Crystallography and Crystal Chemistry
VIII International School-Conference of Young Scientists ICYS-2023

Operando studies of structure evolution in battery materials

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PhD in **Chemistry, Assistant Professor**

Center for **Energy Science** and **Technology**

Skoltech, Moscow, Russian Federation

November 9th, 2023

School logistics: lecturers and tutors

Lecturers

Prof. D. Aksyonov (Skoltech)
Prof. S. Levchenko (Skoltech)
Prof. O. Shmatova (Skoltech)
Dr. R. Eremin (AIRI)
Dr. I. Trussov (KazNU)
Dr. Z. Bobyleva (MSU)
Dr. A. Volkov (Skoltech)
Dr. M. Zakharkin (MSU)
Dr. A. Savina (Skoltech)
Prof. S. Fedotov (Skoltech)

Group	Friday Nov 10th (14:00 -18:00)	Saturday Nov 11th (13:20-18:20)	Sunday Nov 12th (13:20-18:00)	Monday Nov 13th (10:00-13:00)
Basic A (15 people)	Python R3-2007	GSASII R3-2015	BVEL R3-2007	
Basic B (14 people)	BVEL R3-2015	Python R3-2007	GSASII R3-2015	
Advanced (9 people)	GSASII R3-2024	BVEL R3-2024	Python R3-2024	GSASII R3-2024

Atomistic modelling

Prof. Dmitry Aksyonov
Dr. Anton Boev
Dr. Andrey Geondzhian

Processing of experimental data

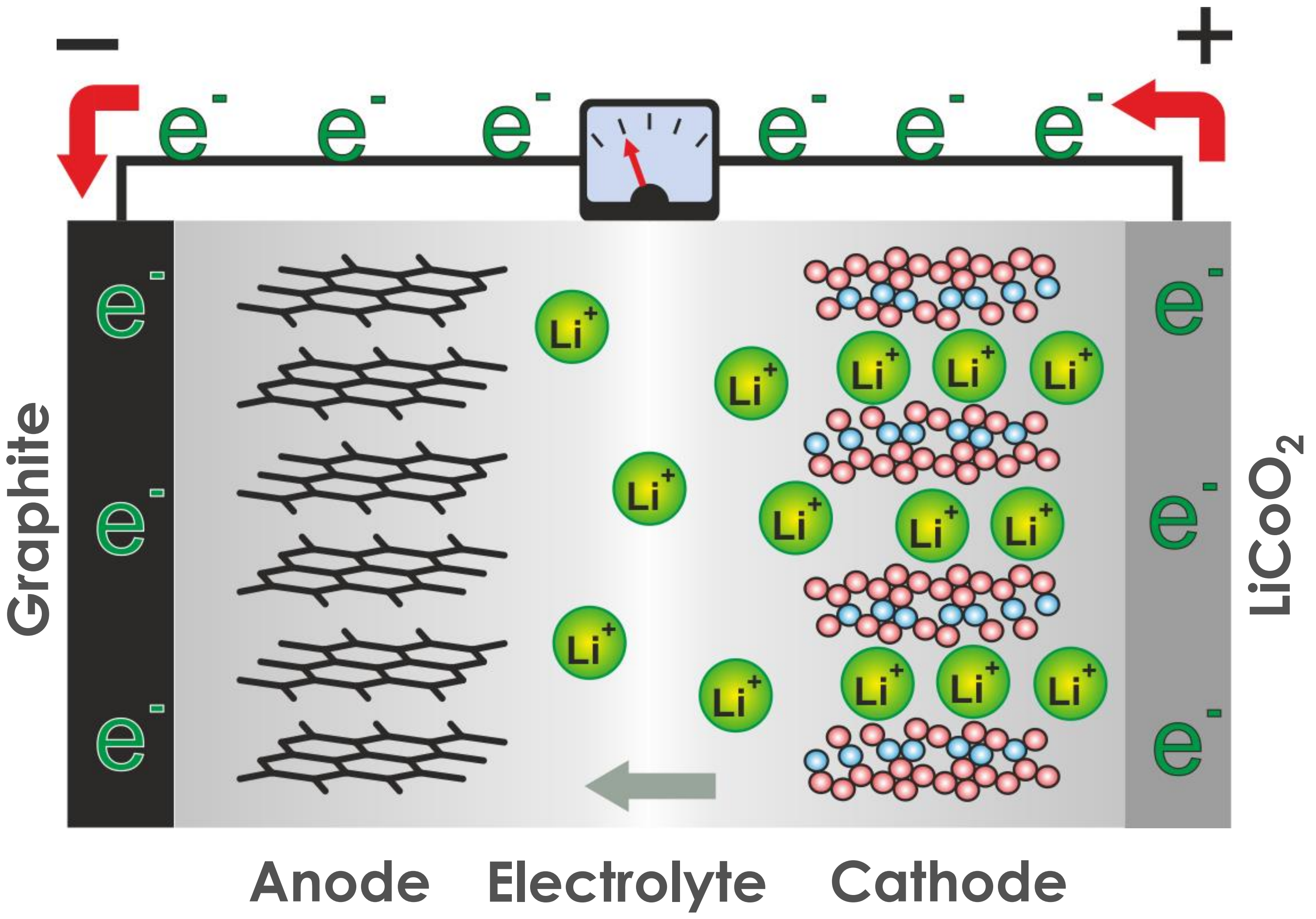
Python
Mr. Mikhail Agapkin
Mr. Nikolay Ovsyannikov

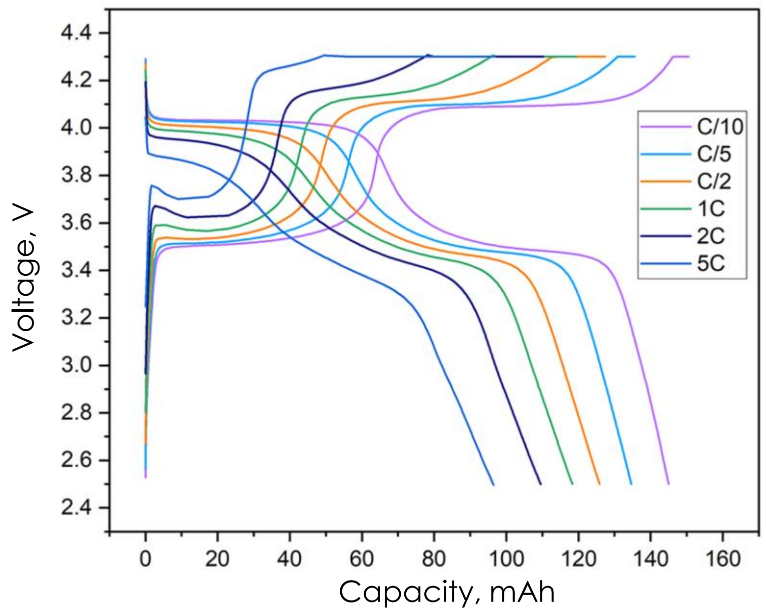
BVEL
Mr. Artem Dembitskiy
Mr. Eugene Nazarov

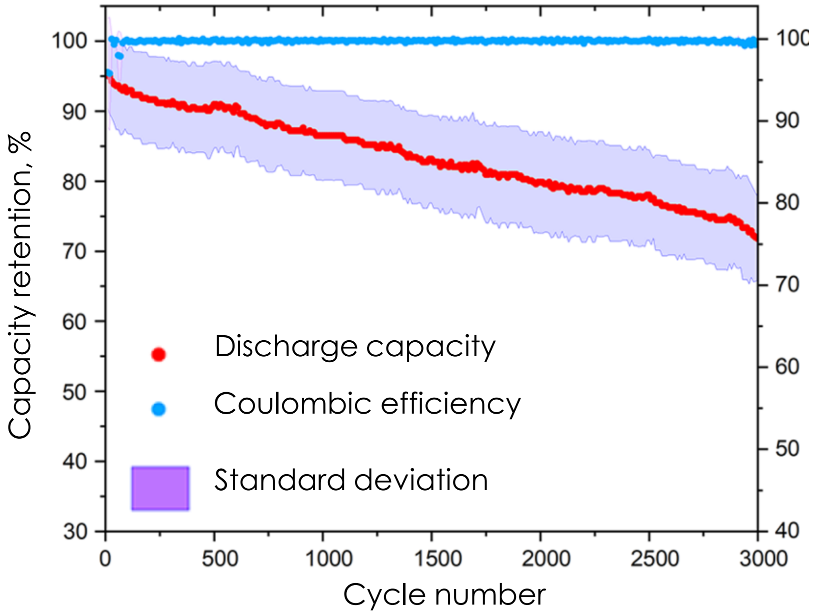
GSAS-II
Dr. Ivan Trussov
Mr. Sergey Marshenya

Logistics and support
Mr. Mikhail Tashlanov

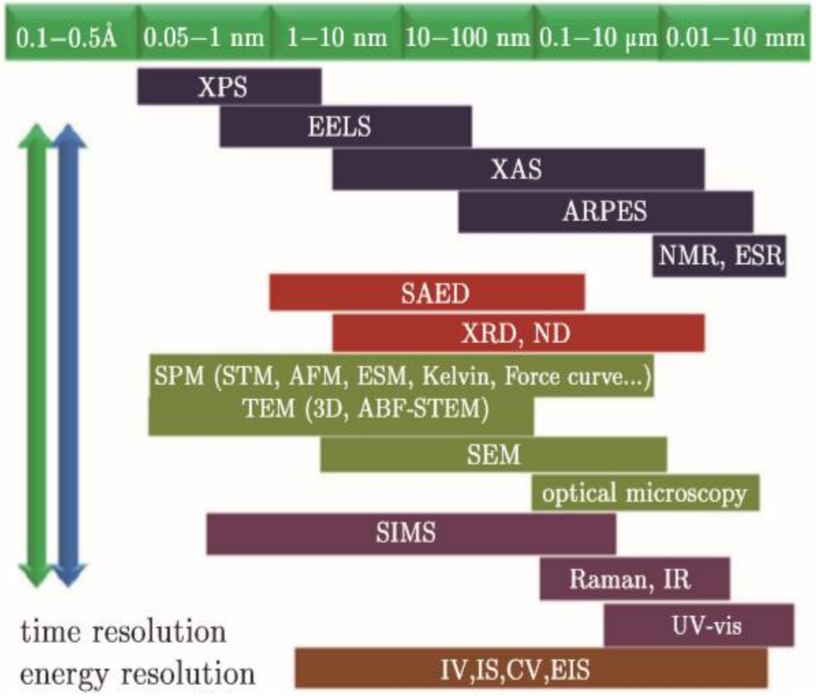
Metal-ion battery

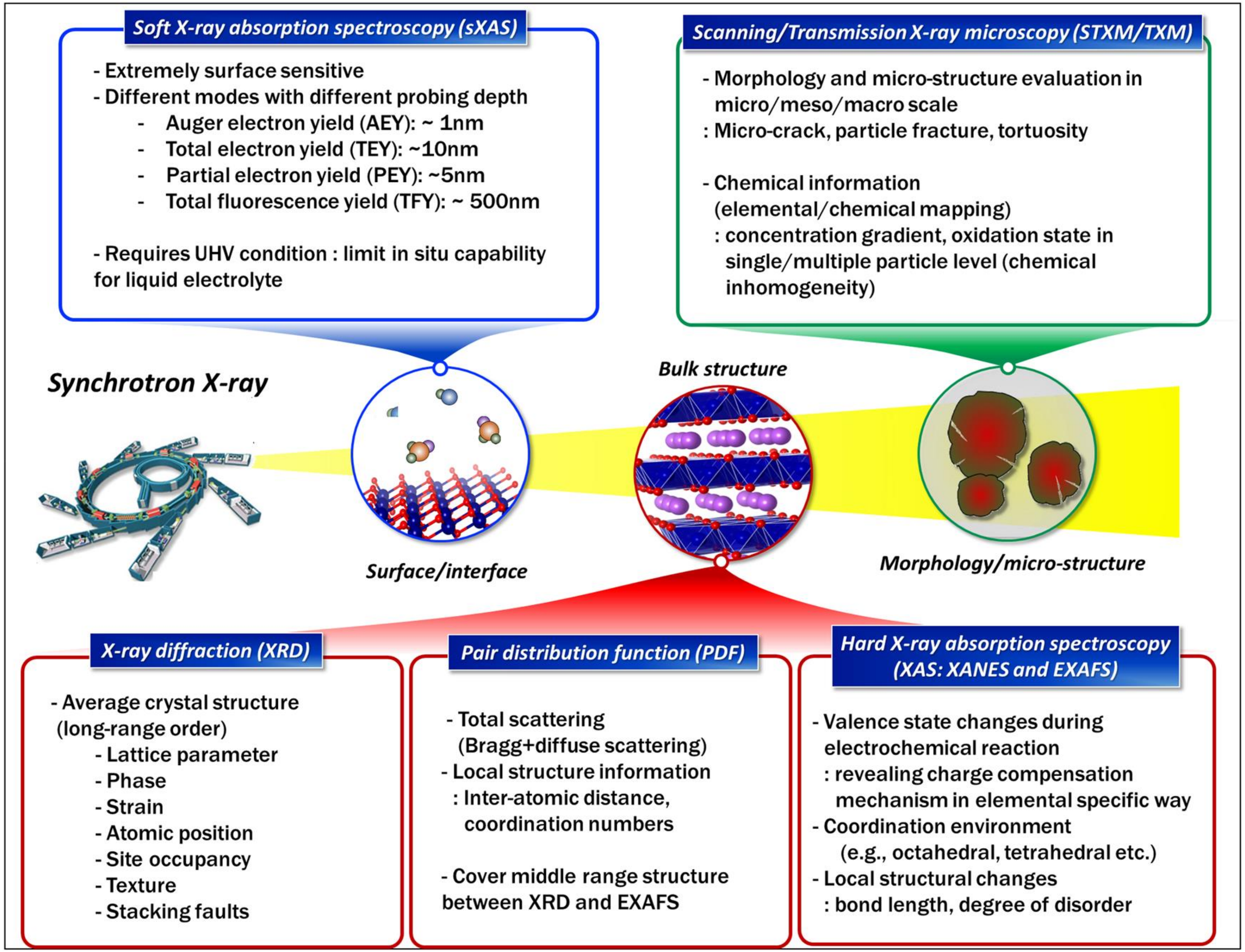






Synchrotron-based X-ray techniques for electrodes





10.1088/1674-1056/25/1/016104
10.1038/s41427-018-0056-z

Type of experiments for studying functional materials

Standard

Without impact
or environment

Ex situ
(off-site)

After impact
Out of environment

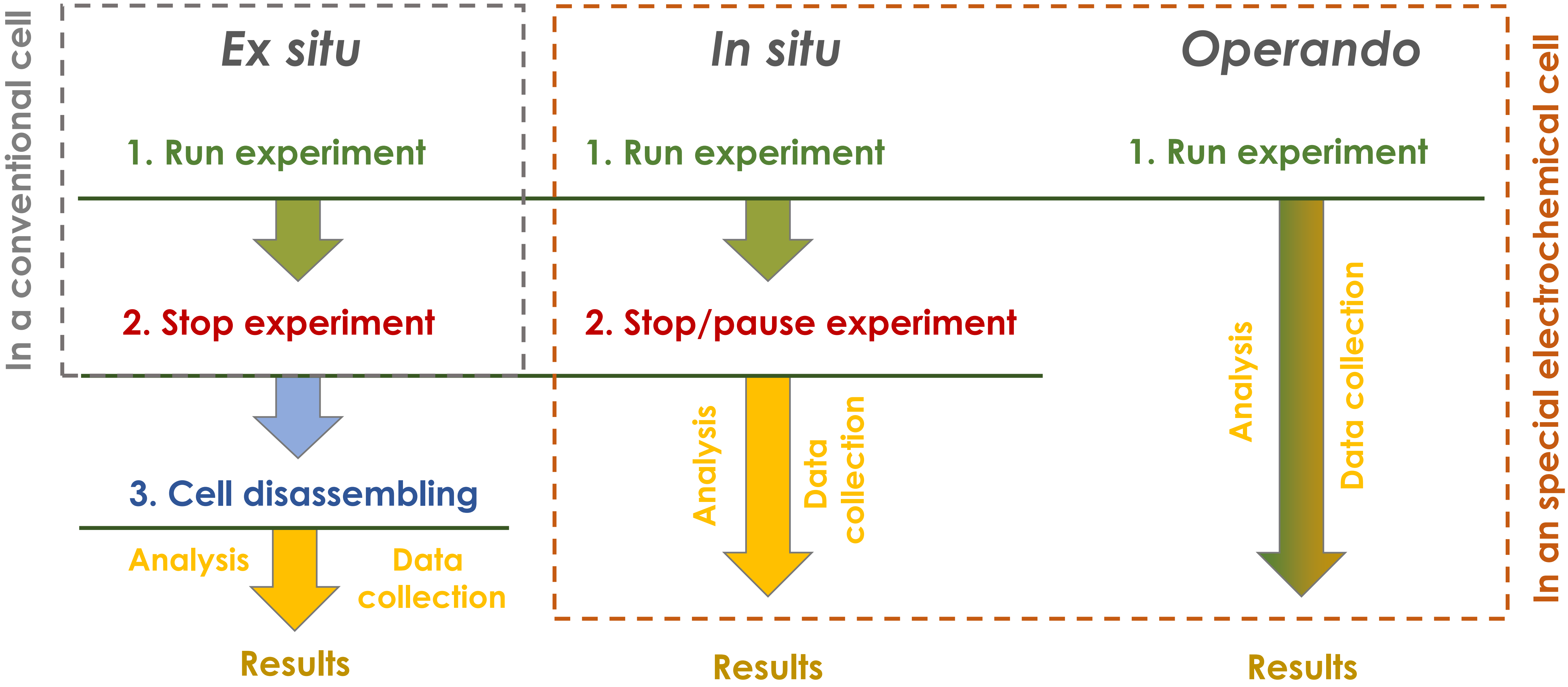
In situ
(on-site)

After impact
In an special environment

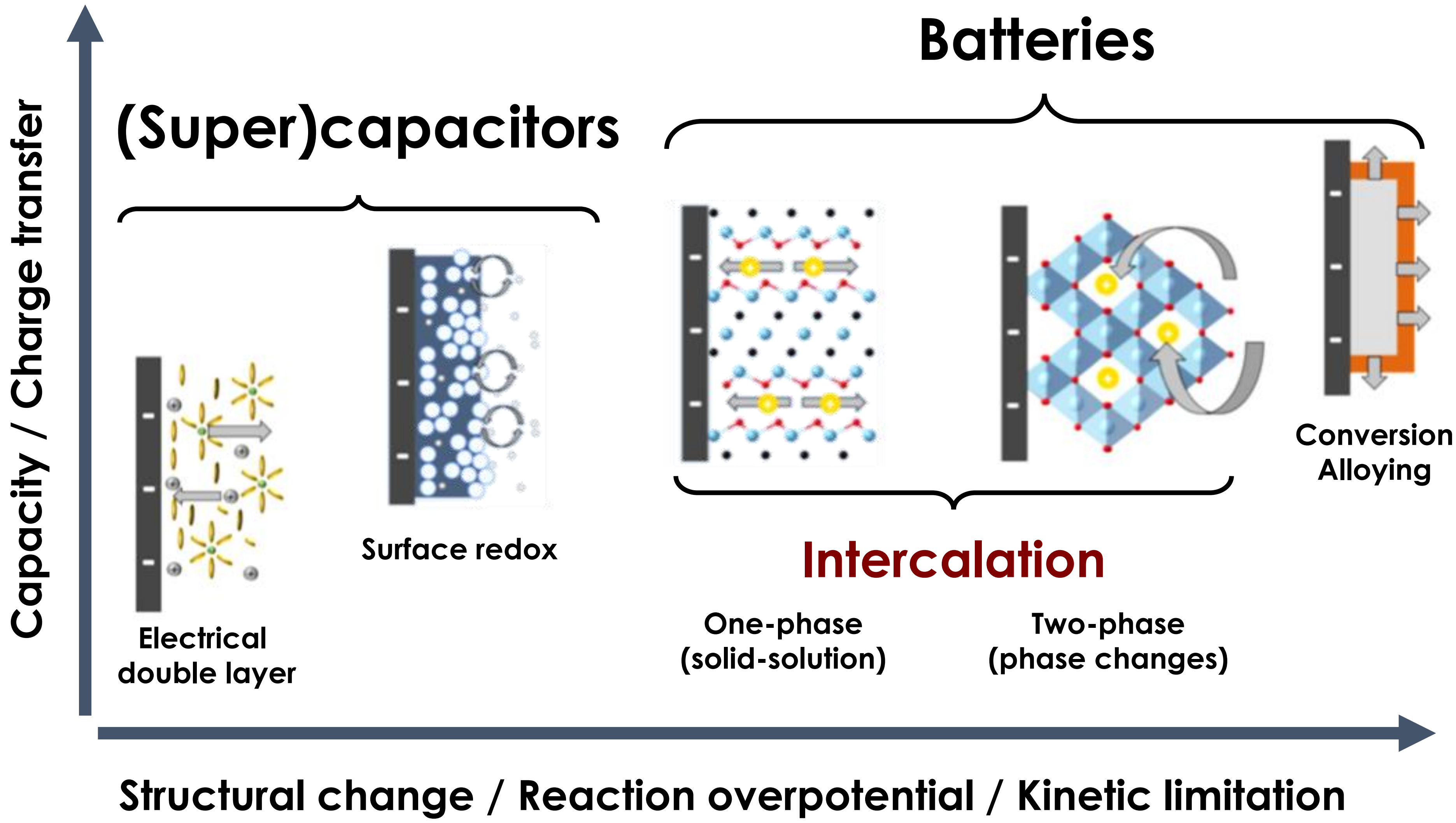
Operando
(working)

Under external impact

Terminology



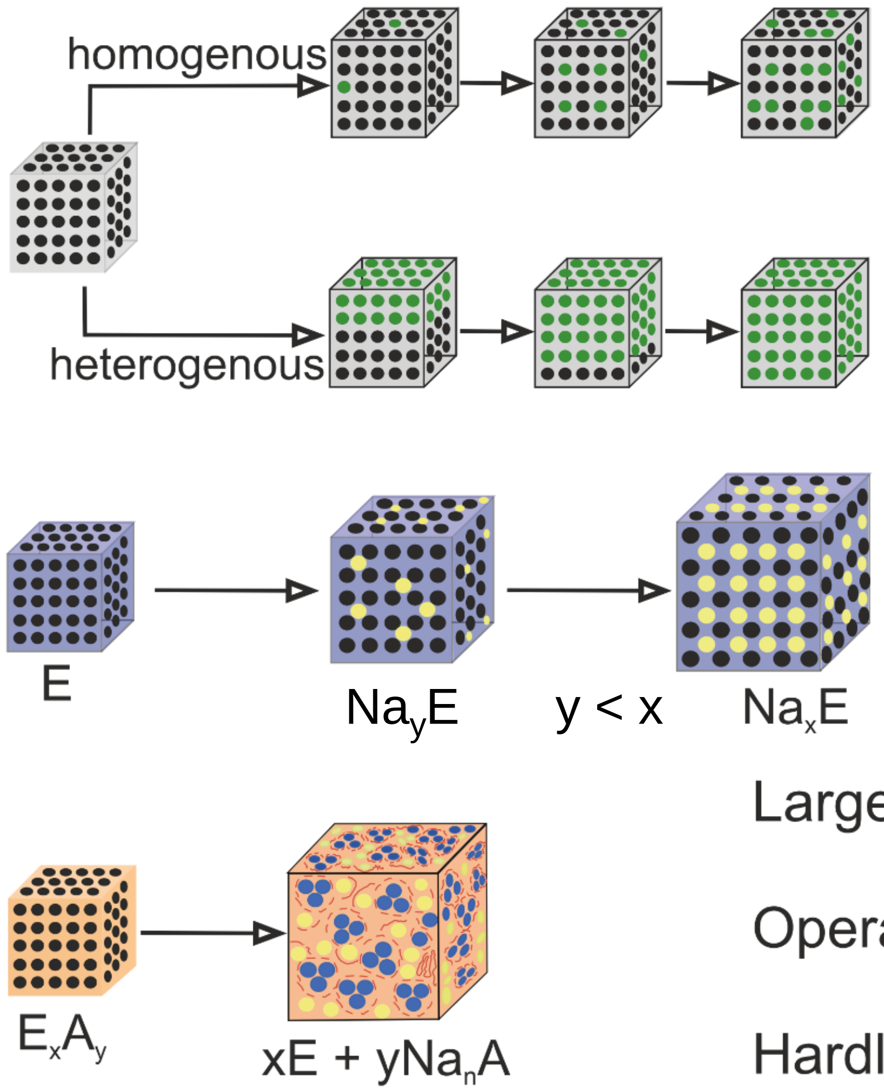
Electrochemical energy storage mechanisms



Chem. Rev. 2020, 120, 6738-6782.

Electrochemical energy storage mechanisms

“Depth” of structural transformation



Intercalation

“Conventional” process

Moderate capacity values

Alloying

Large capacity values

Huge volume changes

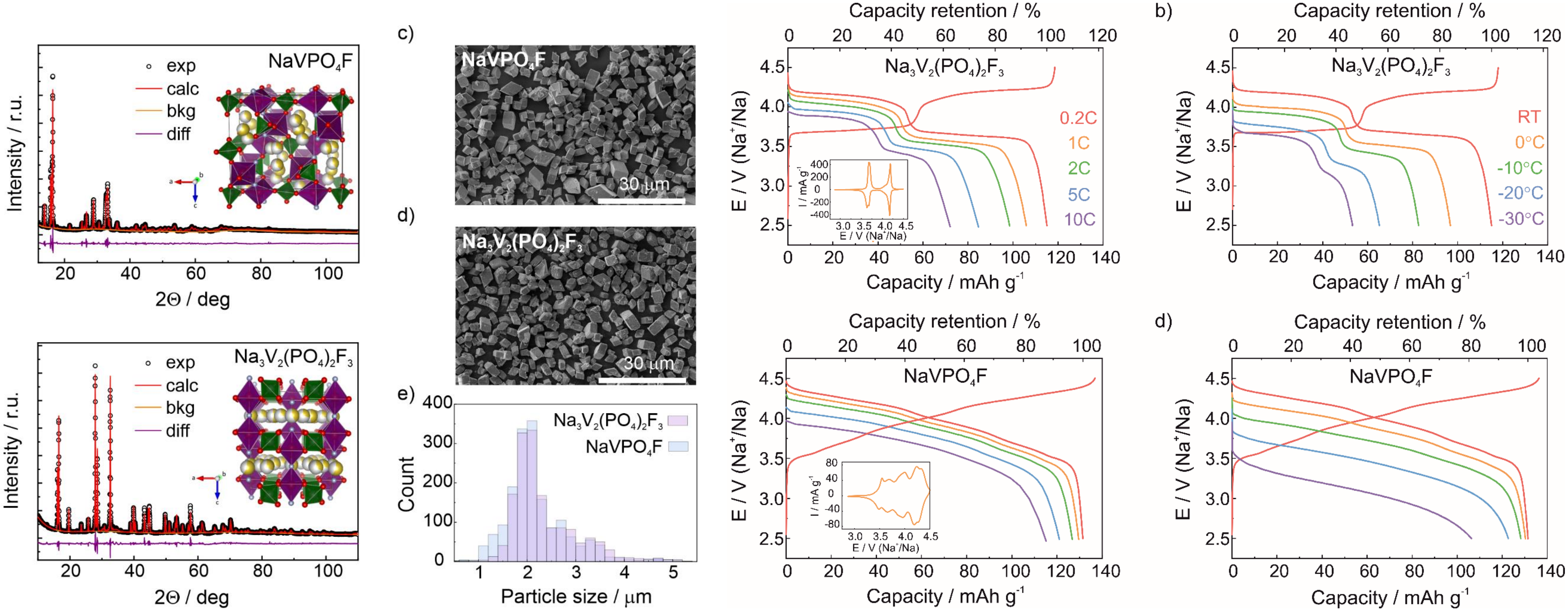
Conversion

Large capacity values

Operating potential hysteresis

Hardly controlable
electrode degradation

Single-phase $NaVPO_4F$ vs. two-phase $Na_3V_2(PO_4)_2F_3$



Better kinetics of $NaVPO_4F$ (single-phase mechanism) = better high-rate and low-temperature performance

Komayko A. I., Shraer S. D. et al, *Appl. Mater. & Interfaces*, 2023

XRD changes vs. de/intercalation mechanism

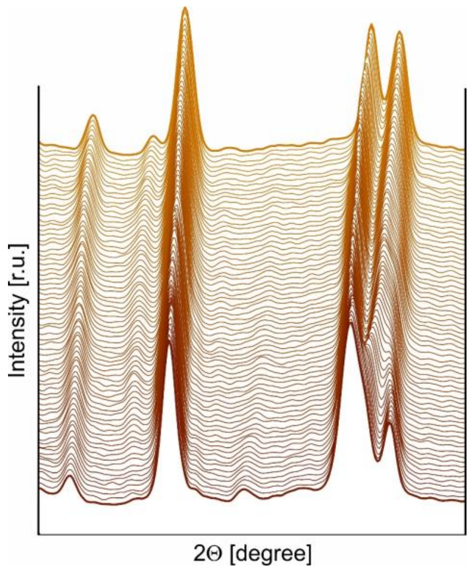
Intercalation

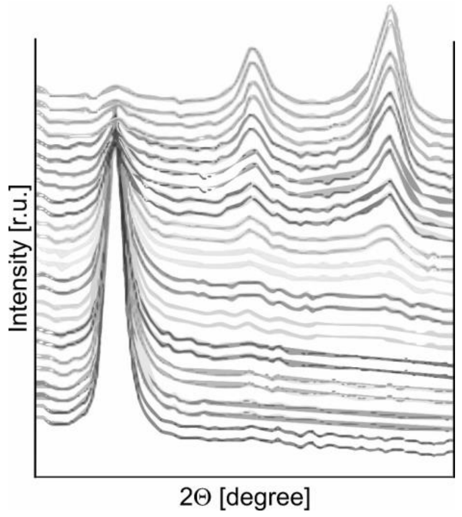
Phase transition

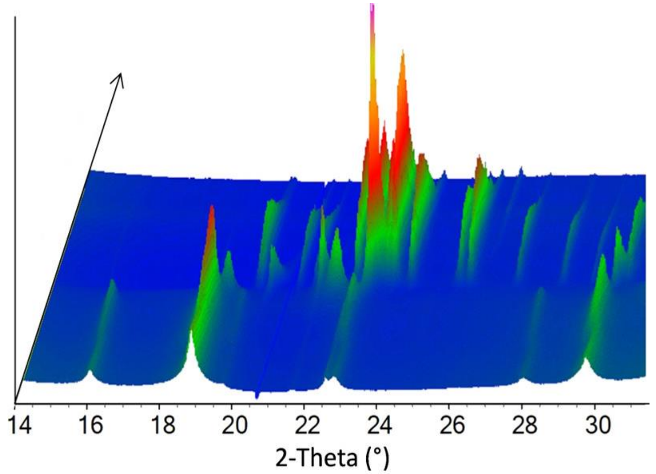
Solid-solution

Two-phase

Conversion







Gradual change of cell parameters

Symmetry preserves

Rapid kinetics

Two phases co-exist with close structures but different cell parameters

Symmetry may change, but may not

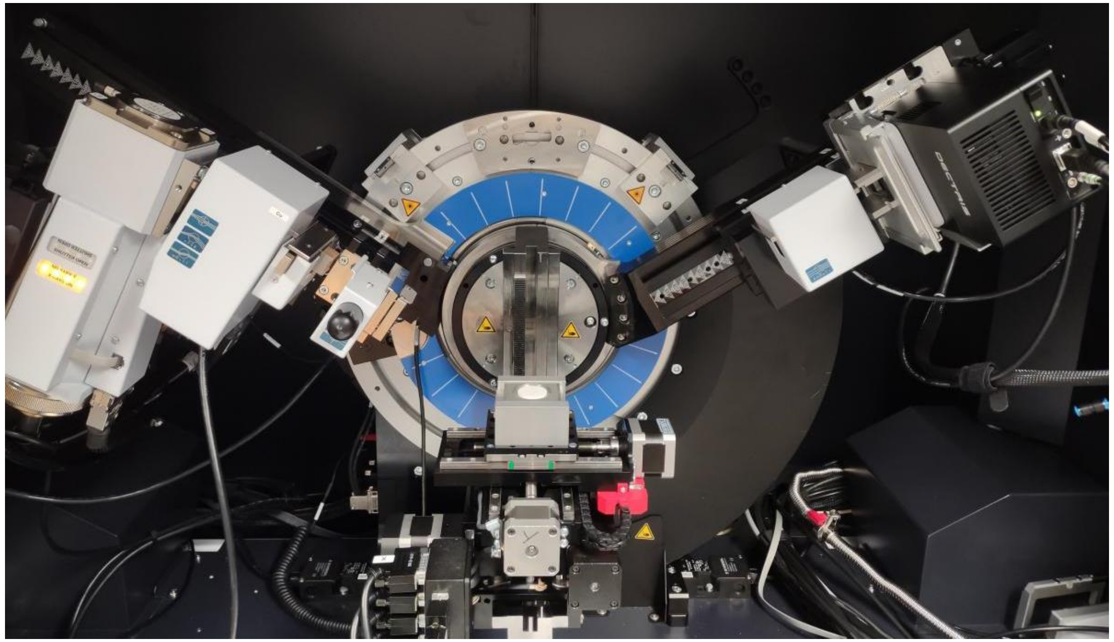
Phase boundary propagation

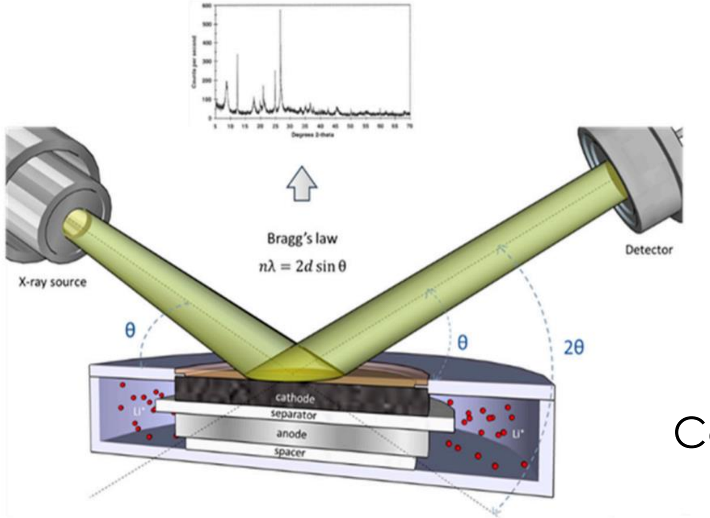
Radically different crystal structure and cell parameters

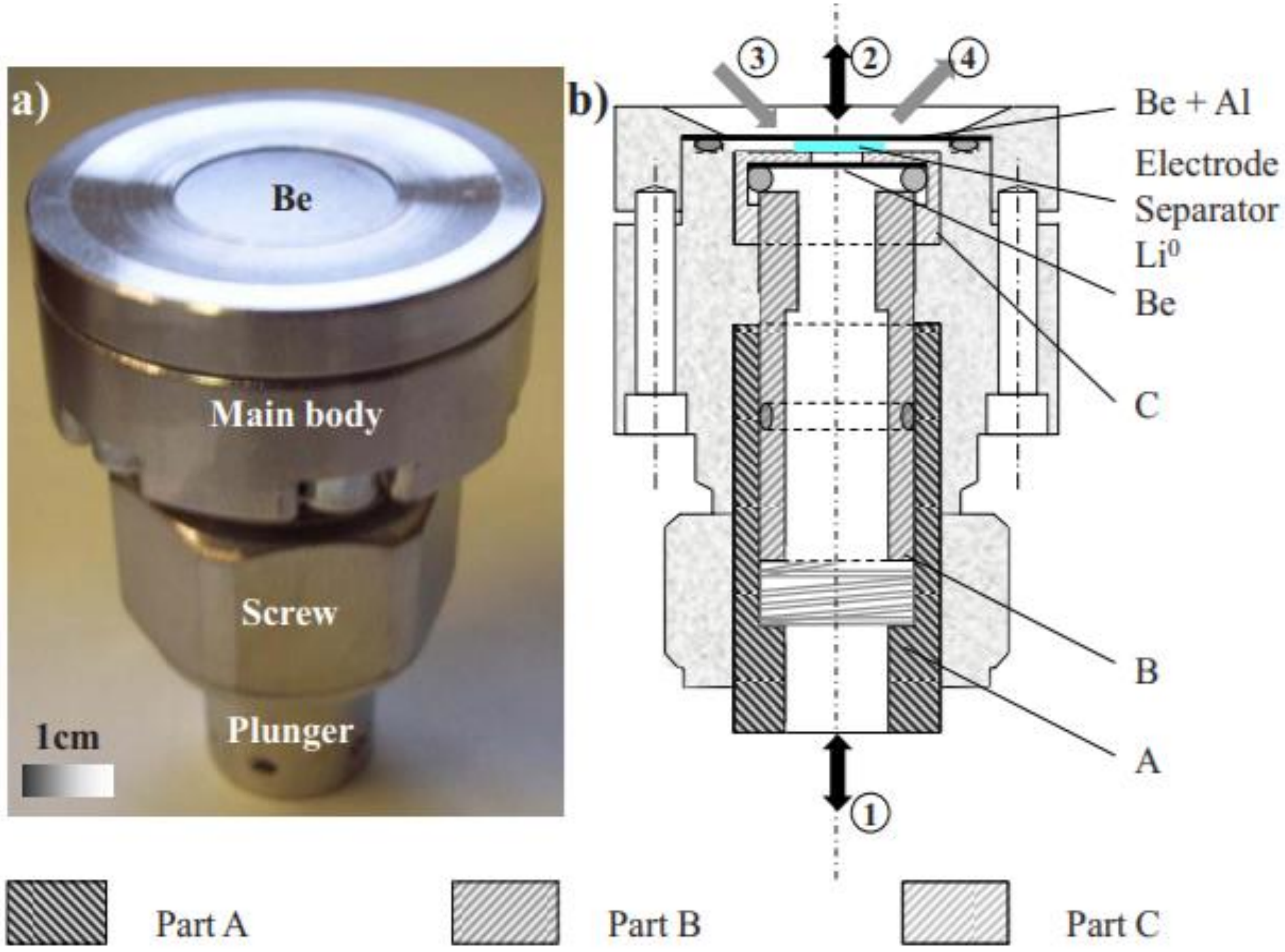
Symmetry most probably changes

$M_xO_y + 2yLi^+ + 2ye = xM + yLi_2O$

Principal scheme and the cell (lab design)



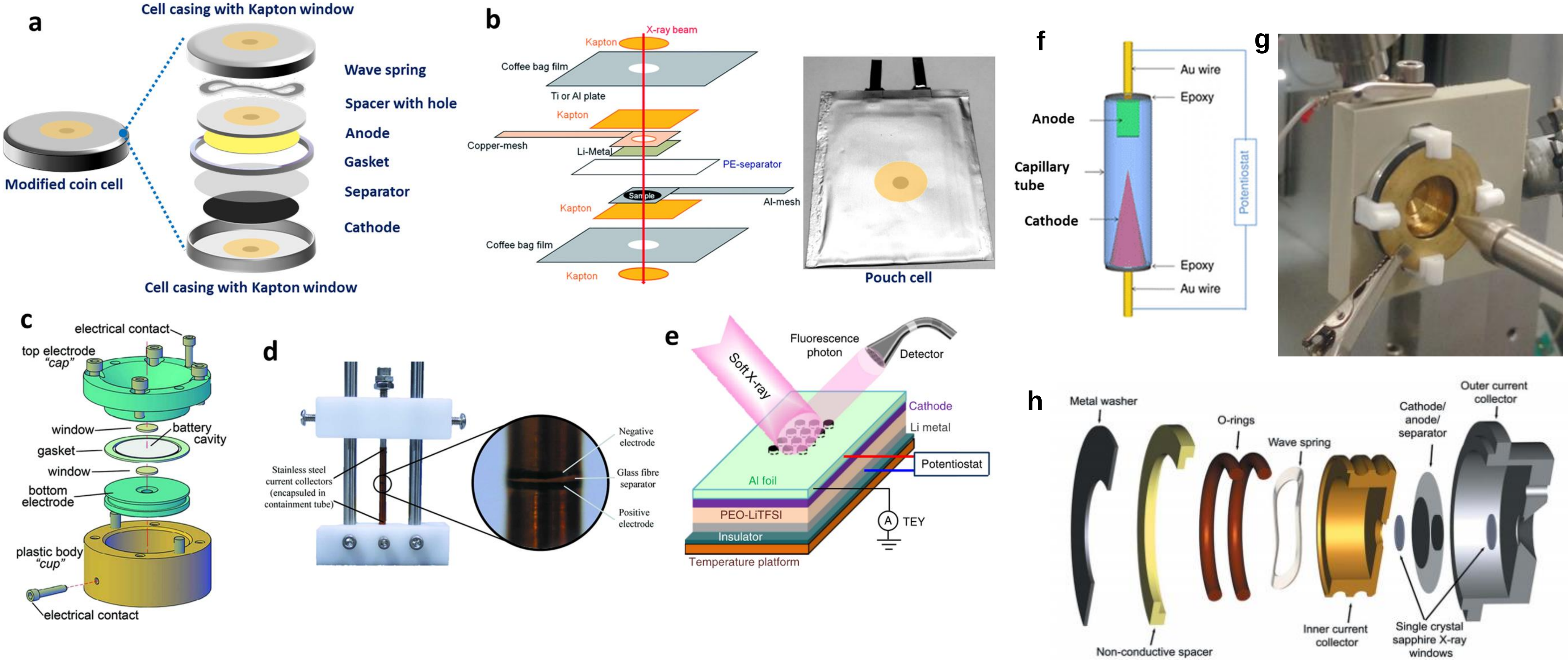




Condens. Matter 2020, 5, 75

J.B. Leriche et al, JES, 2010

Operando electrochemical cells



10.1002/smtd.201900223

10.1038/s41427-018-0056-z

J. Synchrotron Rad. (2018). 25, 468–472

Operando electrochemical cells: requirements

At the synchrotron:

- easy to assemble/disassemble at synchrotron facilities;
- able to be incorporated into the existing beamline setup and should fit properly in X-ray optics;
- electrochemical potentiostat mounted or supplied;

The casing:

- a cell case made from low X-ray absorption materials to avoid blockage of outgoing X-rays;
- one hole for reflection mode and two holes for transmission mode are covered with X-ray transparent materials;
- Interference from inactive cell components minimized

X-rays:

- energy of X-rays determines the materials the construction of the cell;
- Beam damage -> intermittent sample probing (beam shutter or moving the sample region off the beam).

Highly reproducible for electrochemical testing

10.1038/s41427-018-0056-z

Operando electrochemical cells: requirements

Cell “windows”
one hole for reflection mode and two holes for transmission mode are covered with X-ray transparent materials (e.g., Kapton film, beryllium, or aluminum foil, etc.)

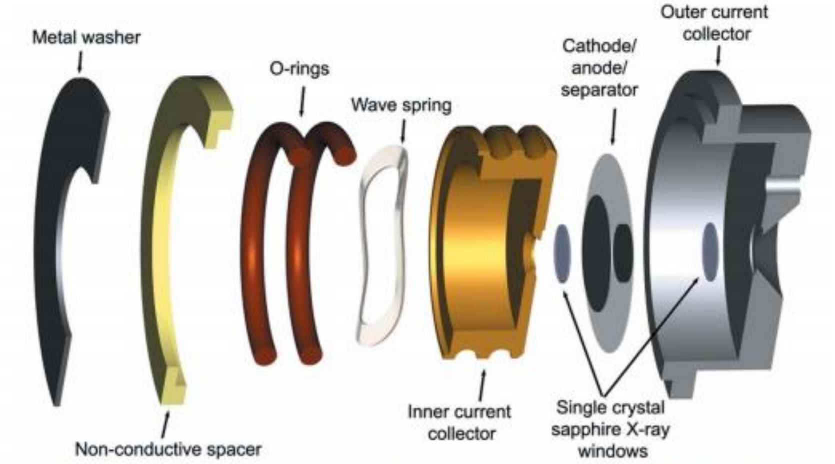
- ideal window material should be as follows:
- chemically and electrochemically stable in the cell during operation (should not react with cell components)
- (b) impermeable to oxygen and moisture;
- (c) stiff to apply uniform pressure to ensure a uniform electrochemical reaction.

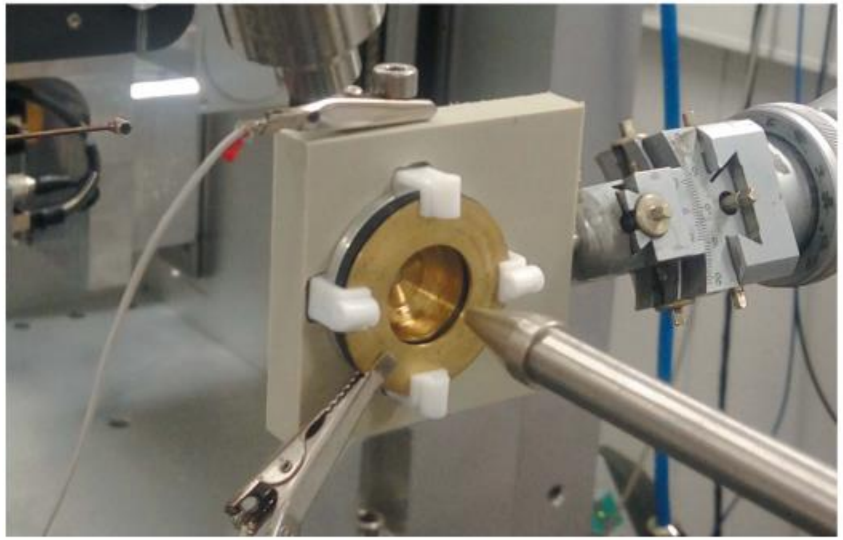
polyimide (Kapton) for hard X-ray, too soft for constant pressure, causing the sample area underneath the window to react abnormally sometimes (e.g., no reaction, delay of the reaction, etc.).
Beryllium - safety hazards, easily oxidized during battery charging, though it is ideal for X-ray transmission.
Thin polyester (Mylar) film for tender X-ray

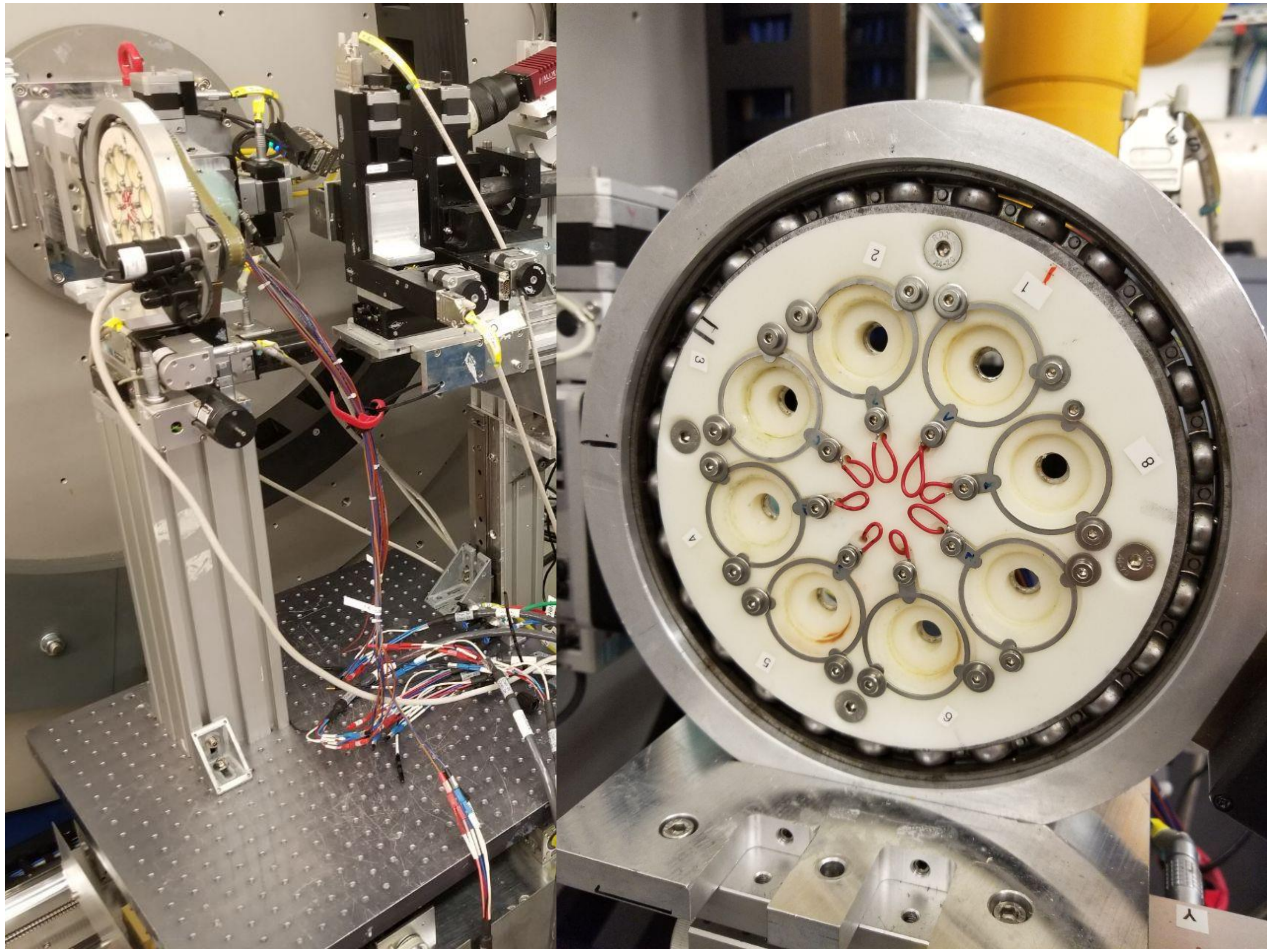
In ultra-high vacuum (UHV) environments are necessary for soft X-ray absorption spectroscopy (sXAS) measurements, an ultrathin **silicon nitride** window or **solid-state electrolyte** or **sapphire**

10.1038/s41427-018-0056-z

Synchrotron operando cells

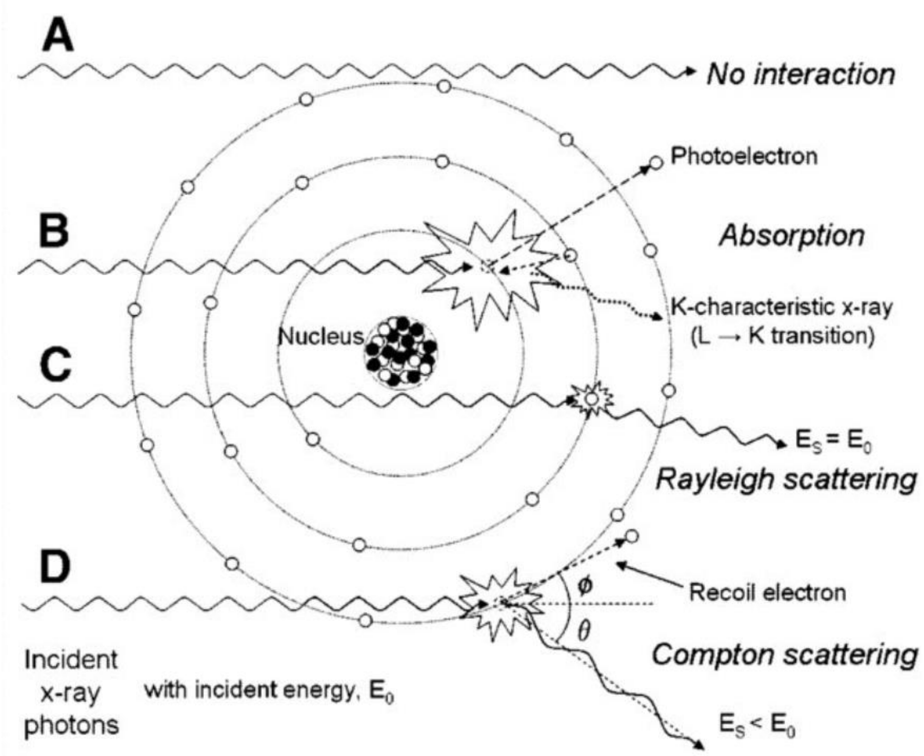


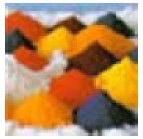


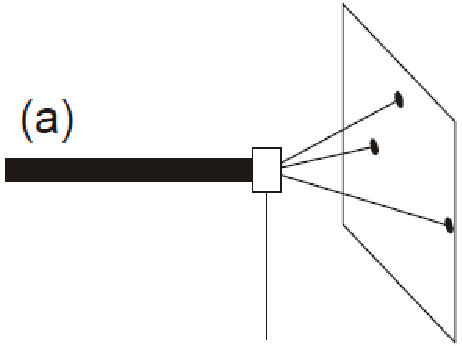


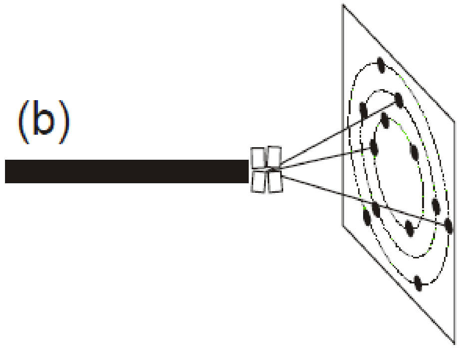
O.A. Drozhzhin et al, J. Synchrotron Rad. (2018). 25, 468–472

Signal formation



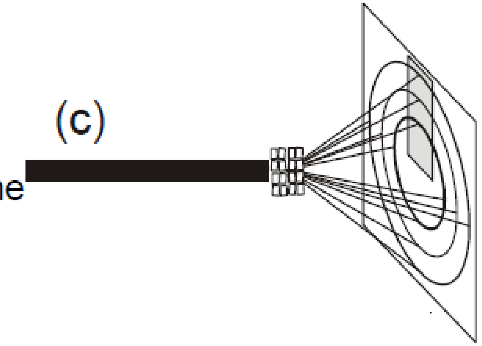


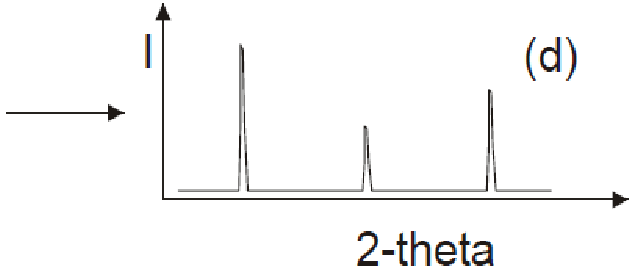




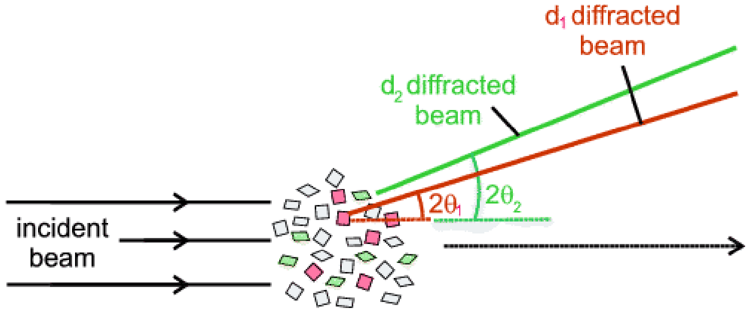
Single crystal

Four differently oriented single crystals

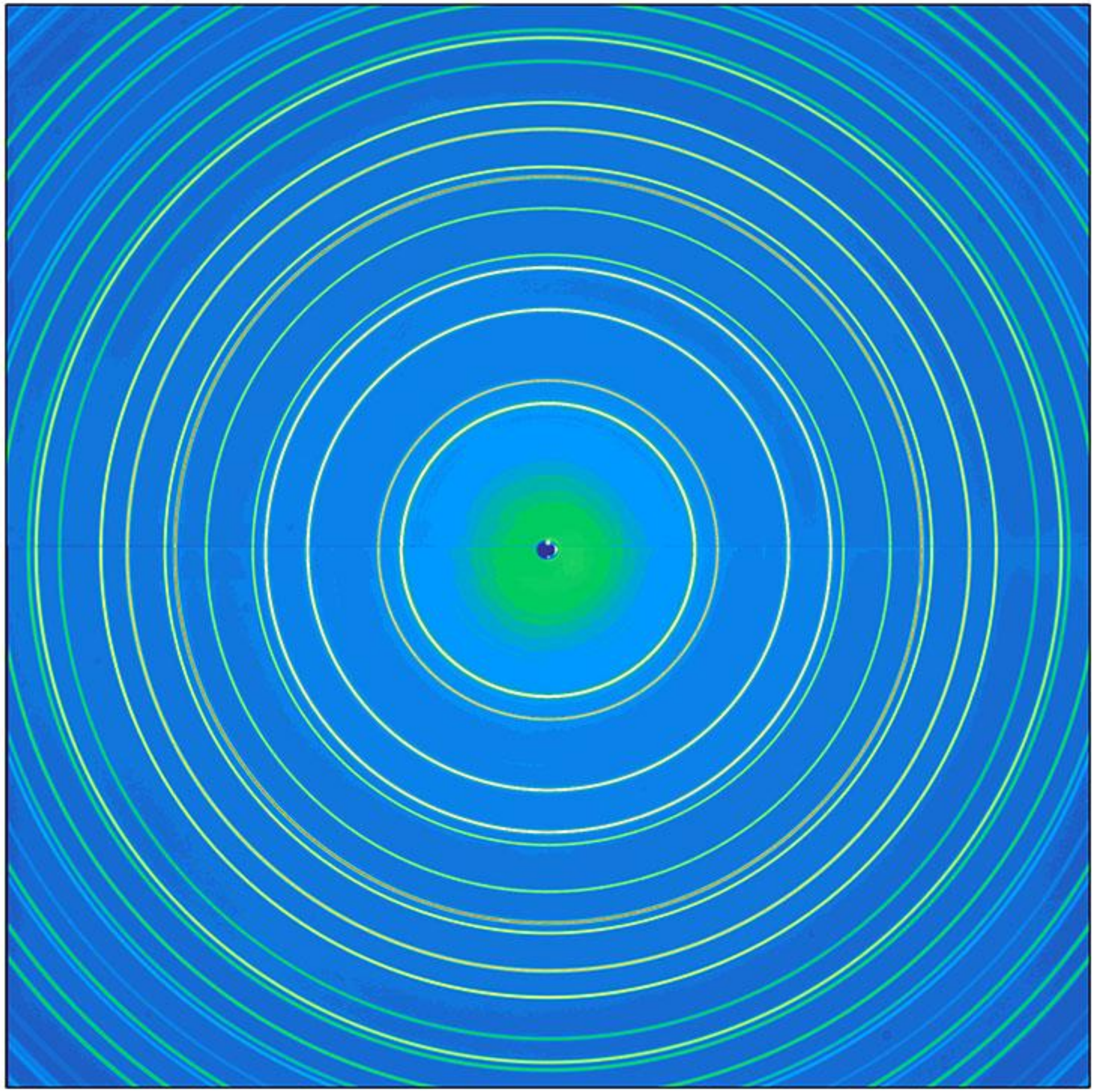




Polycrystalline material

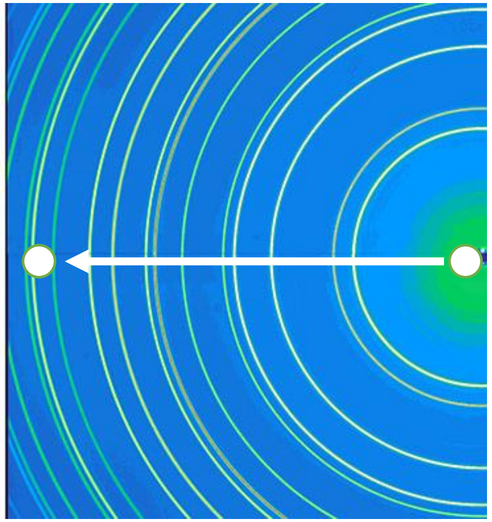


Signal formation



Detectors type

0D (scintillation)

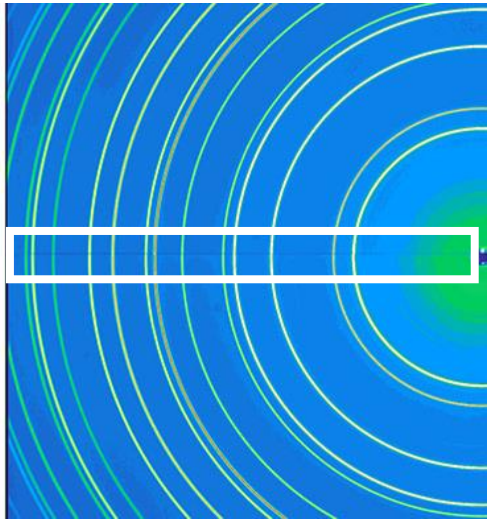


Small spot measured

Scan necessary

Long measuring time

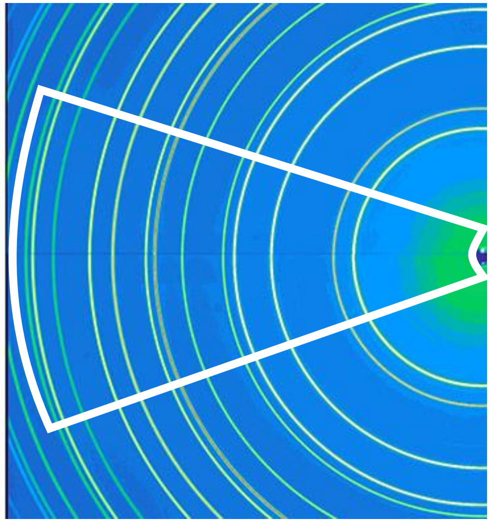
1D (position sensitive, PSD)



Simultaneous measurement

Medium measuring time

2D



Monocrystals
Oriented samples

Fast measuring time

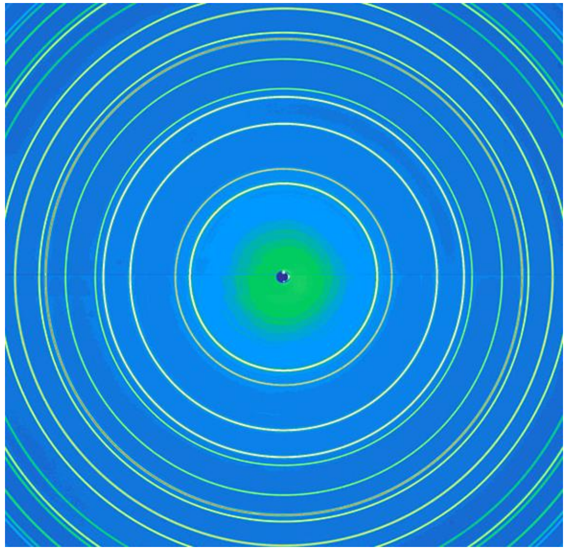
Instant measuring time

Detectors type

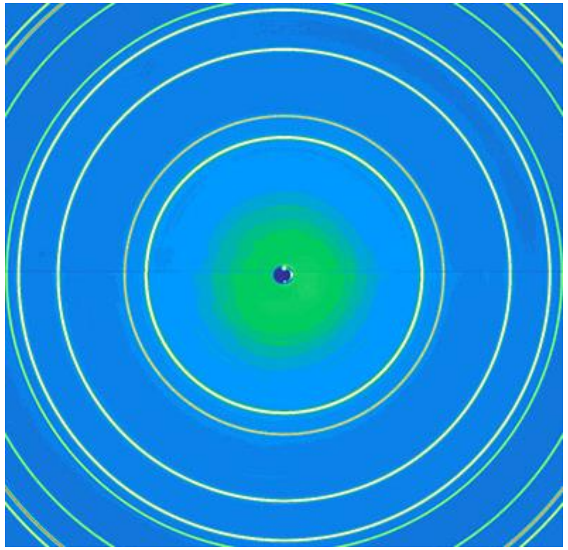
Perkin Elmer

DECTRIS

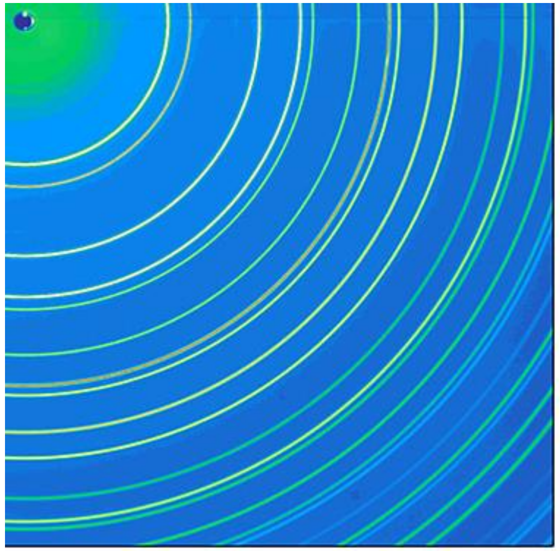
Detectors positioning



Close to the sample



Far from the sample



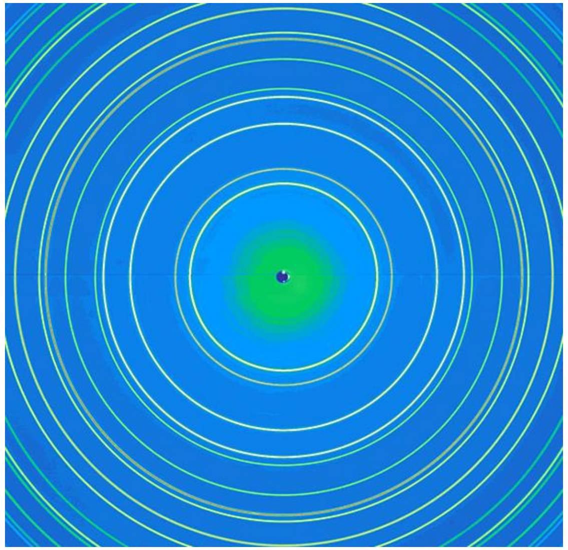
Shifted against the beam

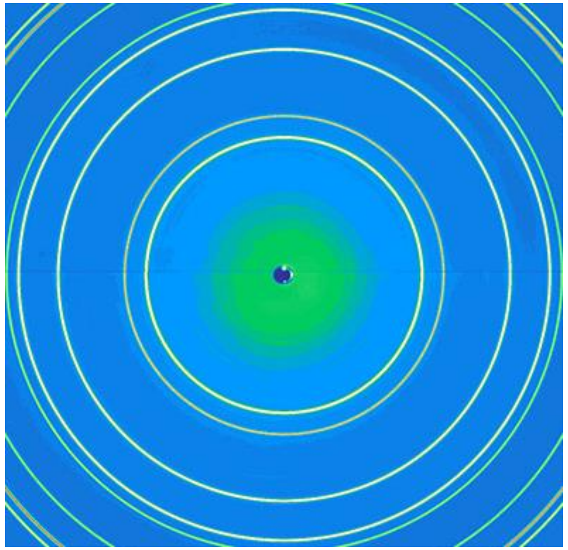
To change the d (Q) space the detector-to-sample distance and detector alignment may be adjusted

The detector-to-sample distance changes affects the resolution

The detector size matters

Detectors positioning

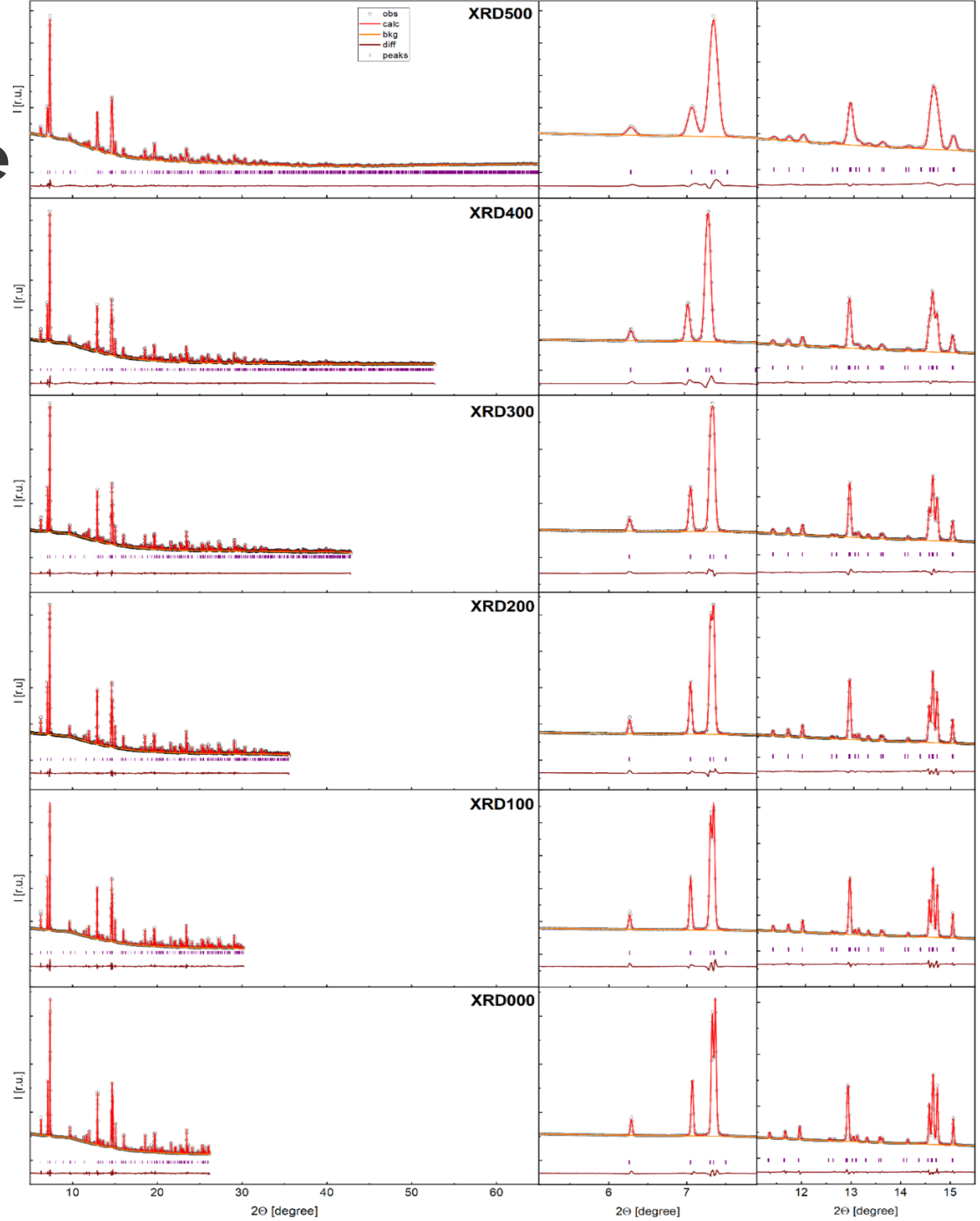




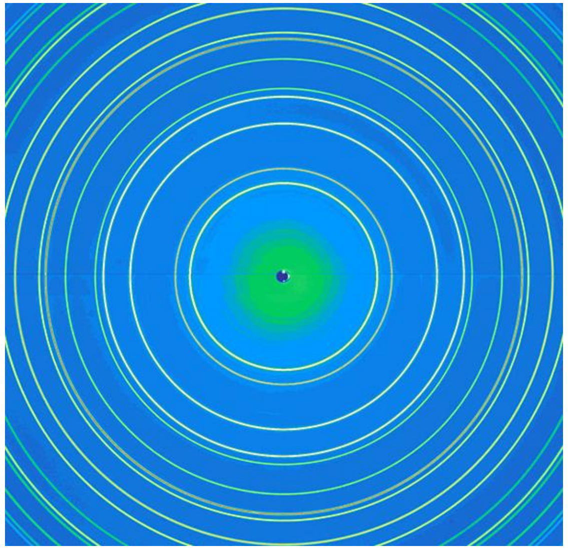
close

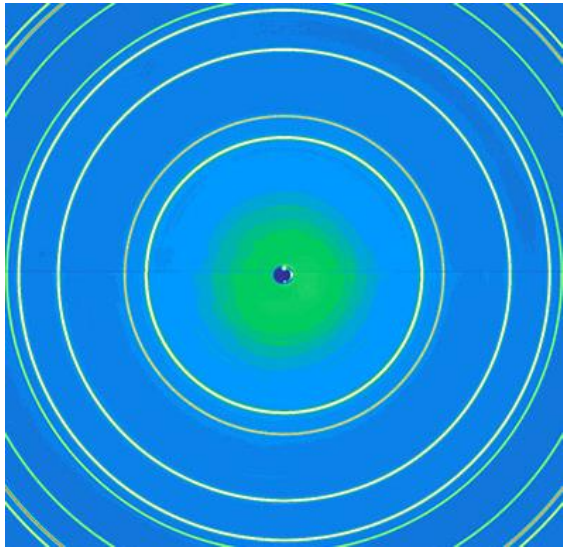
Towards the sample

far



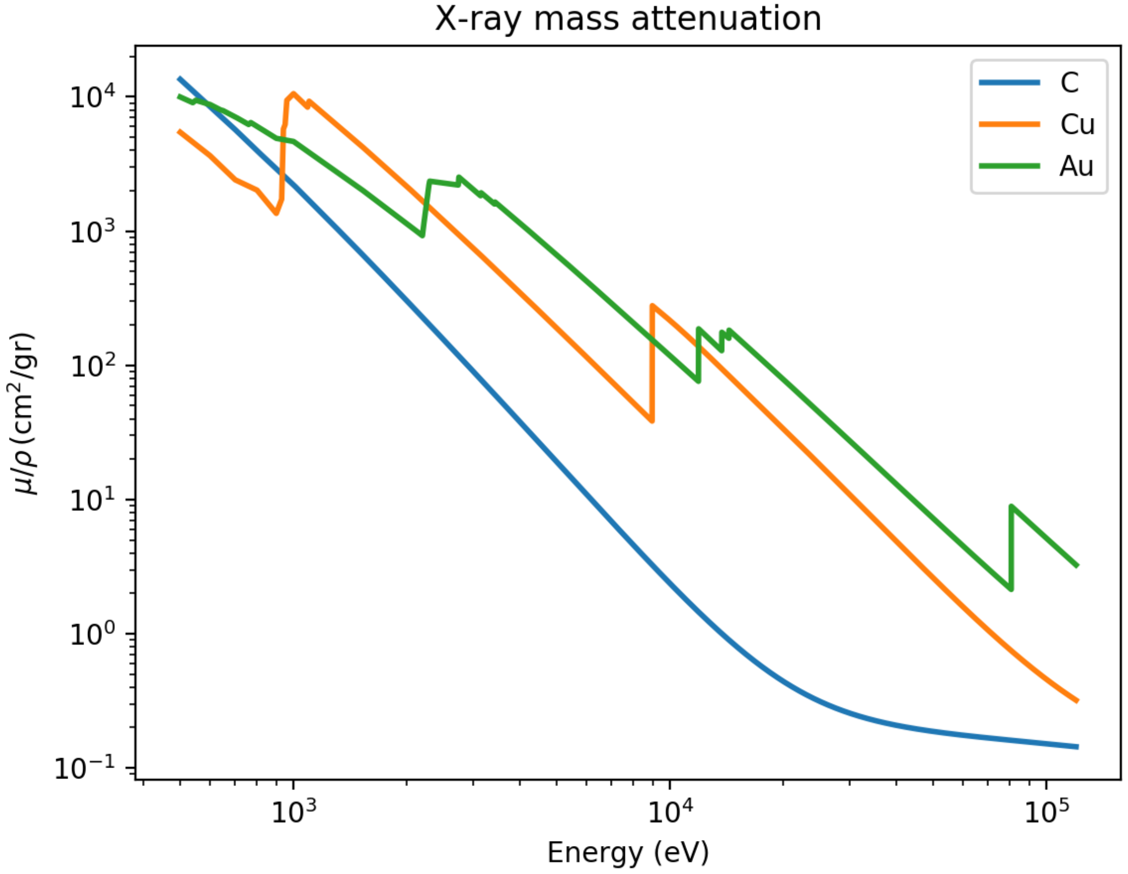
X-ray wavelength



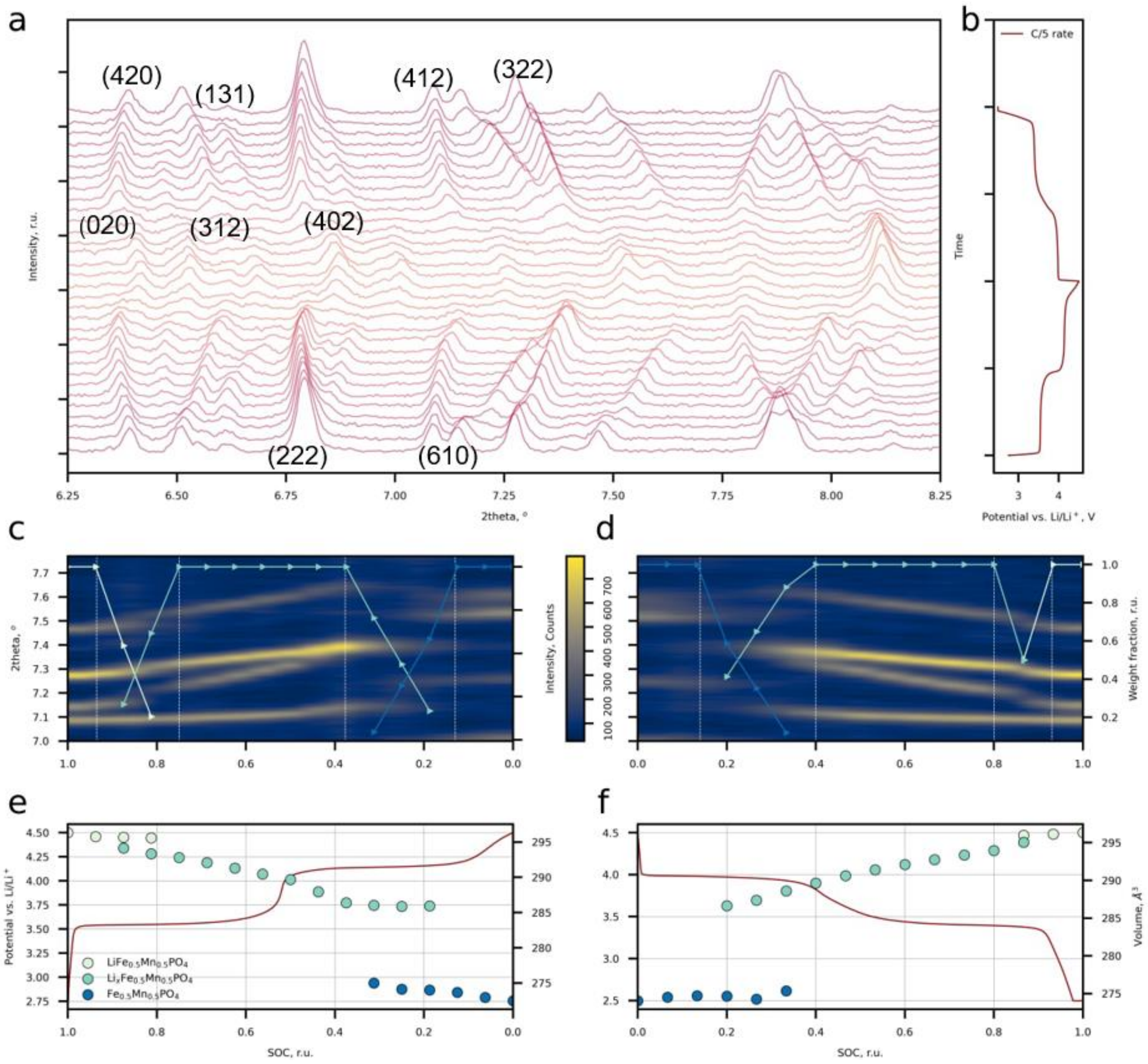


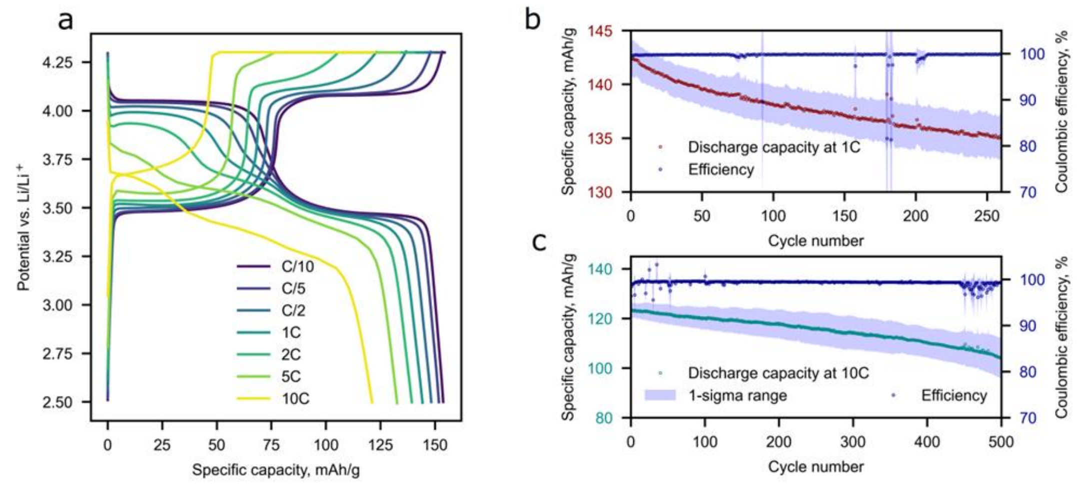
$2d\sin\theta = k\lambda$

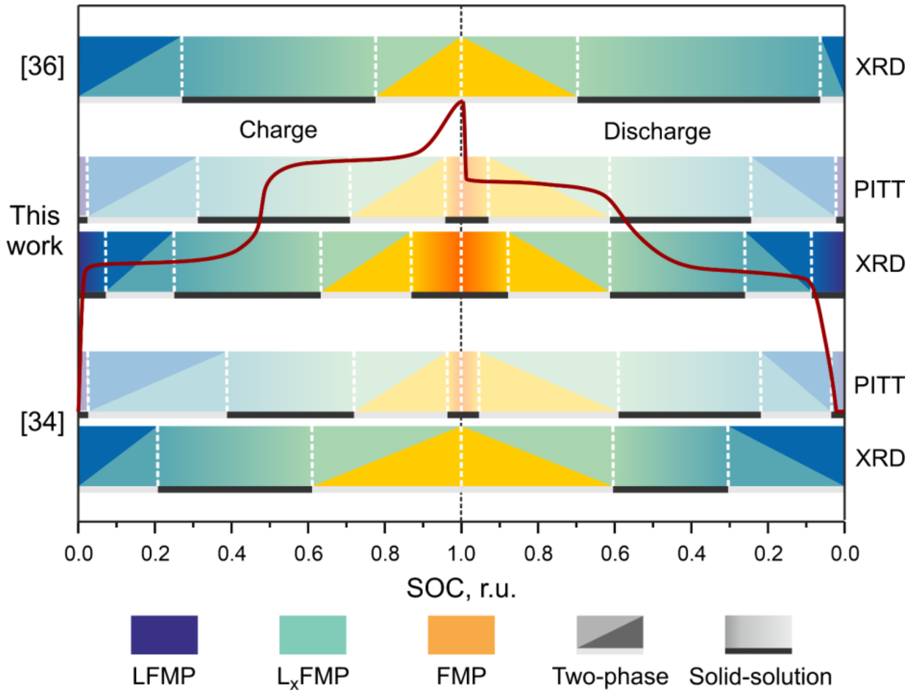
X-ray absorption vs. energy (wavelength)



Li-rich $LiMn_{0.5}Fe_{0.5}PO_4$

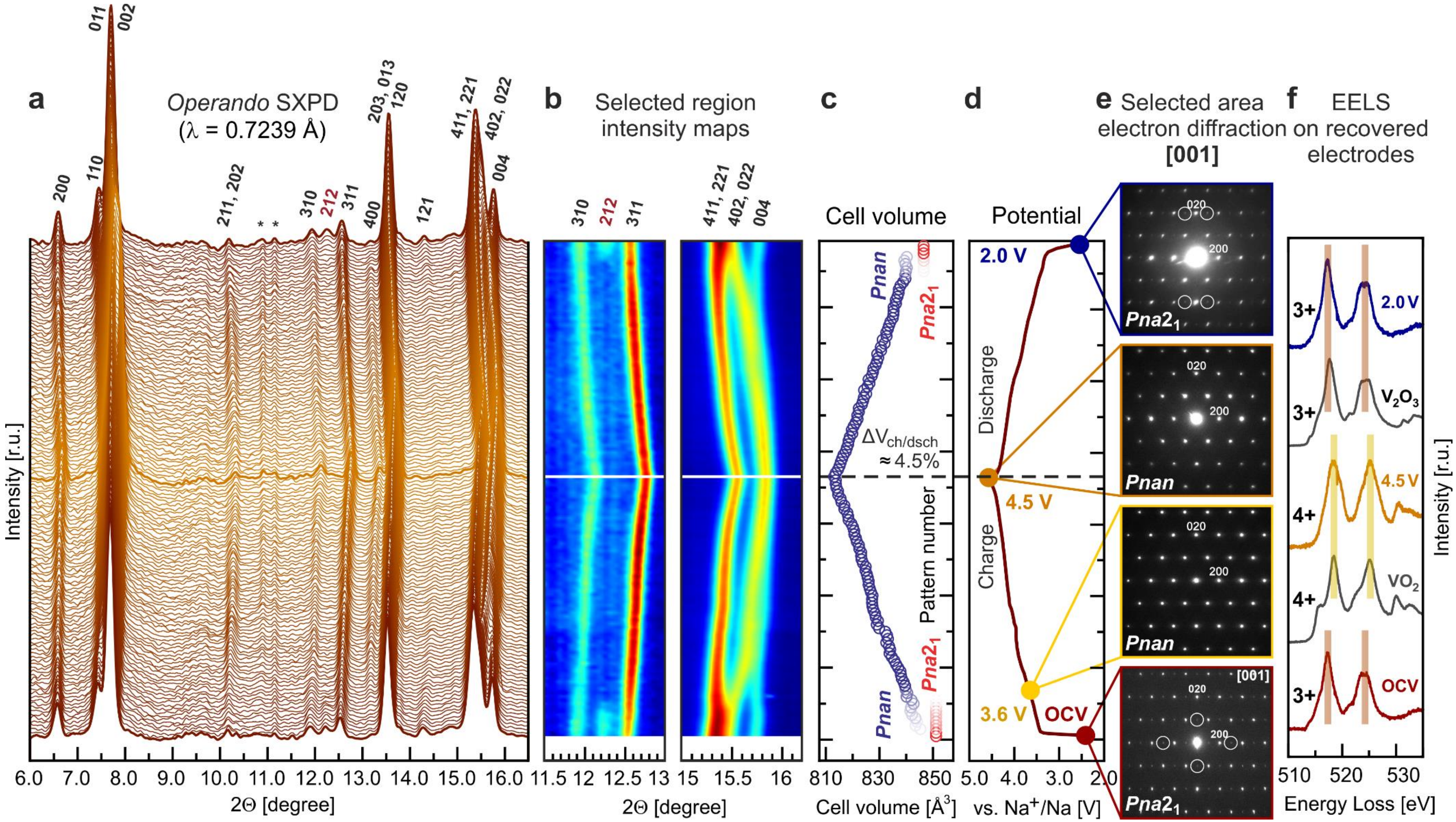






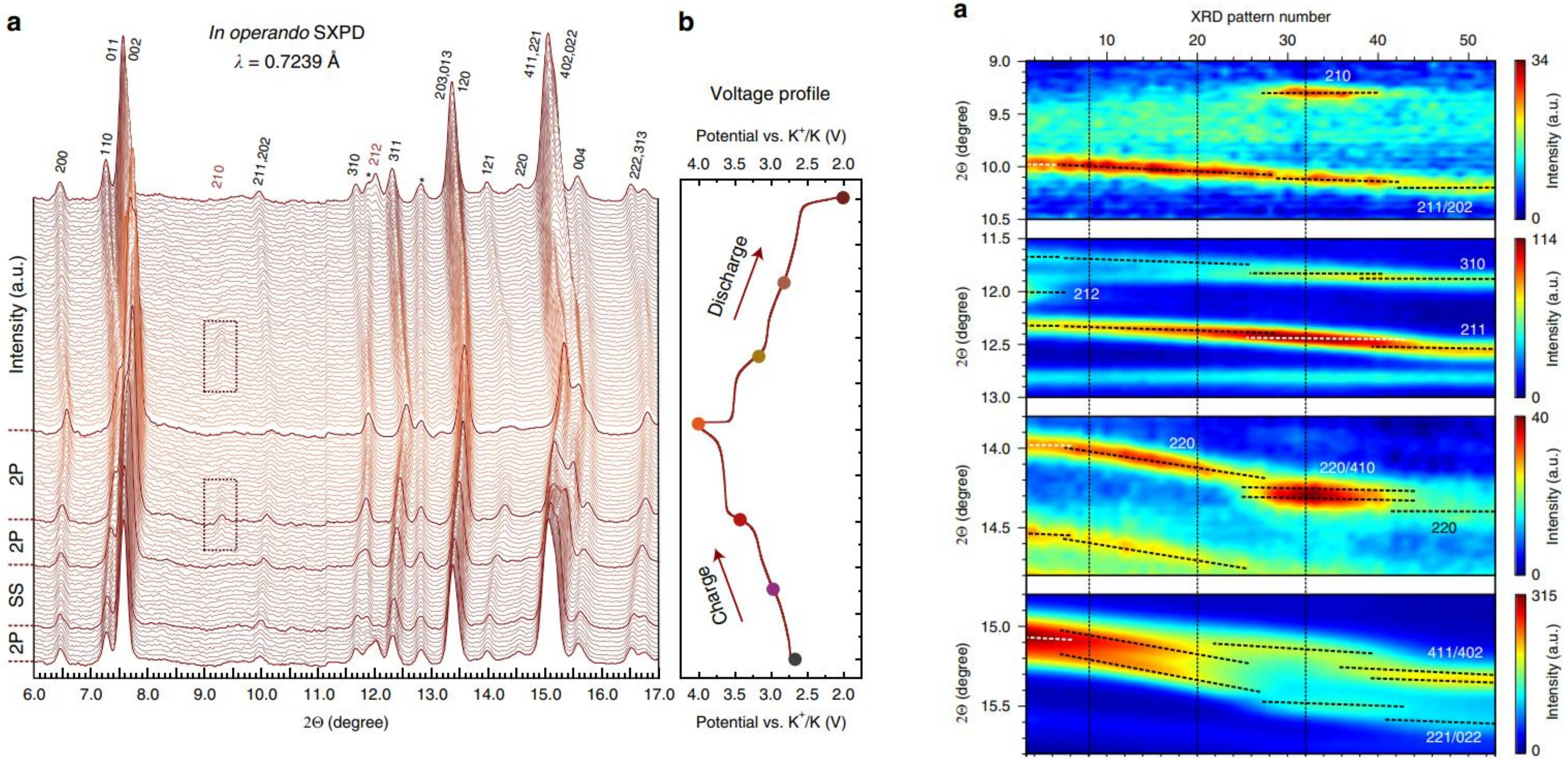
https://doi.org/10.1039/D2YA00292B

$NaVPO_4F$



S. Shraer et al. Nat. Comm. 2022

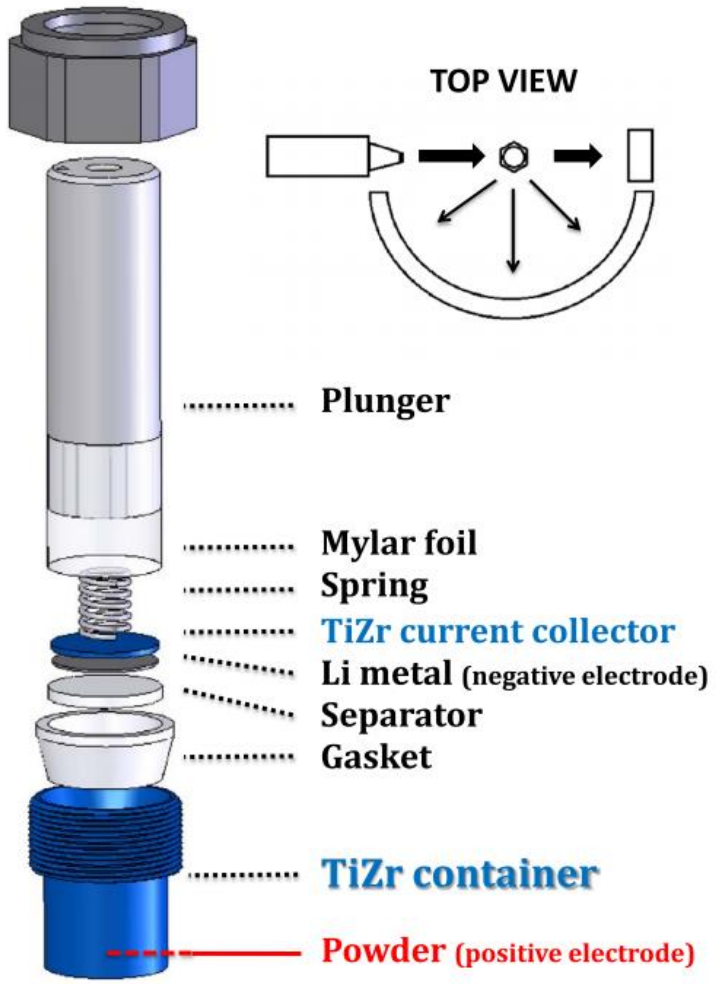
$KTiPO_4F$: structural evolution



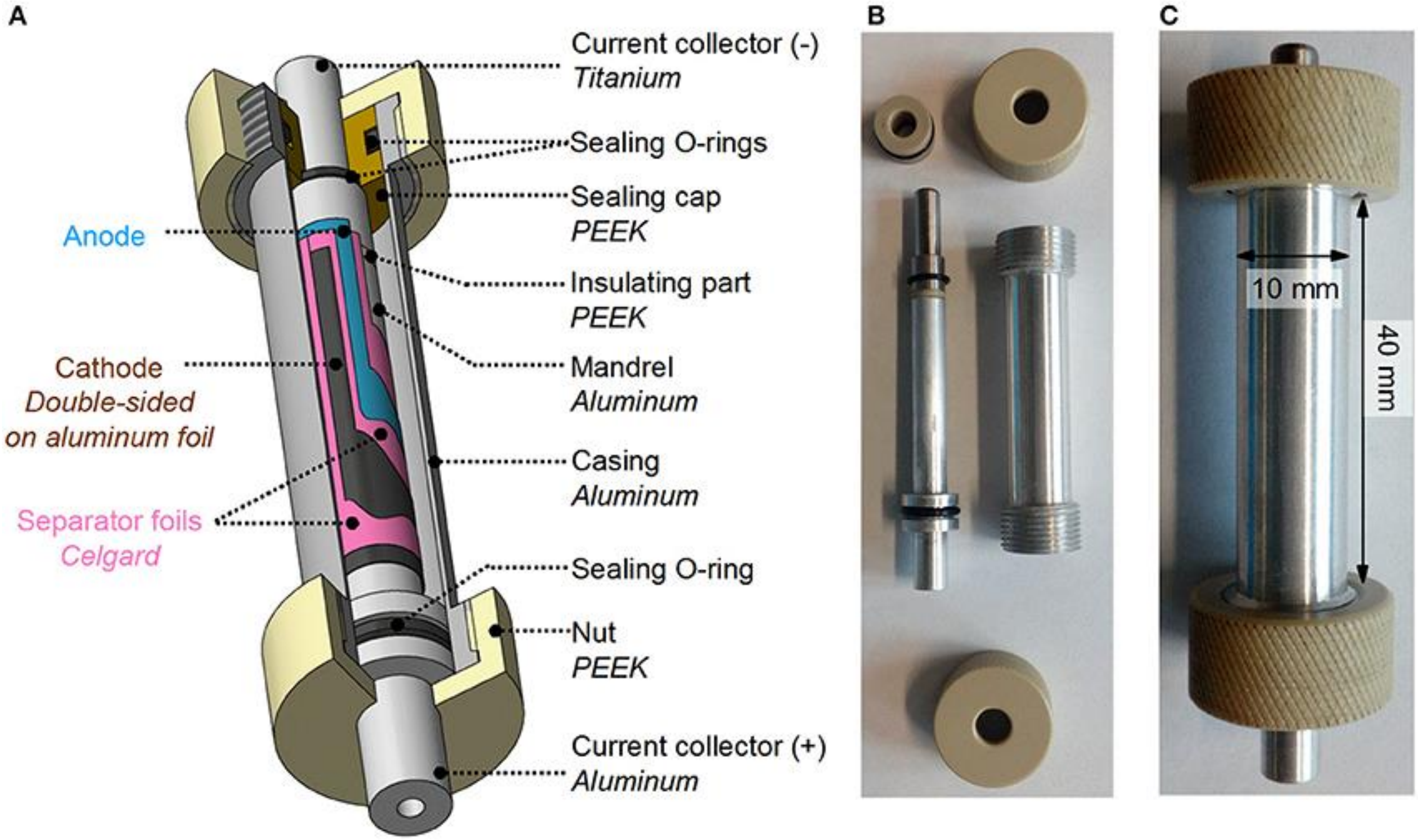
Phase separation with ordering of charges at Ti1 and Ti2

Fedotov S. S., et al *Nat. Commun. 11 (2020)* 1-11

Neutron diffraction operando cell



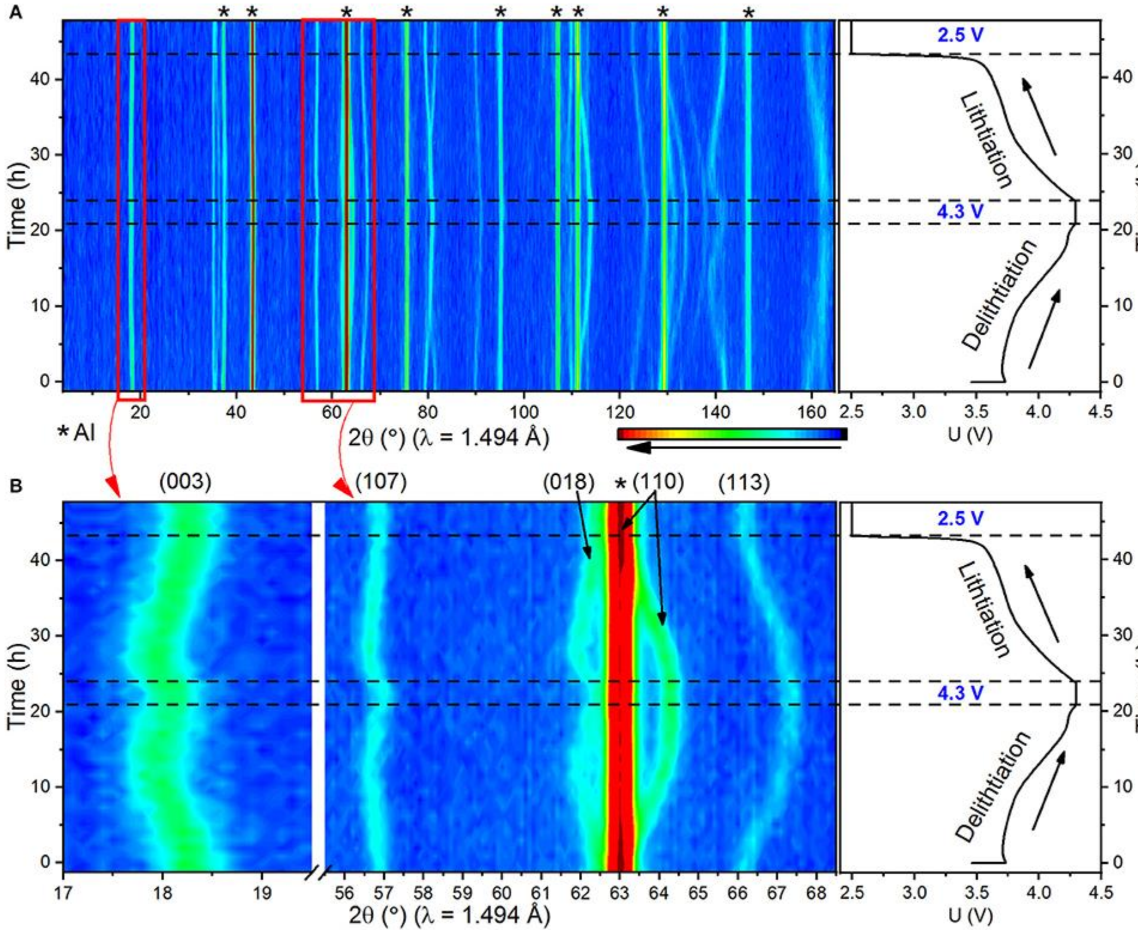
https://doi.org/10.3389/fenrg.2018.00076



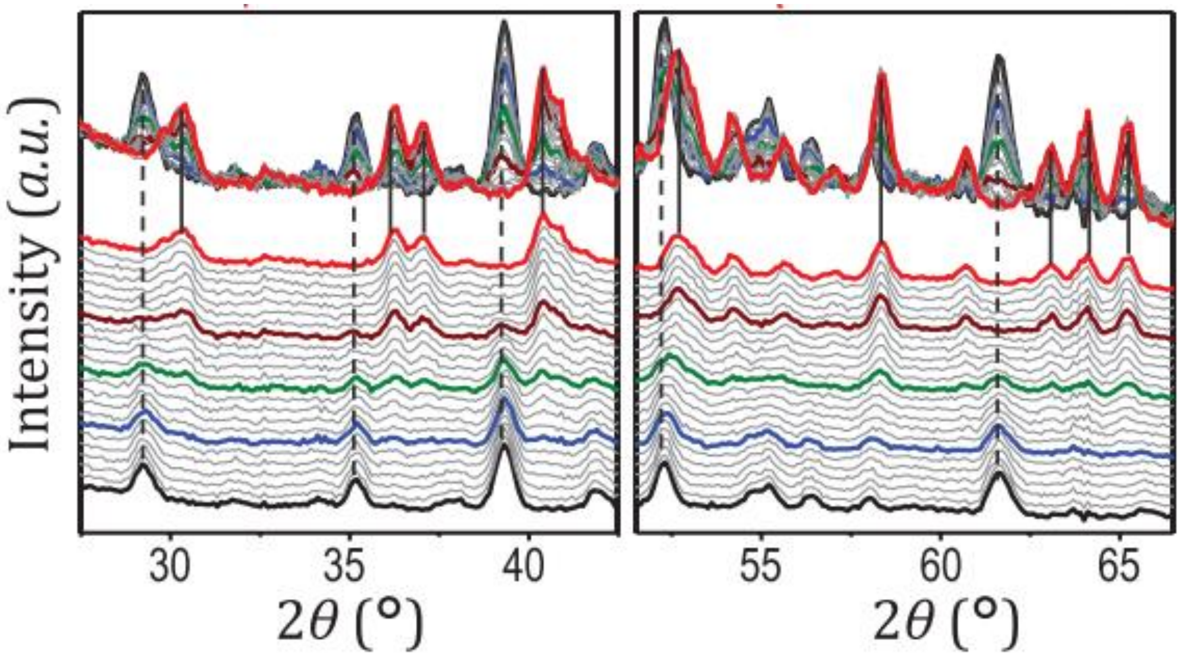
https://doi.org/10.3389/fenrg.2018.00076

Neutron diffraction

$Li(NiCoMn)O_2$ 622



$LiFePO_4$



Thank you for your attention!


Mr. Semyon Shraer


Mr. Nikita Luchinin


Mrs. Polina Morozova


Mr. Sergey Marshenya


Mr. Bulat Matsaev


Mr. Artem Dembitskiy


Dr. Ivan Trussov


Dr. Sergey Ryazantsev


Prof. Olga Shmatova


Mr. Eugene Nazarov


Mr. Anatoly Morozov


Prof. Victoria Nikitina


Prof. Dmitry Aksyonov


Prof. Artem Abakumov


Prof. Evgeny Antipov

RFBR RUSSIAN FOUNDATION FOR BASIC RESEARCH
#21-53-12039

RSF Russian Science Foundation
#23-73-10125

Skoltech Translational Research & Innovation program

Elettra Sincrotrone Trieste

Energy Technology for Better Life
Skoltech Startup

ICr Lab

Skoltech
Skolkovo Institute of Science and Technology

Thx!