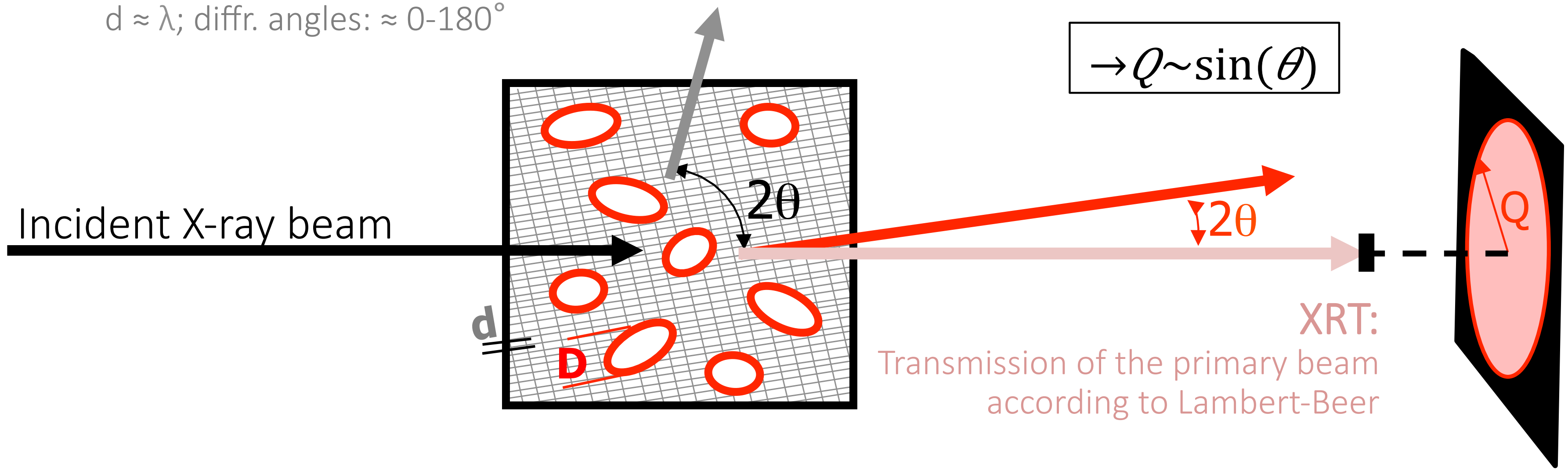
Adapted from F. Béguin, V. Presser, A. Balducci and E. Frackowiak, *Advanced Materials*, 2014, **26**, 2219-2251.

Introduction

X-ray scattering experiment at Synchrotron:

WAXS:
diffraction (peaks)/scattering from atoms or molecules on crystal lattice/disordered structure;
d ≈ λ; diffr. angles: ≈ 0-180°

SAXS:
diffuse scattering from particles, **pores**,...
(electron density fluctuations);
D >> λ; scattering angles: ≈ 0-10°



Why using a Synchrotron Radiation Source?

- Provides extremely high photon flux
- Time resolutions below one second easily achievable **(compared to Lab: ≈ 30min)**

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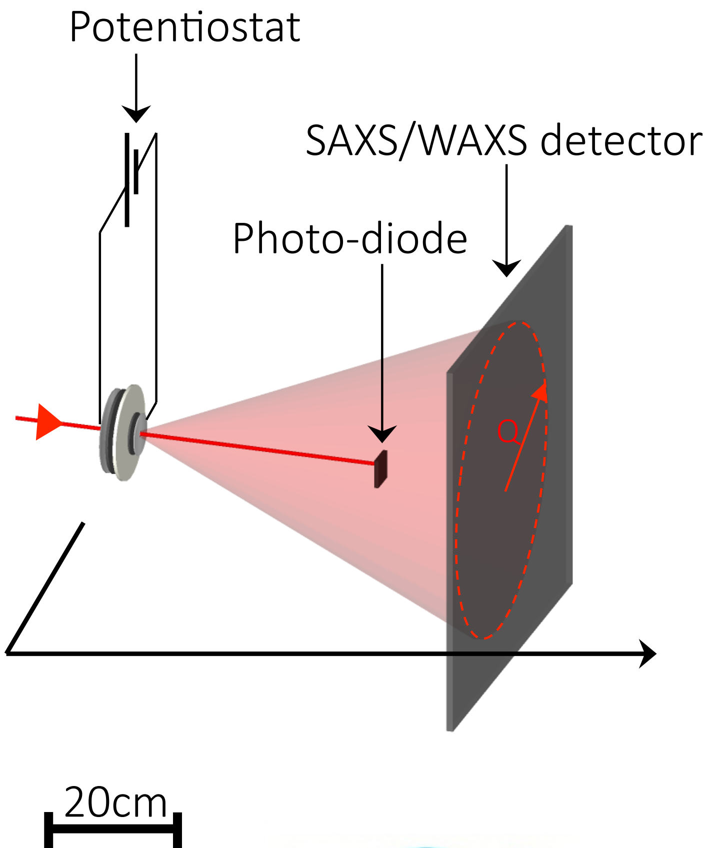
Principle - experiment



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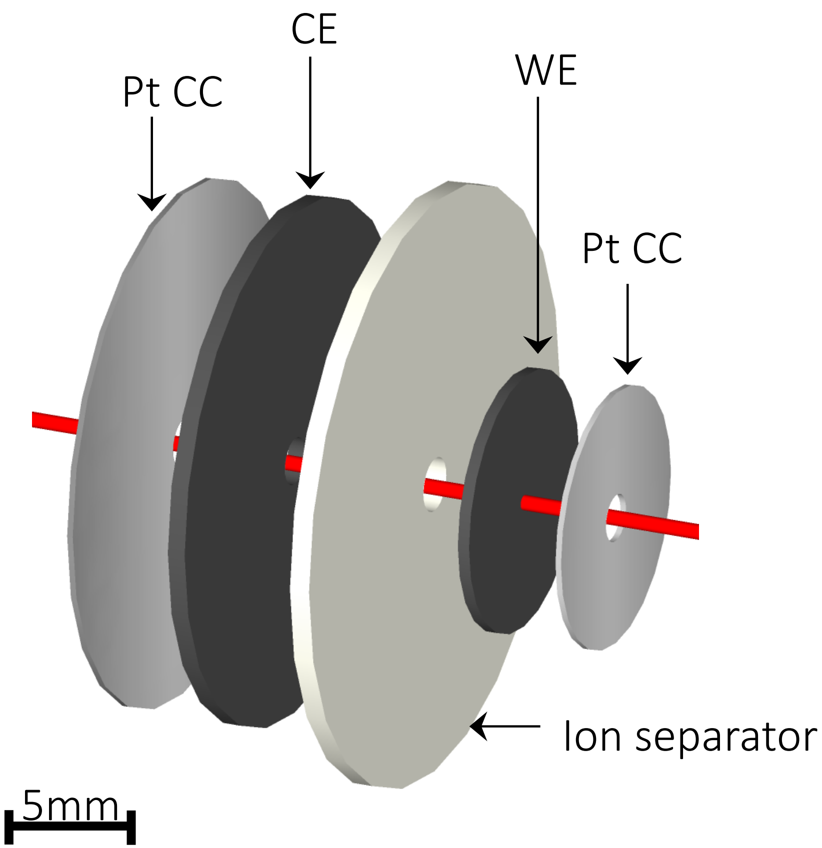

In-situ cells

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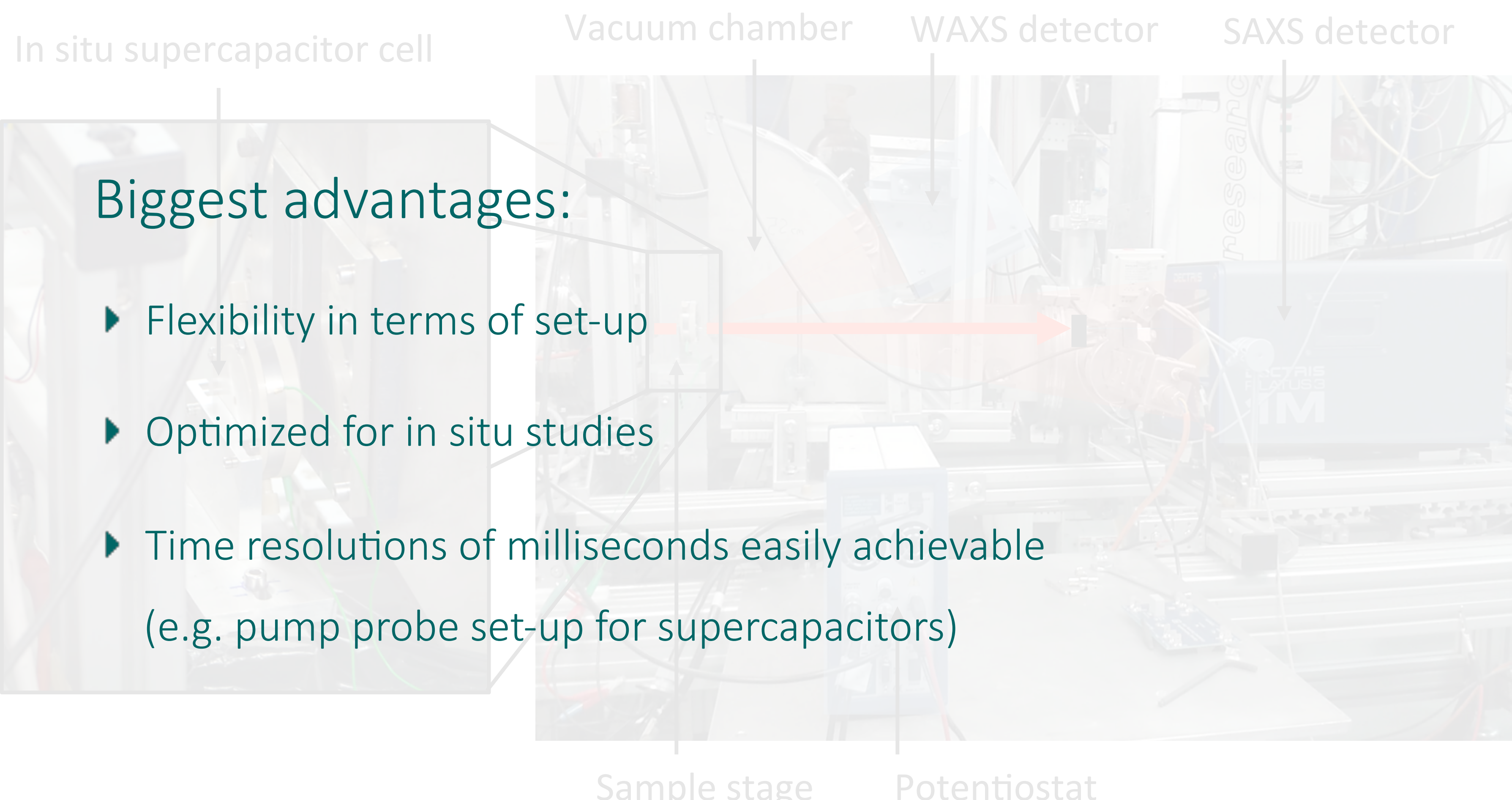
Experimental set-up at ELETTRA

- Austrian SAXS Beamline (TU Graz) at ELETTRA



Biggest advantages:

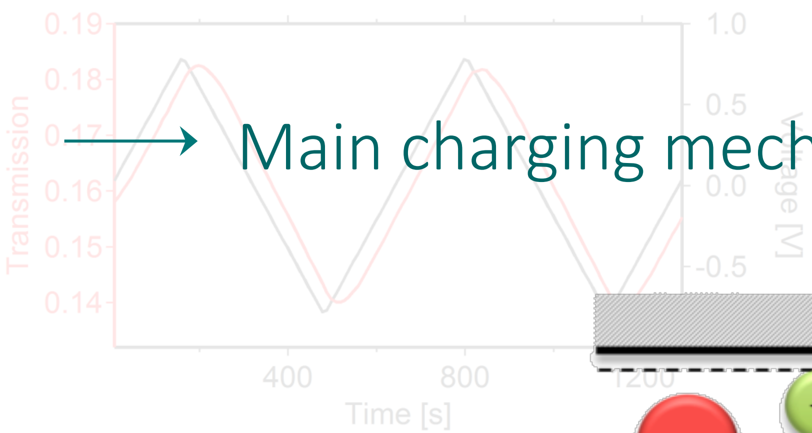
- Flexibility in terms of set-up
- Optimized for in situ studies
- Time resolutions of milliseconds easily achievable (e.g. pump probe set-up for supercapacitors)

X-ray transmission: counting the ion flux

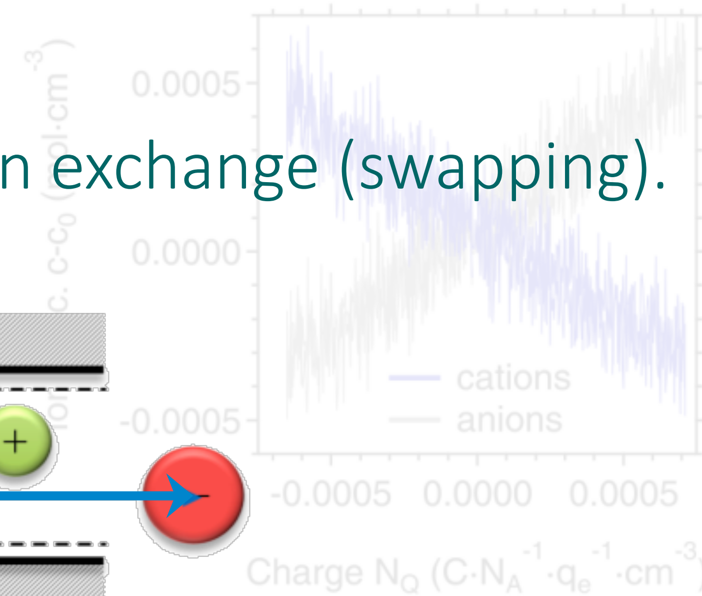
Here: AC2 (pore size 0.9 nm) with 1M CsCl;

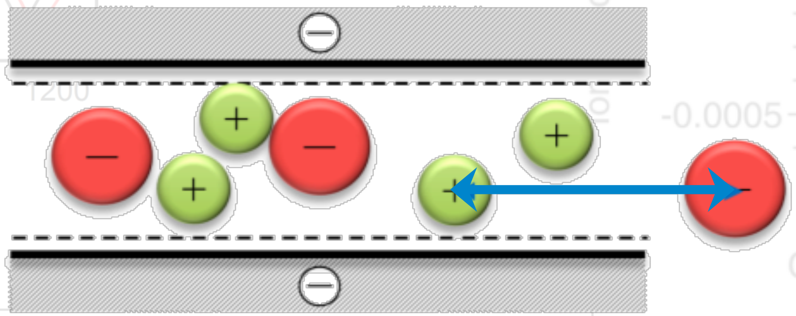
Cyclic voltammetry (+-0.6 V) with 0.5 mv/s

Integral ion concentration change:



→ Main charging mechanism is ion exchange (swapping).





Transmission (Lambert-Beer Law):

$$-\ln(\tau) = [c_{cat} M_{cat} (\mu/\rho)_{cat} + c_{an} M_{an} (\mu/\rho)_{an} + c_{H2O} M_{H2O} (\mu/\rho)_{H2O}] d_{el} + C$$

Voltage < 0 | Voltage > 0

$$Charge\ Q = \int I(t)dt / q_e N_A Volume_{el} = c_{an} - c_{cat}$$

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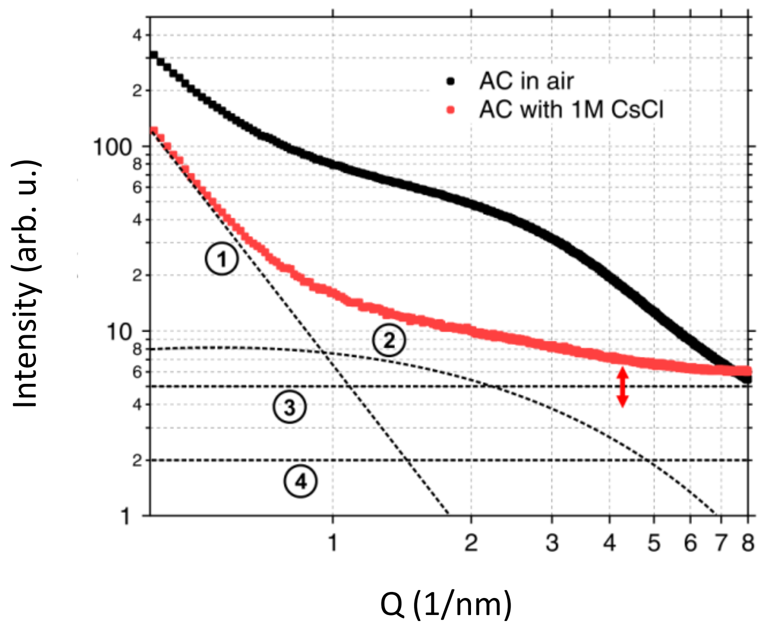
First outcomes from SAXS



1 Porod contribution

2 SAXS contribution (nanopores)

3 Electrolyte structure factor

4 Carbon structure factor

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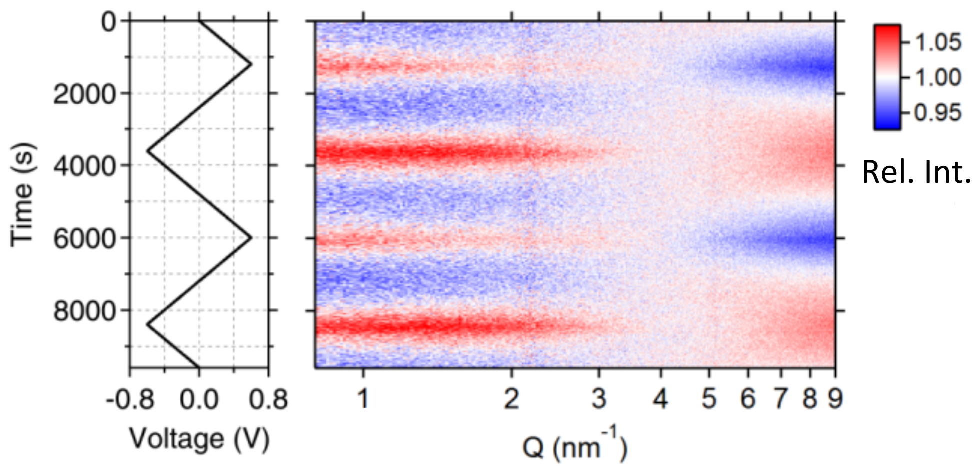

- Rich on information, but interpretation difficult
- We see ion concentration changes.
- And collective structural rearrangement of ions.
- Comprehensive data analysis approach necessary

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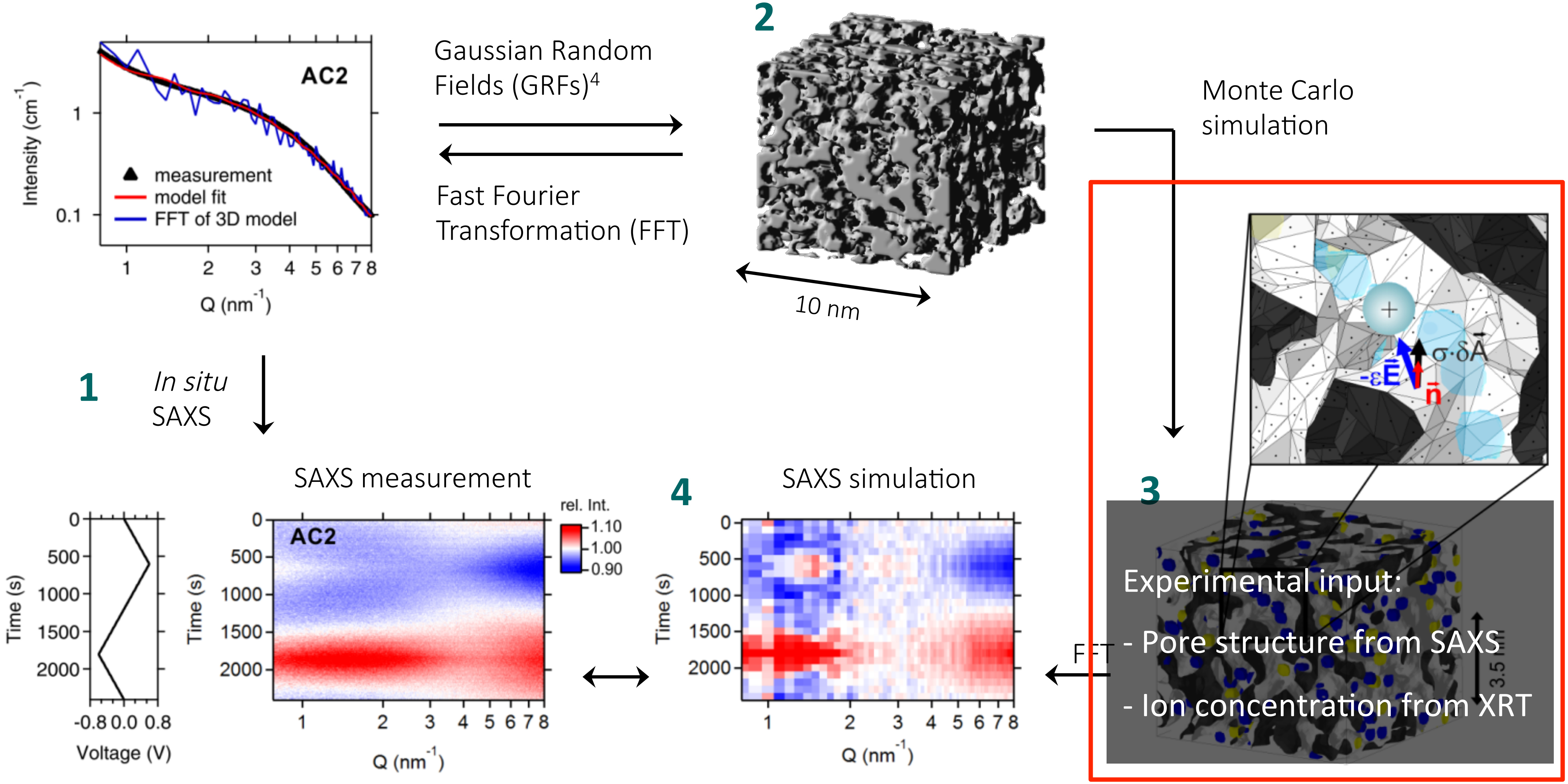
Our data analysis approach



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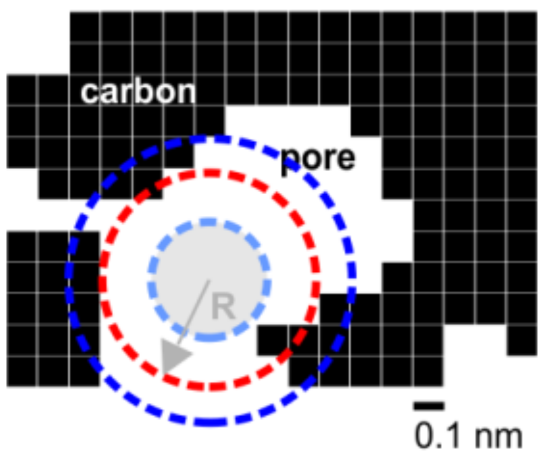
Analyzing the real space data

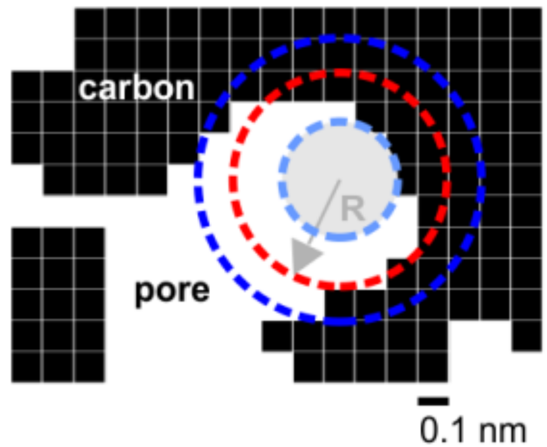
The **degree of confinement (DoC)** and the degree of desolvation (DoDS)

Small DoC, DoDS



Apply voltage →

Large DoC, DoDS



R – bare ion
R – hydrated ion
R – cut-off

$$DoC = \sum_i 1/R_{i,C}^2 \Big/ \sum_i 1/R_i^2 \quad for\ R_i < R_{cut-off}$$

$$DoDS = \sum_i V_i / V_{HS} \quad for\ R_i < R_{HS}$$

- The DoC precisely accounts for the ion position in a disordered pore structure.
- The DoDS is proportional to the number of released water molecules within the hydration shell.

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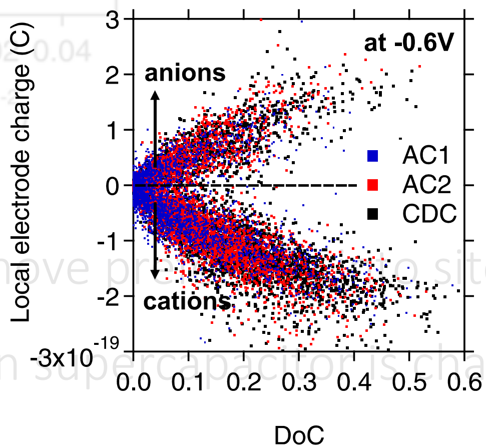
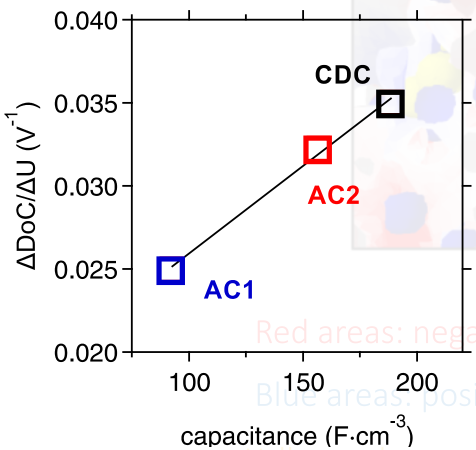
Quantifying ion confinement

As a voltage is applied ions rearrange on a local scale, i.e. they change their DoC

- Counter-ion – counter-ion repulsion is effectively screened in sites with high DoC!
- Confinement and desolvation conclusively determine the electrode performance.
- Ions are stored most effectively in sites with high DoC.





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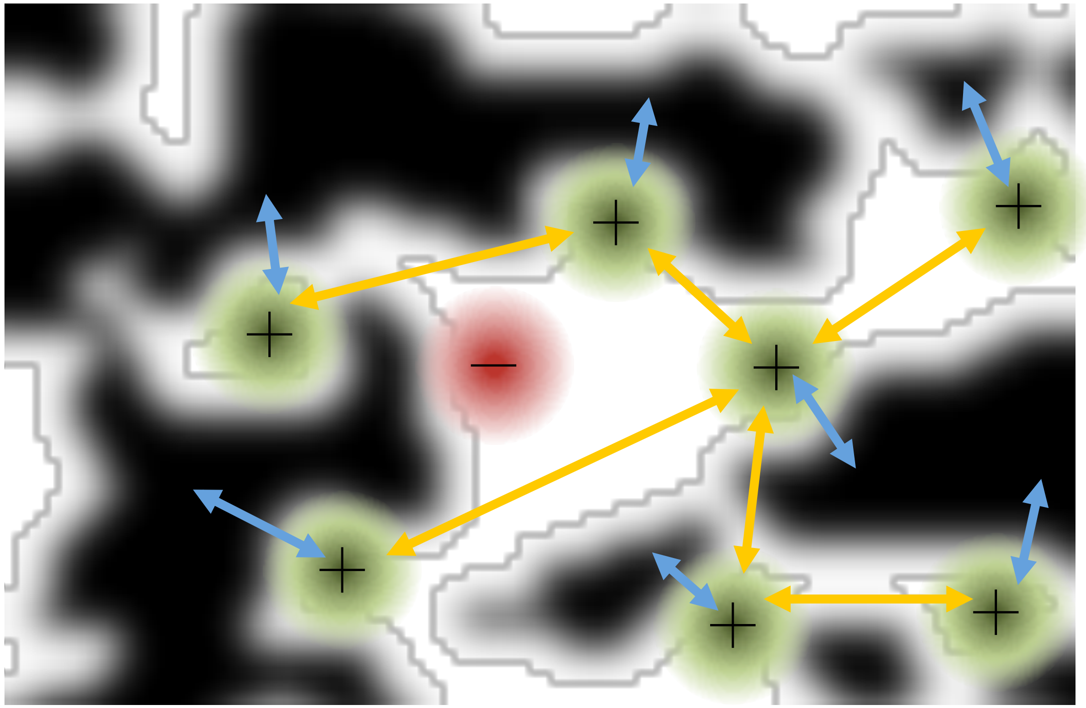
Ion charge storage in nanoporous carbons

Electrode charge = 6 e⁻



1) Global concentration change: XRT
2) Local ion rearrangement: SAXS
   i. to minimize repuls. interact. of counter-ions
      → minimized in sites with high DoC
   ii. Ion-ion correlations remain constant
   iii. If number of sites with high DoC ↑
      → counter-ion density ↑
      → capacitance ↑

EDLC performance: we need pore structures, providing the maximum amount of pore sites with high DoC.

Thank you for your attention!