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Operando powder X-ray diffraction

in application to battery materials

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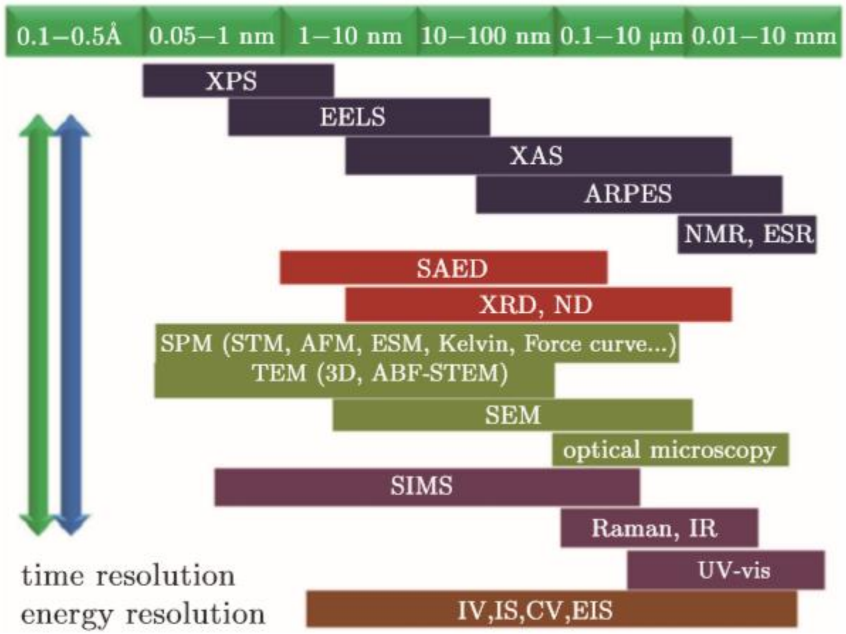
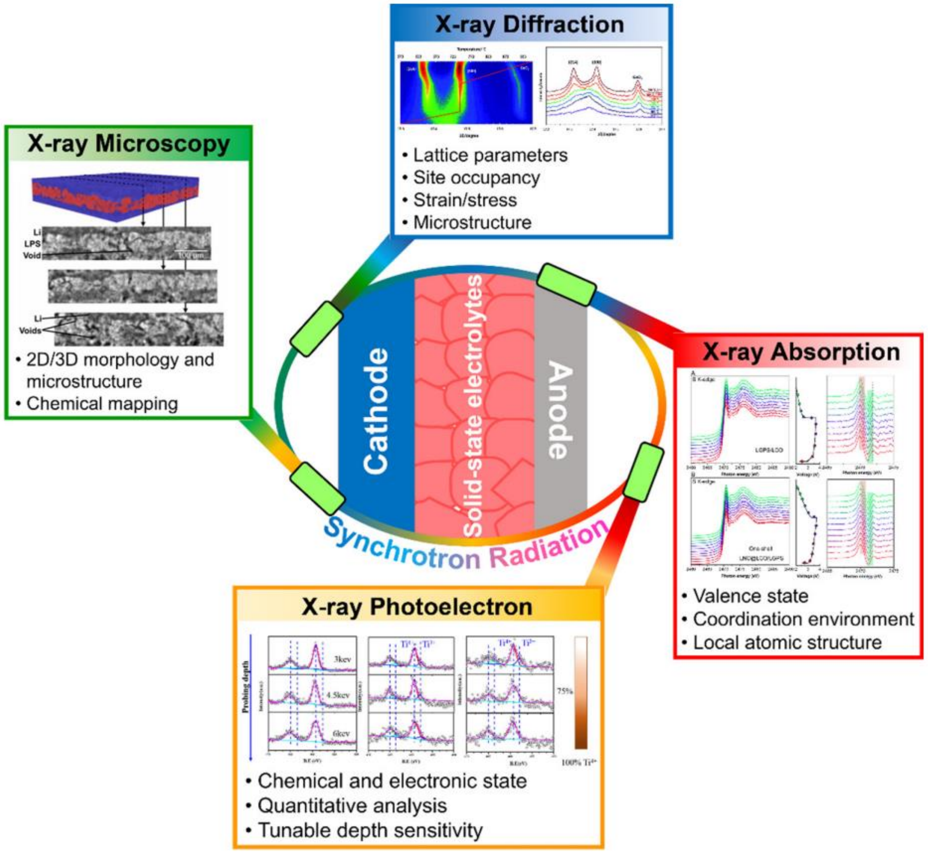
ICYS-2021, Moscow, November 13th, 2021

Characterization techniques





10.1088/1674-1056/25/1/016104

10.1016/j.mattod.2020.01.018

Terminology

Ex situ

1. Run electrochemical experiment
2. Stop experiment
3. Cell disassembling
4. Analysis

In a conventional cell

In situ

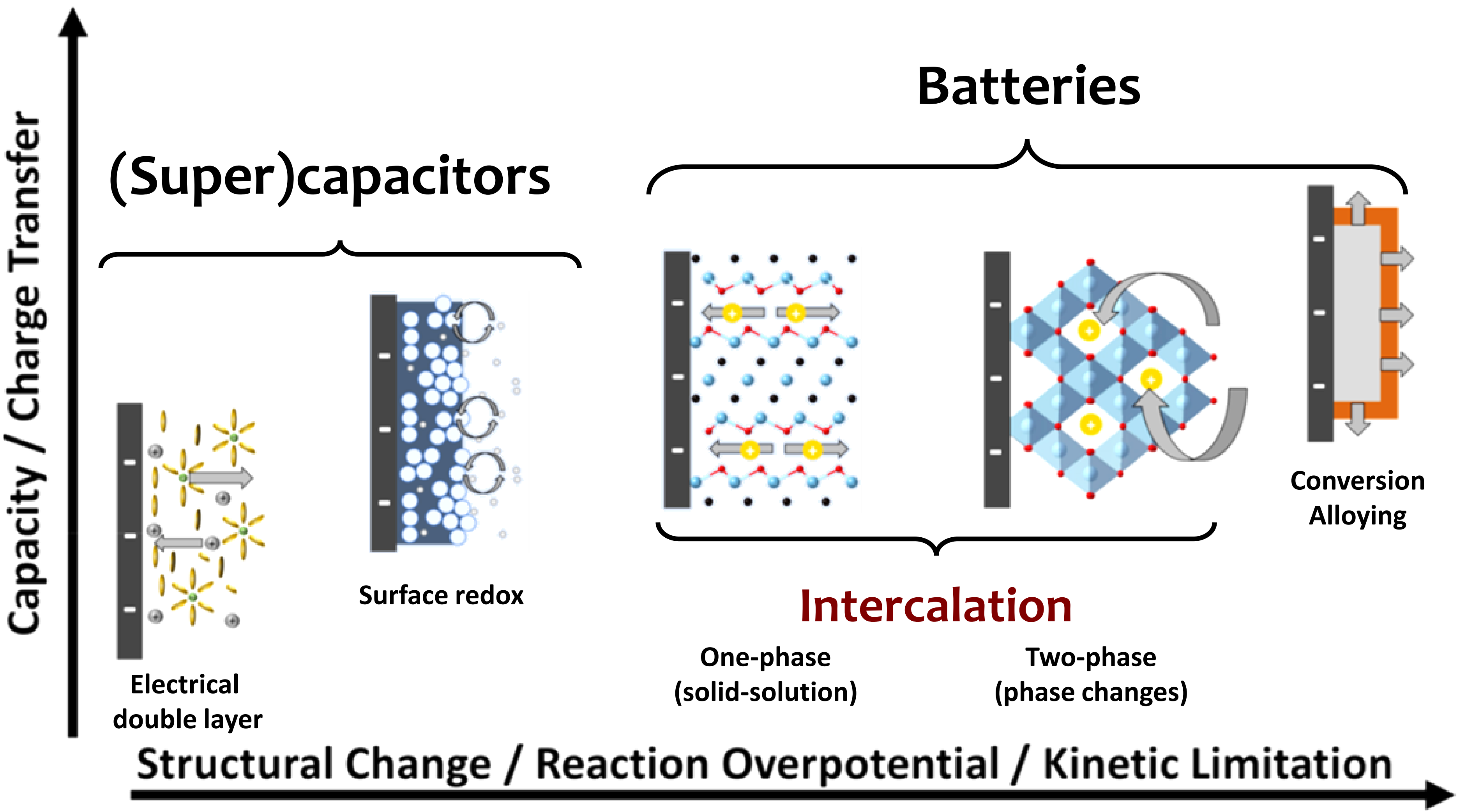
1. Run electrochemical experiment
2. Stop experiment
3. Analysis

Operando

1. Run electrochemical experiment
1. Analysis

In an special electrochemical cell

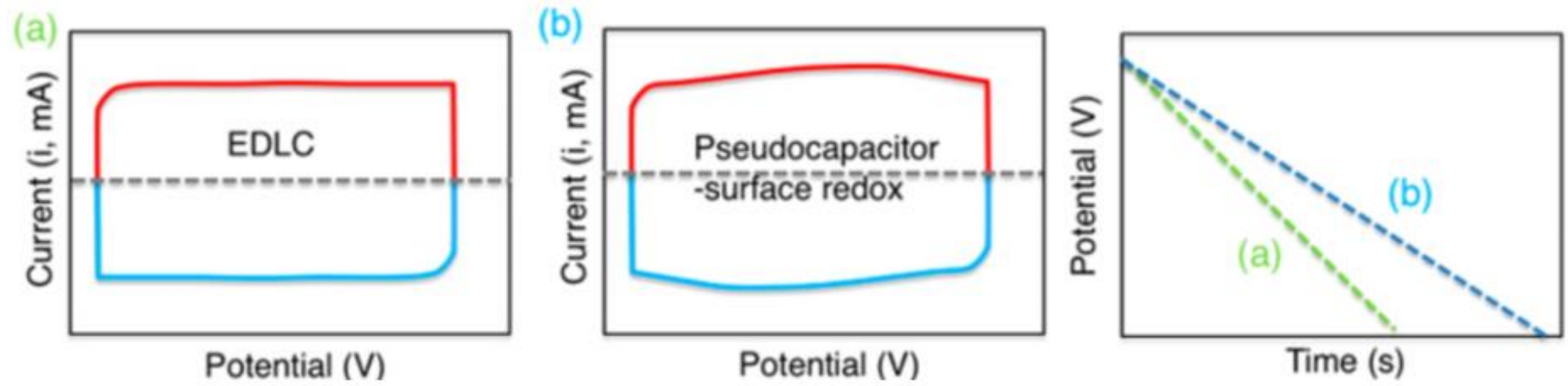
Electrochemical energy storage mechanisms



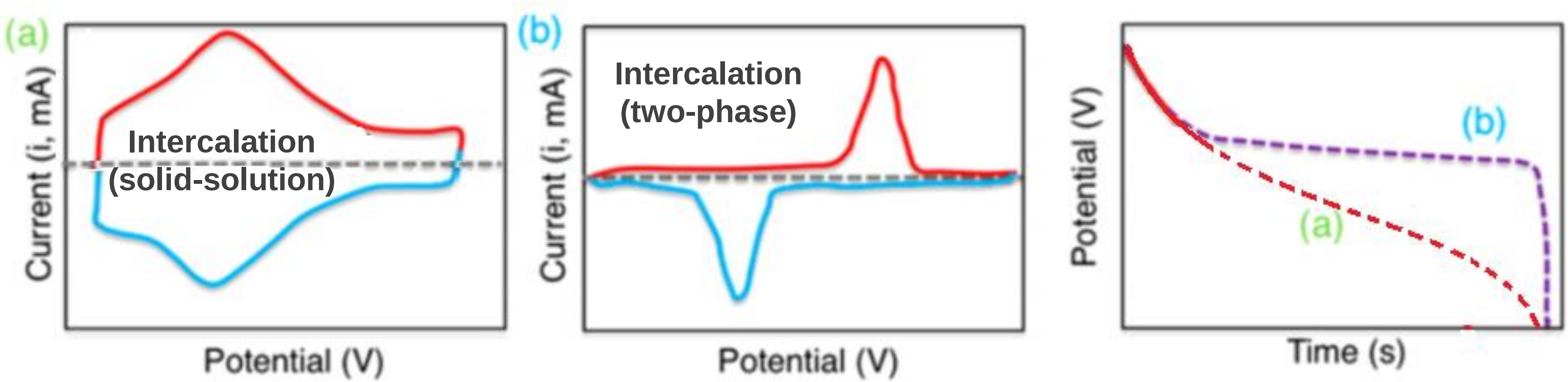
Fleischmann S. et al. Chem. Rev. 2020, 120, 6738-6782.

Electrochemical energy storage mechanisms

(Super)capacitors



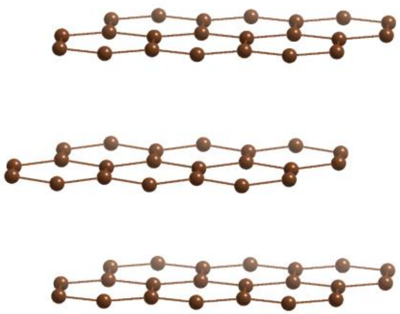
Batteries



Fleischmann S. et al. Chem. Rev. 2020, 120, 6738-6782.

Graphite intercalation compounds (GICs)

Intercalation, 1841 – graphite bisulfate

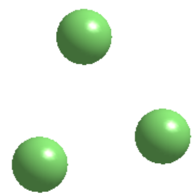


Graphite

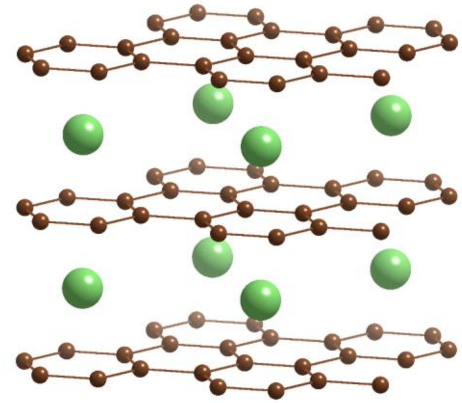
$d = c/2 =$ 3.354 Å

+

Li^+

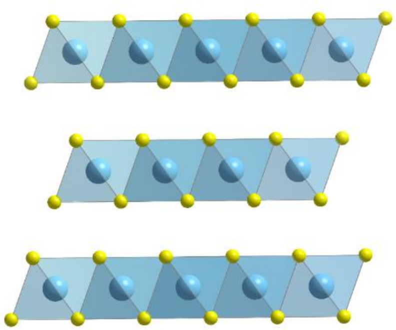


→



Li_xC_6

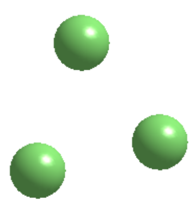
$c =$ 3.706 Å ΔV ~ 10%



TiS_2

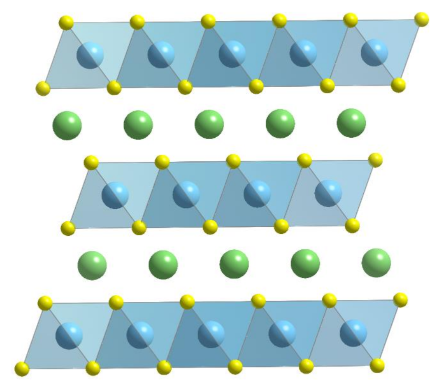
+

Li^+



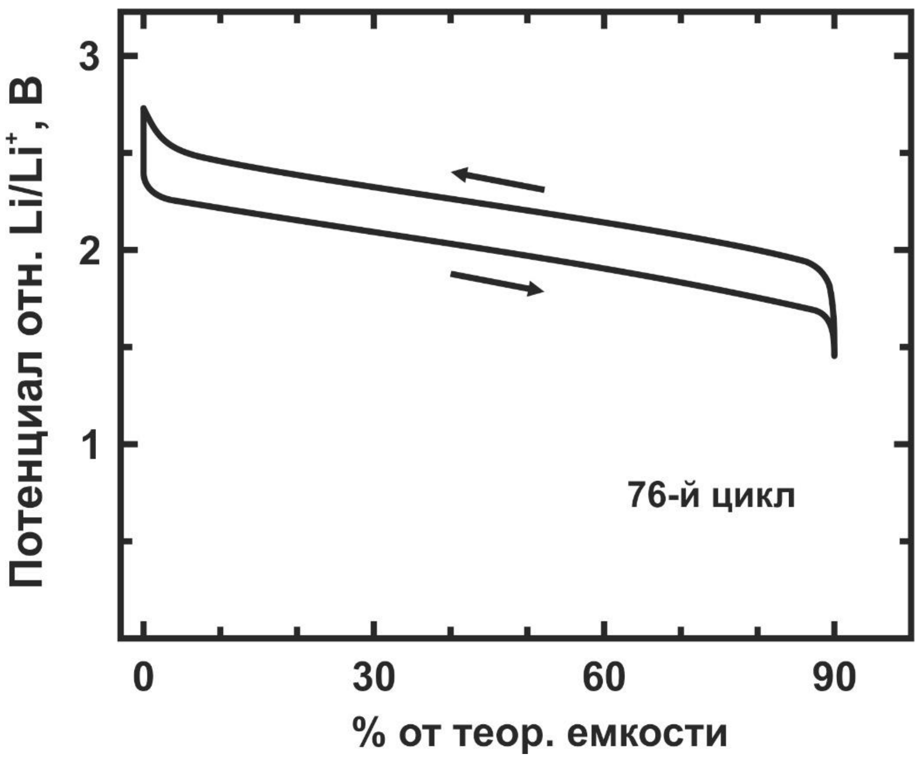
Li_xTiS_2 solid-solution

→



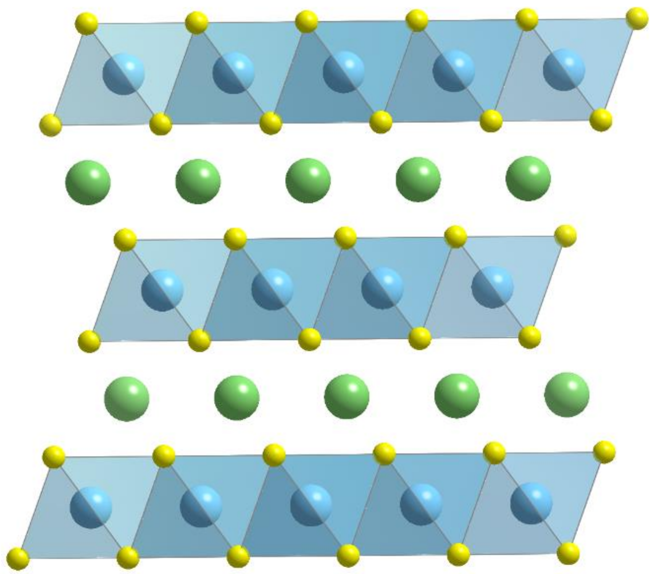
Li_xTiS_2

Intercalation cathode materials



Potential is around 2.0 V vs Li/Li$^+$

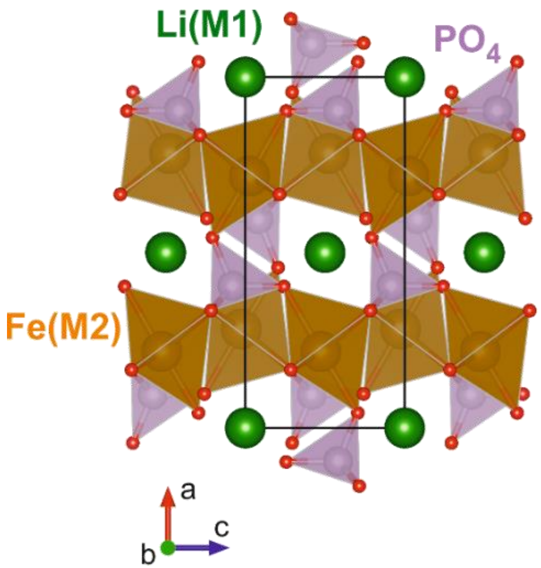
Li/TiS_2 battery by EXXON in 1980-s



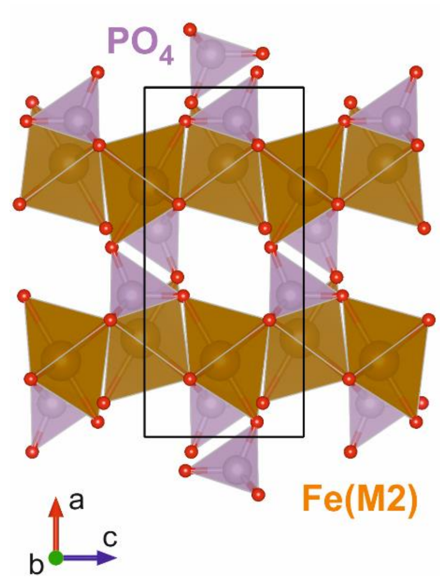
Li_xTiS_2

Li_xTiS_2 solid-solution

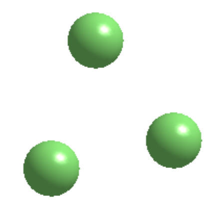
Intercalation cathode materials

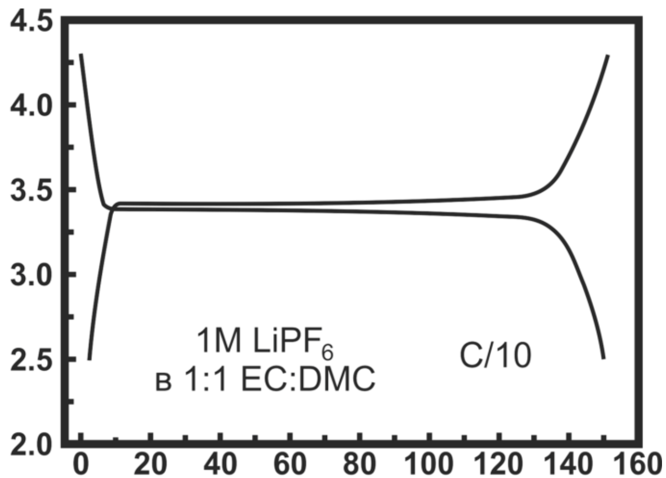


$LiFePO_4$ Triphylite



$FePO_4$ Heterosite





~3.43 V vs. Li^+/Li

Two-phase mechanism

Electrochemical energy storage mechanisms

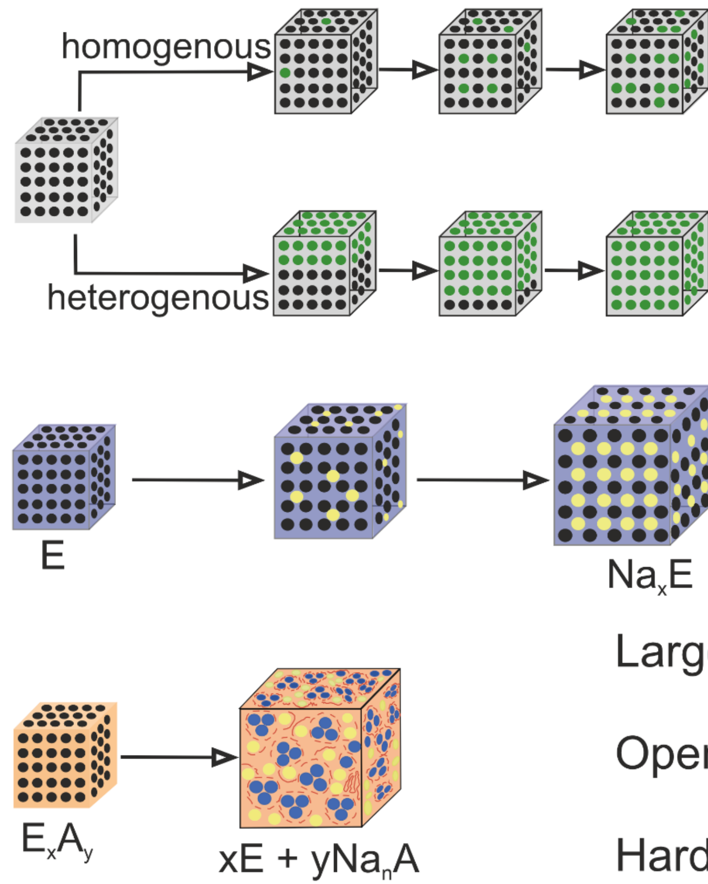
Reaction mechanisms with alkali metal cation

"depth" of structural transformation

intercalation

alloying

conversion



"Conventional" process

Moderate capacity values

Large capacity values

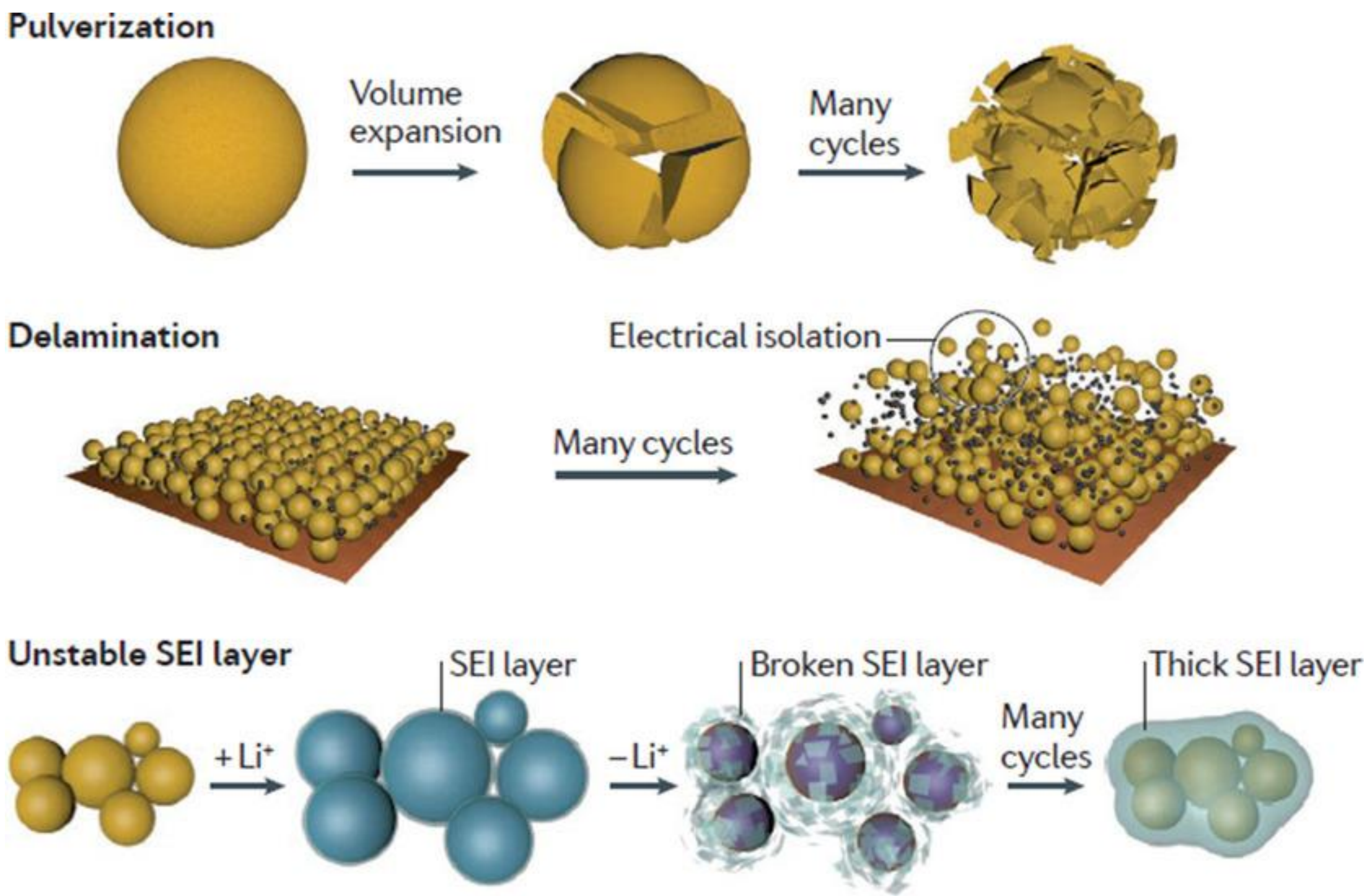
Huge volume changes

Large capacity values

Operating potential hysteresis

Hardly controlable
electrode degradation

Conversion and alloying

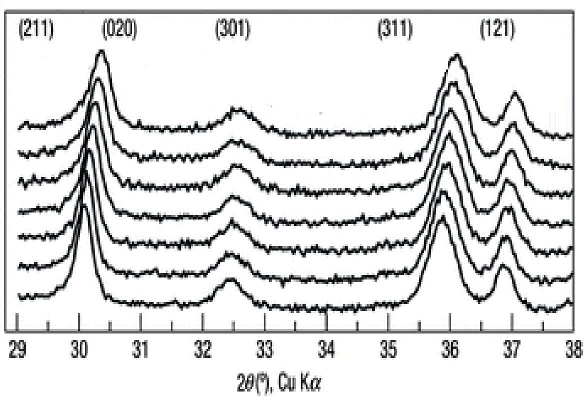


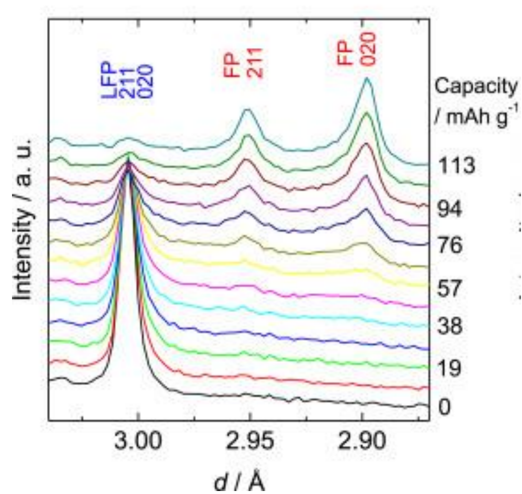
XRD changes vs. de/intercalation mechanism

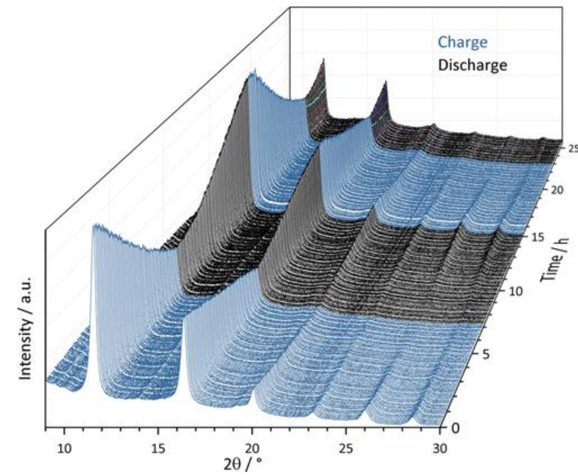
Intercalation (Solid-solution, Two-phase)

Phase transition (Two-phase, Conversion)

Solid-solution | Two-phase | Conversion

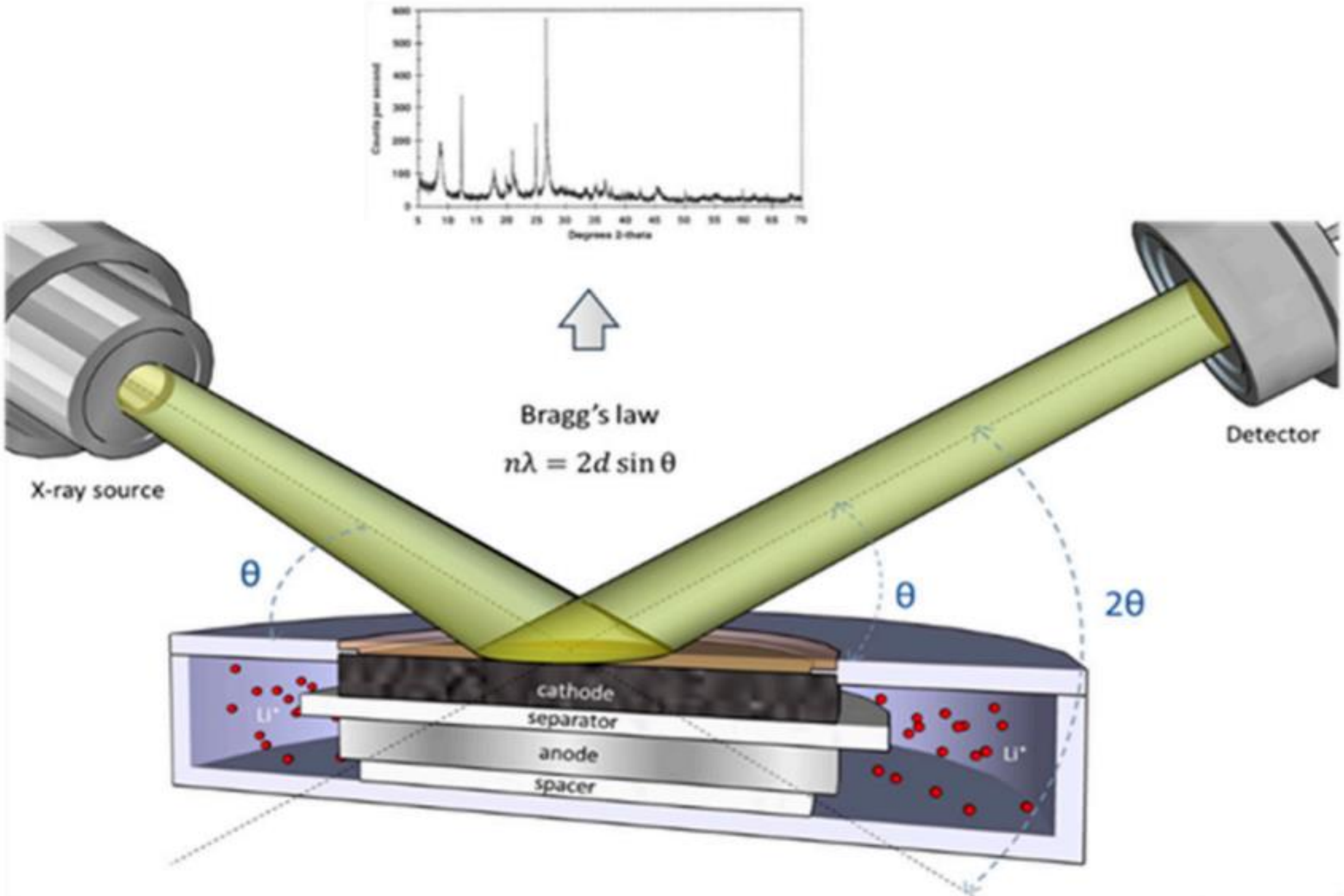






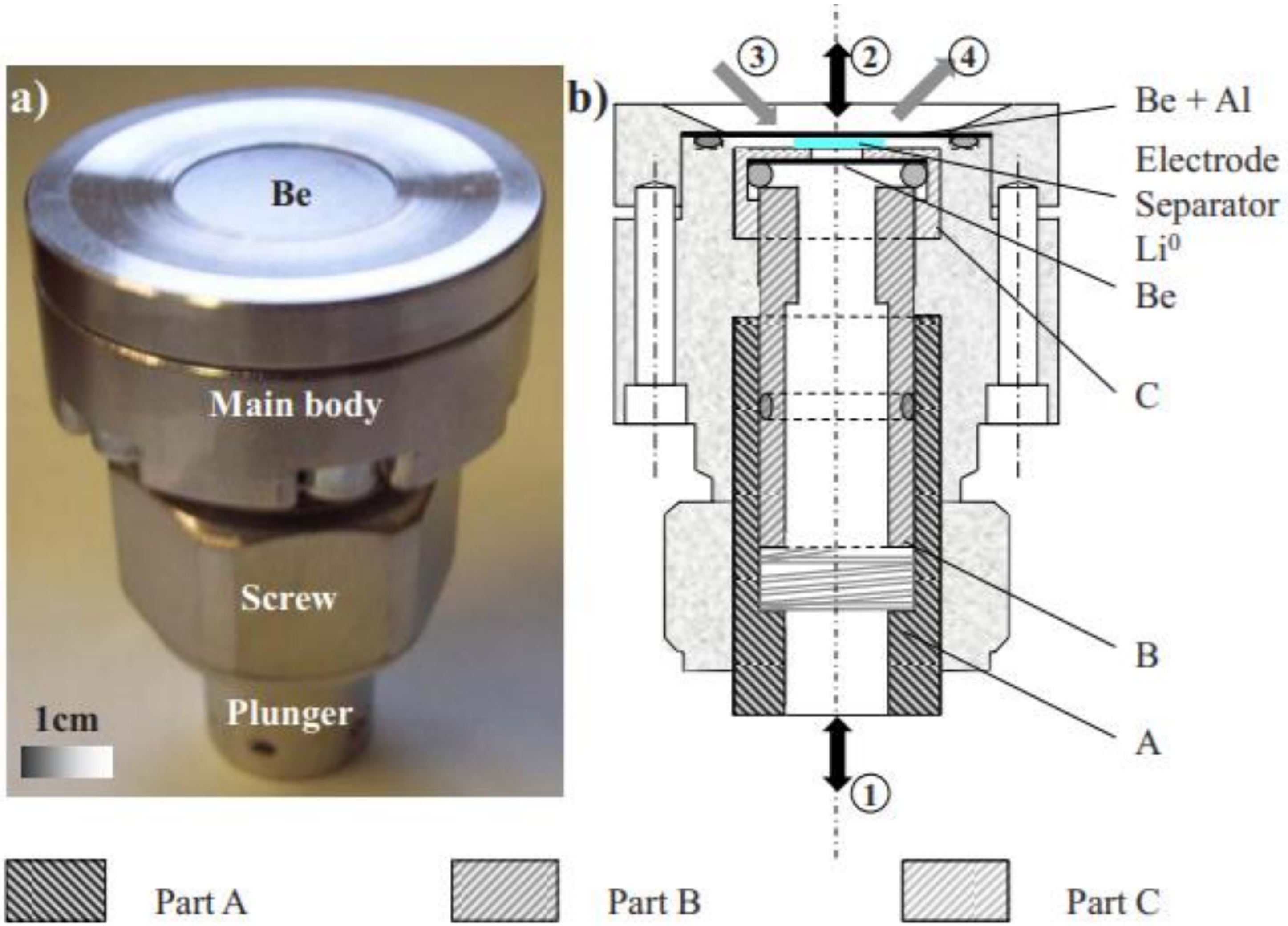
Solid-solution	Two-phase	Conversion
Gradual change of cell parameters	Two phases co-exist with different cell parameters	Radically different crystal structure and cell parameters
Symmetry preserves	Symmetry may change	Symmetry most probably changes
Rapid kinetics	Phase boundary propagation	$M_xO_y + 2yLi^+ + 2ye = xM + yLi_2O$

Principle scheme



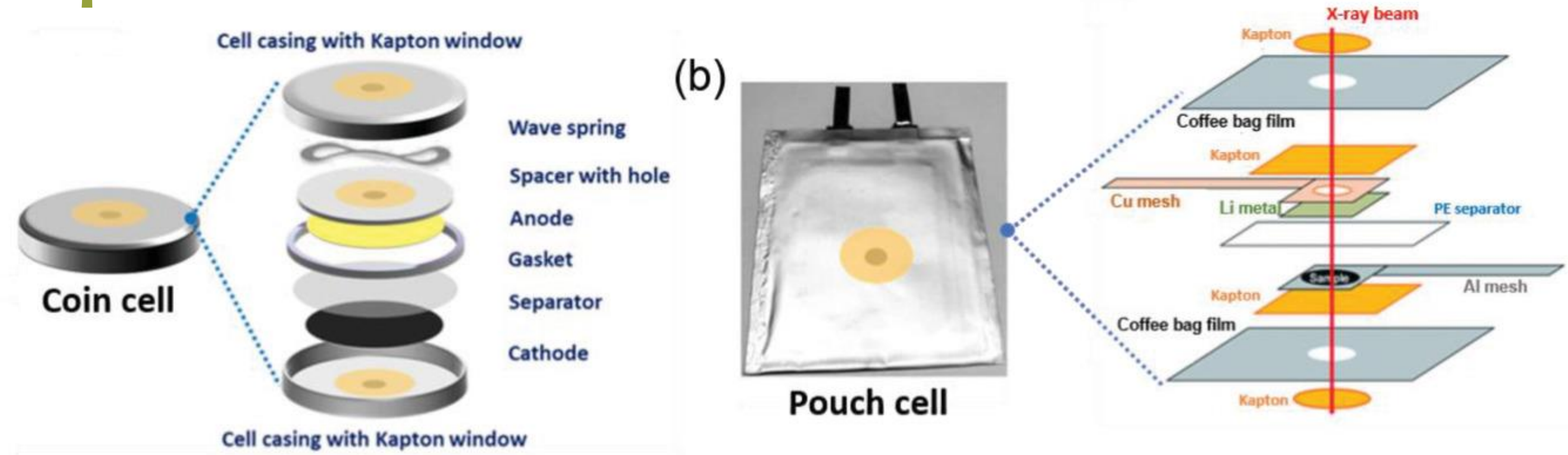
Condens. Matter 2020, 5, 75

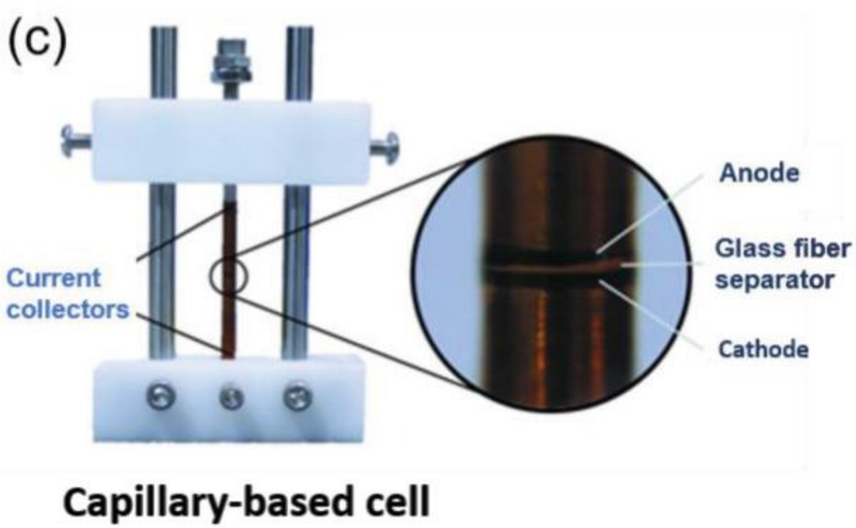
Electrochemical cell

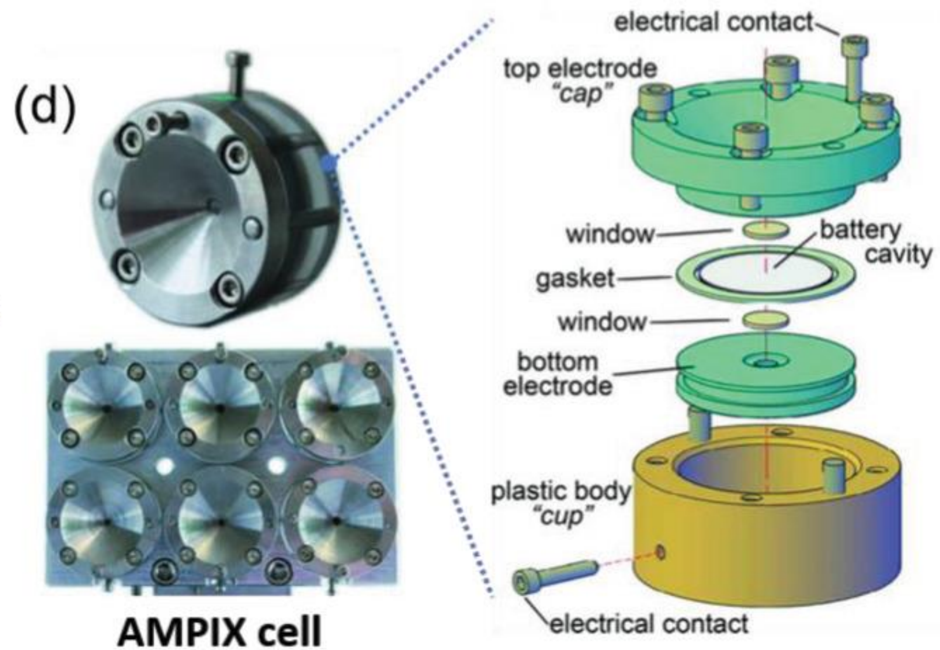


J.B. Leriche et al, JES, 2010

Operando electrochemical cells

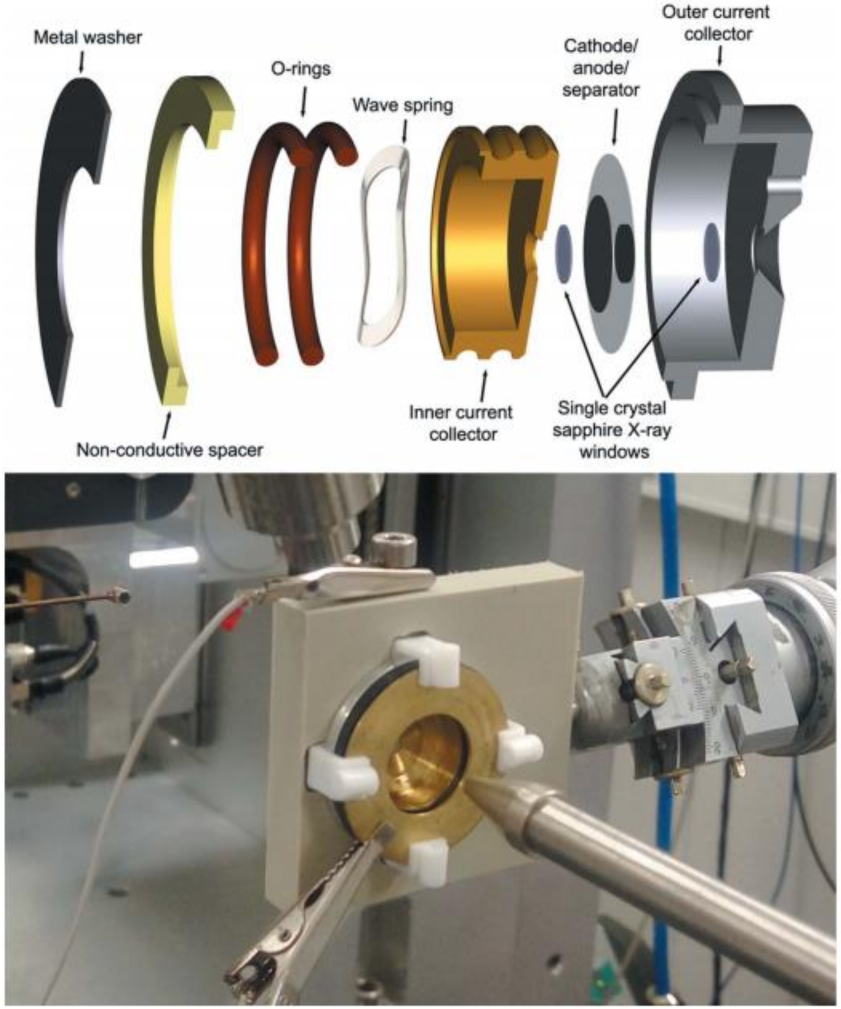






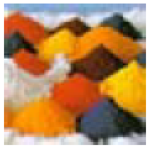
https://doi.org/10.1002/smtd.201900223

Synchrotron operando cells: ESRF BM01

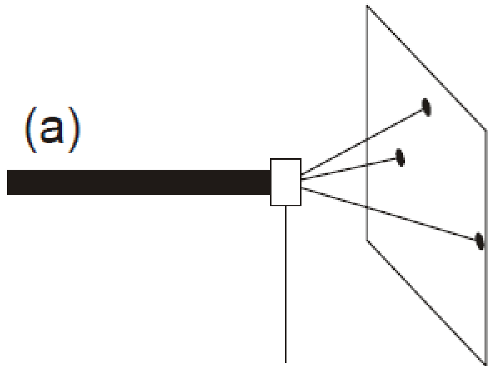


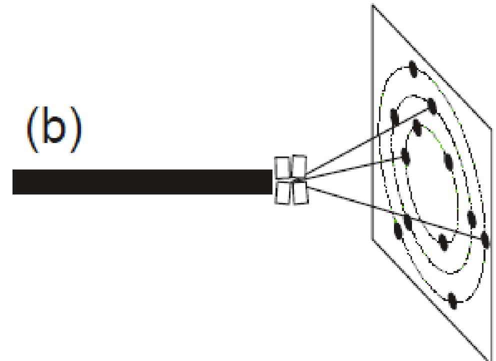
O.A. Drozhzhin et al, J. Synchrotron Rad. (2018). 25, 468–472

Signal formation



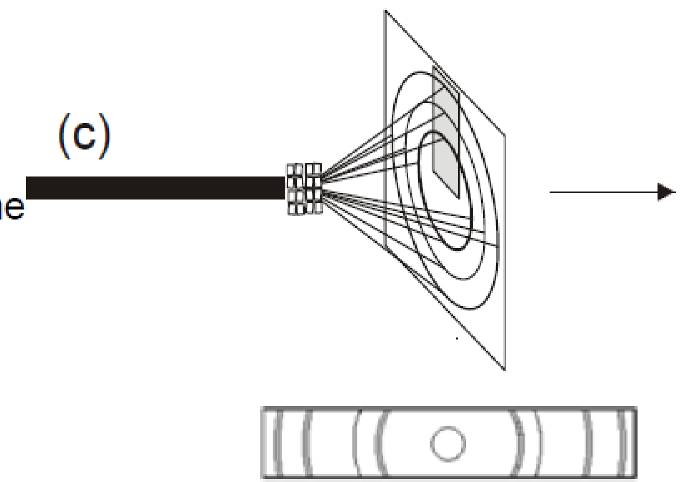
Single crystal

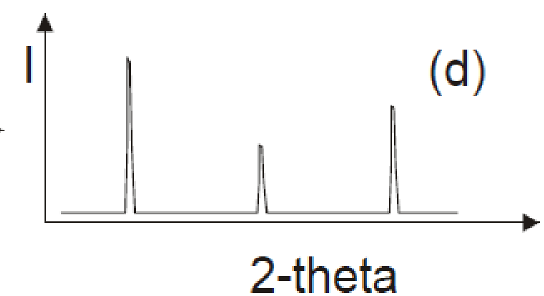




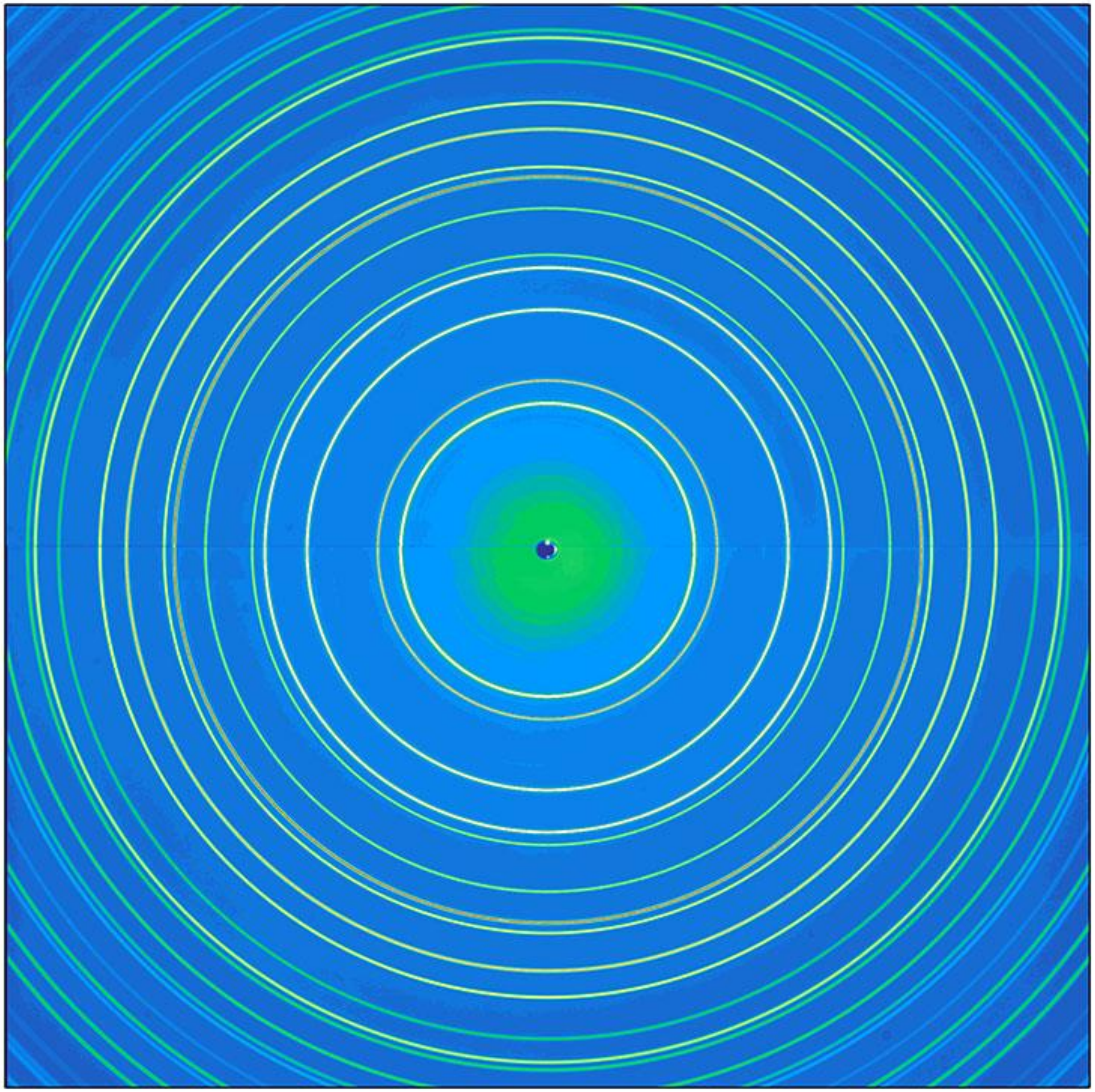
Four differently oriented single crystals

Polycrystalline material



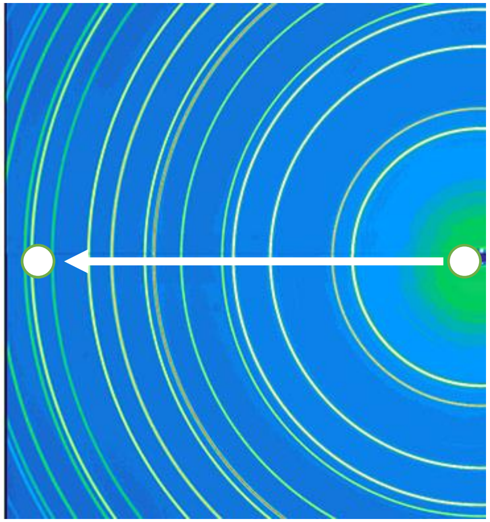


Signal formation



Detector types

0D (scintillation)

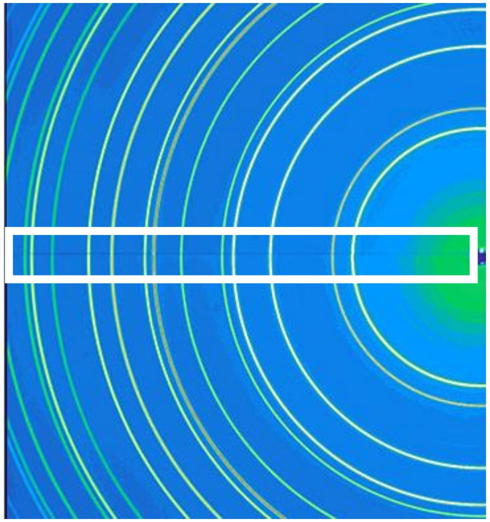


Small spot measured

Scan necessary

Long measuring time

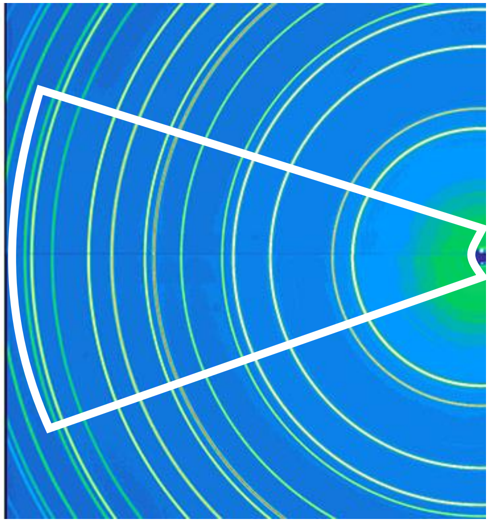
1D (position sensitive, PSD)



Simultaneous measurement

Medium measuring time

2D



Monocrystals
Oriented samples

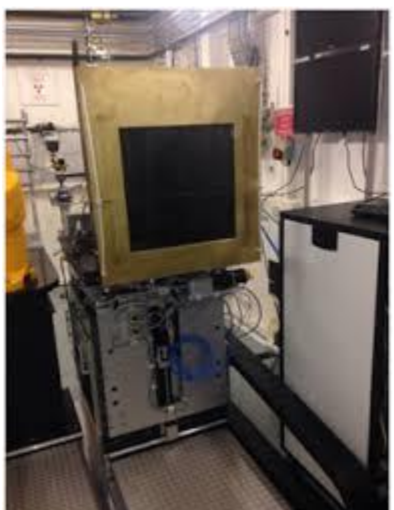
Fast measuring time

Instant measuring time

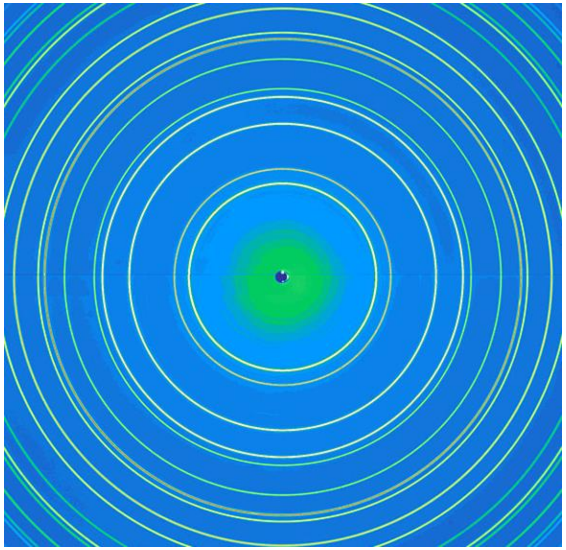
Detector types

Perkin Elmer

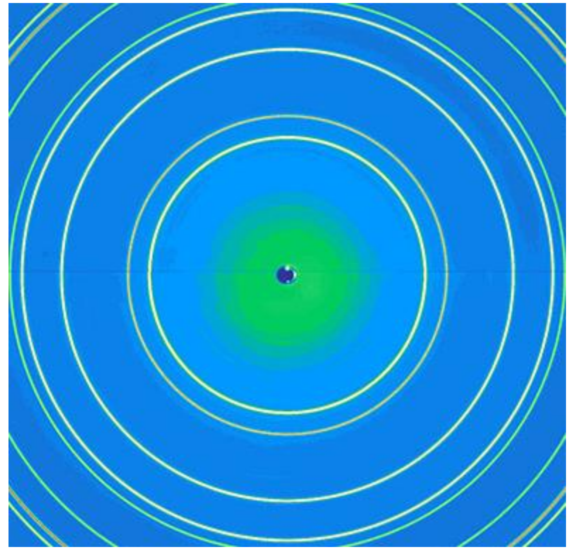
DECTRIS



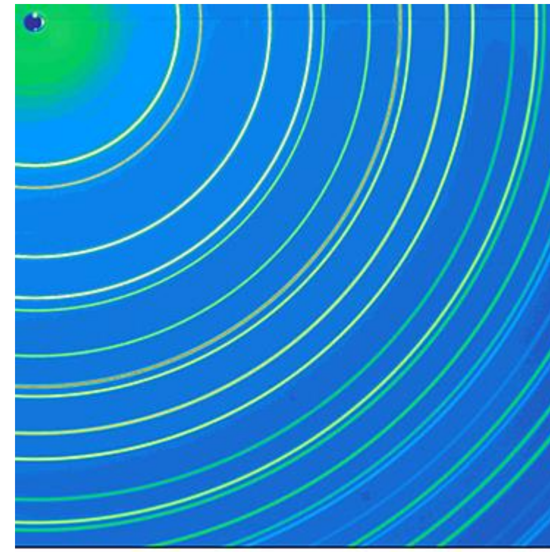
Detector positioning



Close to the sample



Far from the sample



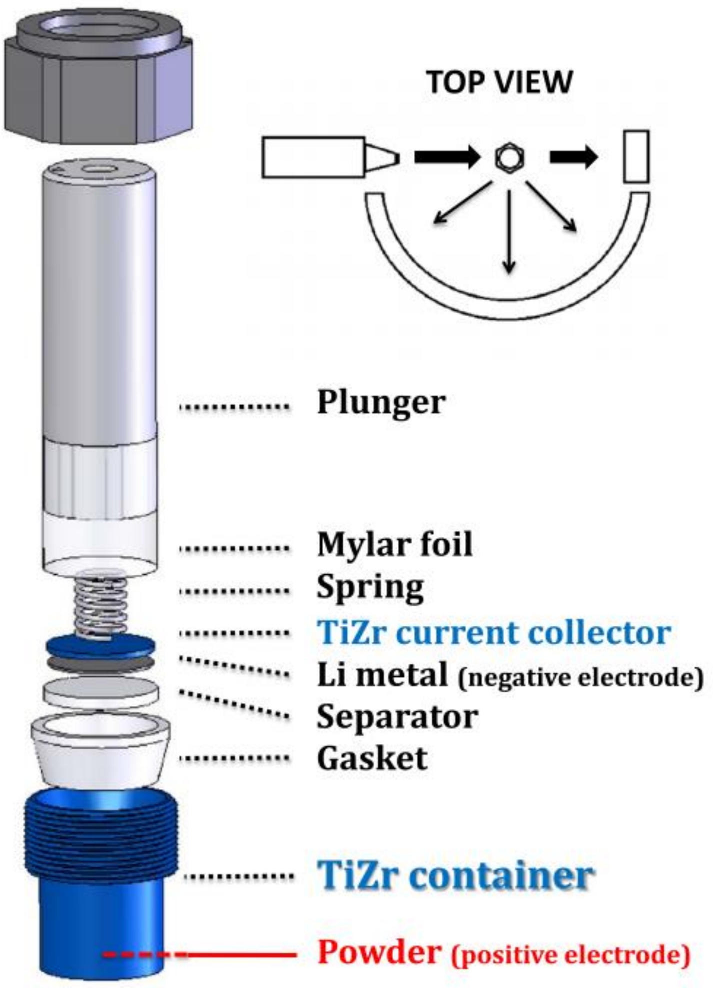
Shifted against the beam

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

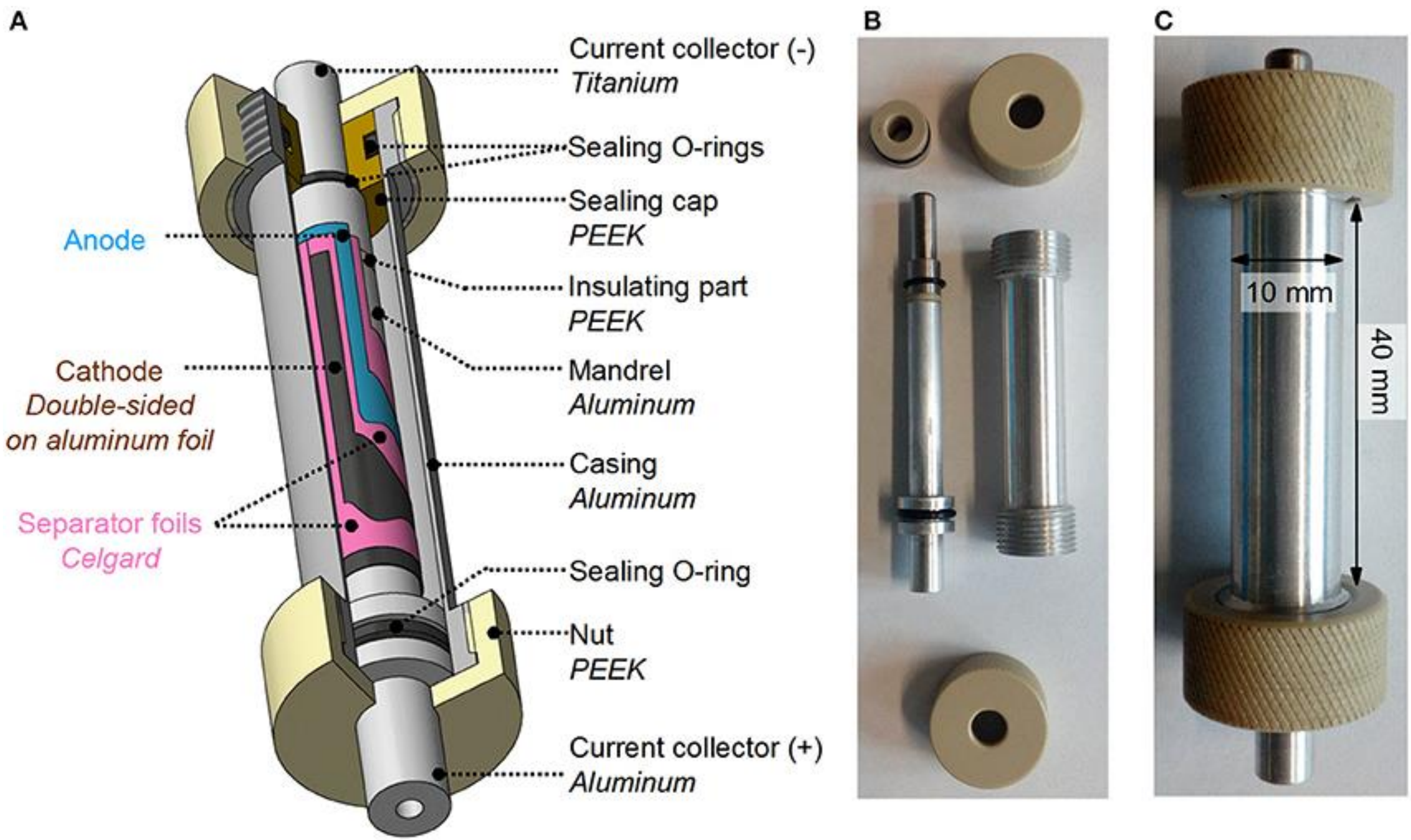
The detector size matters

Neutron diffraction: operando cells



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

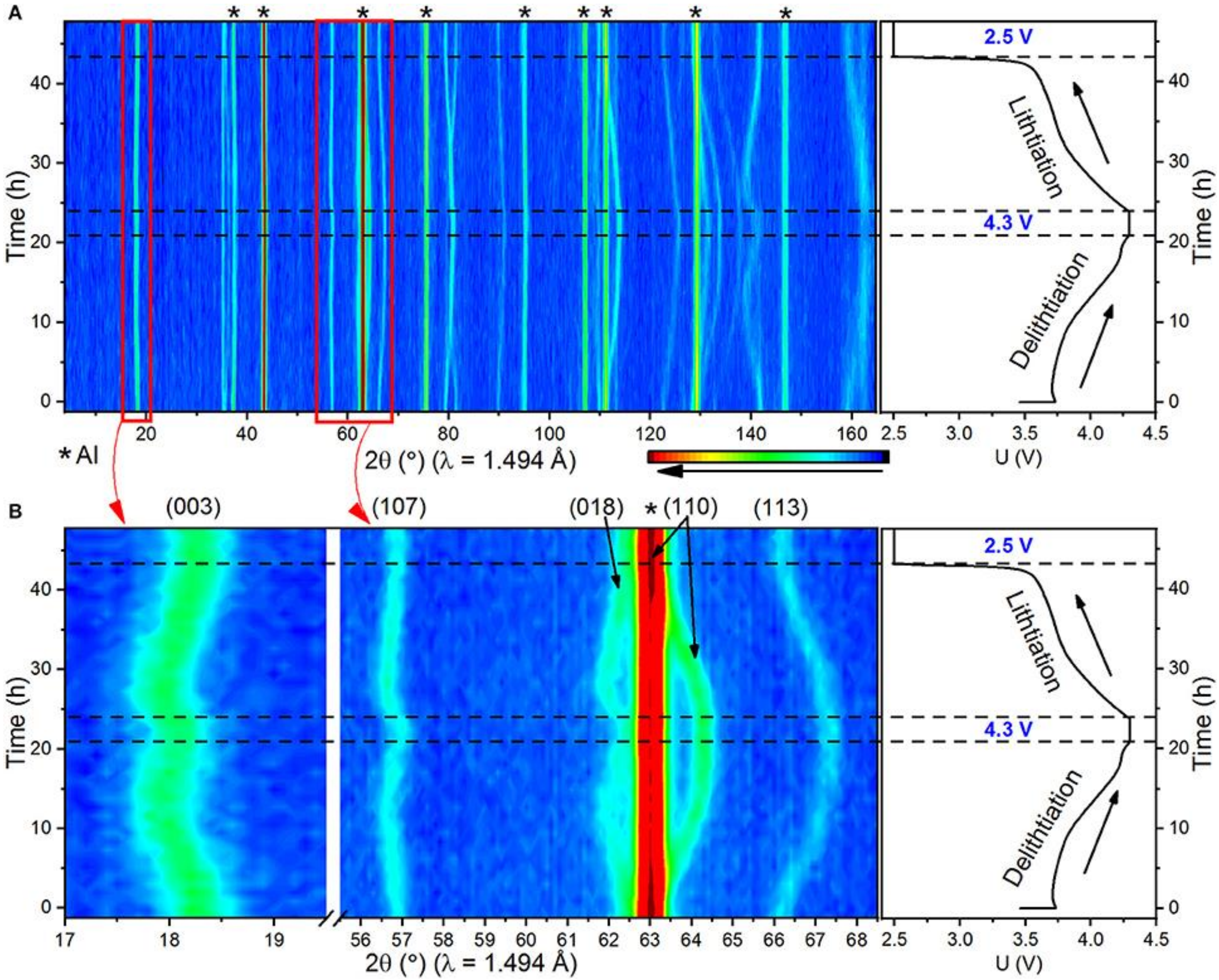
Neutron diffraction: operando cells



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

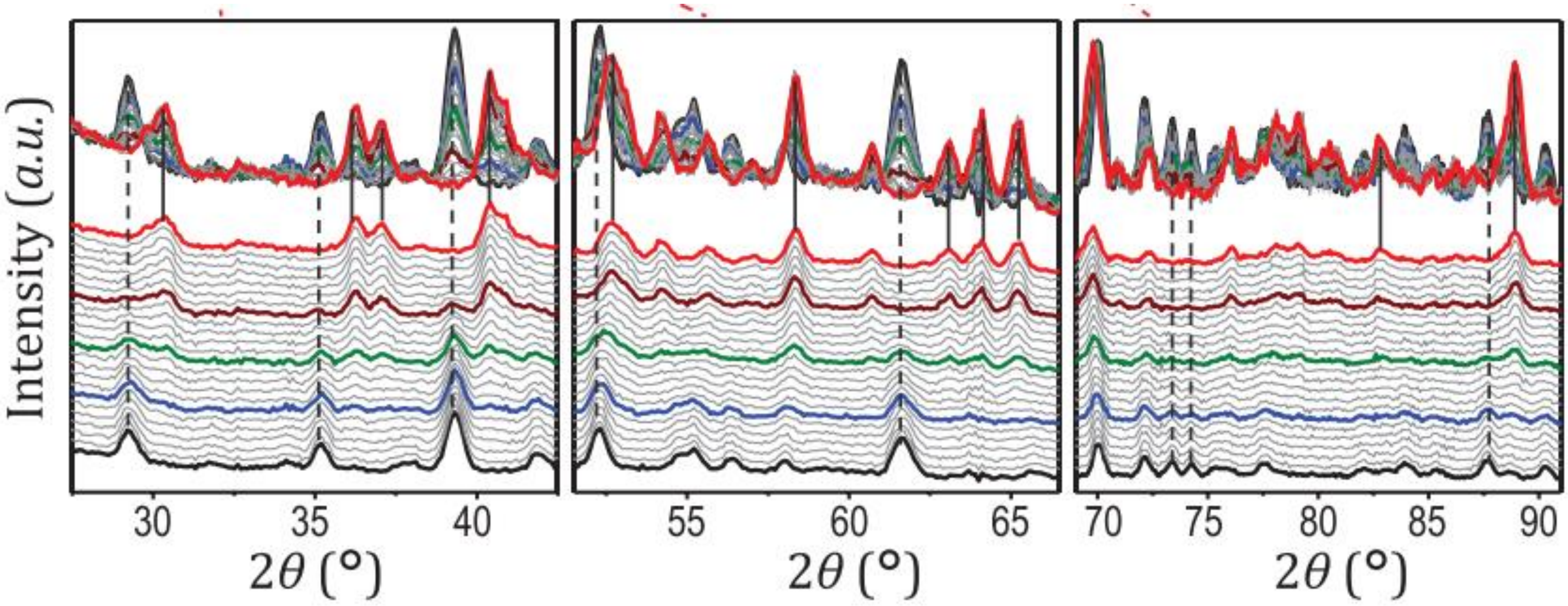
Neutron diffraction NMC 622

Li(NiCoMn)O_2 622

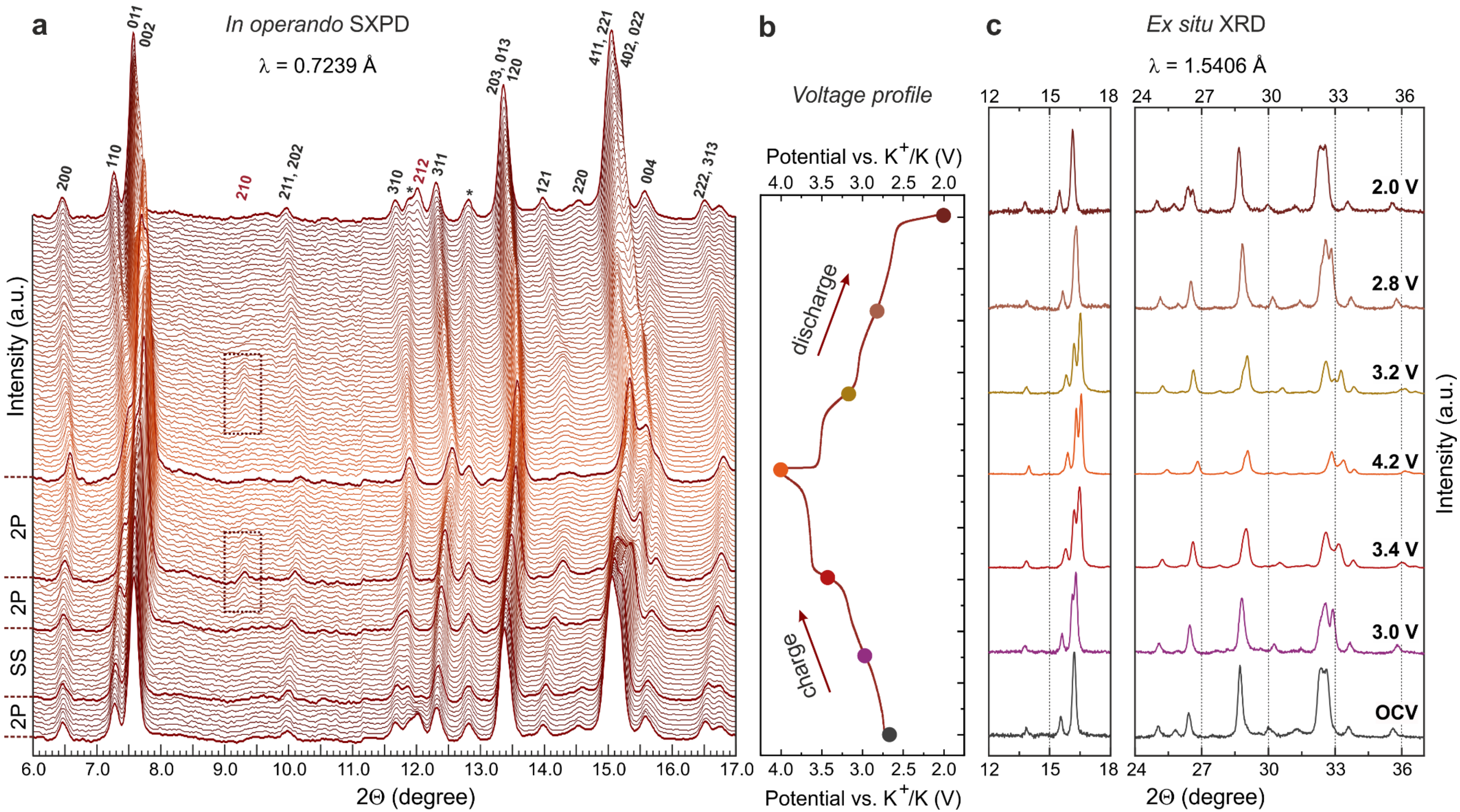


Neutron diffraction

$LiFePO_4$

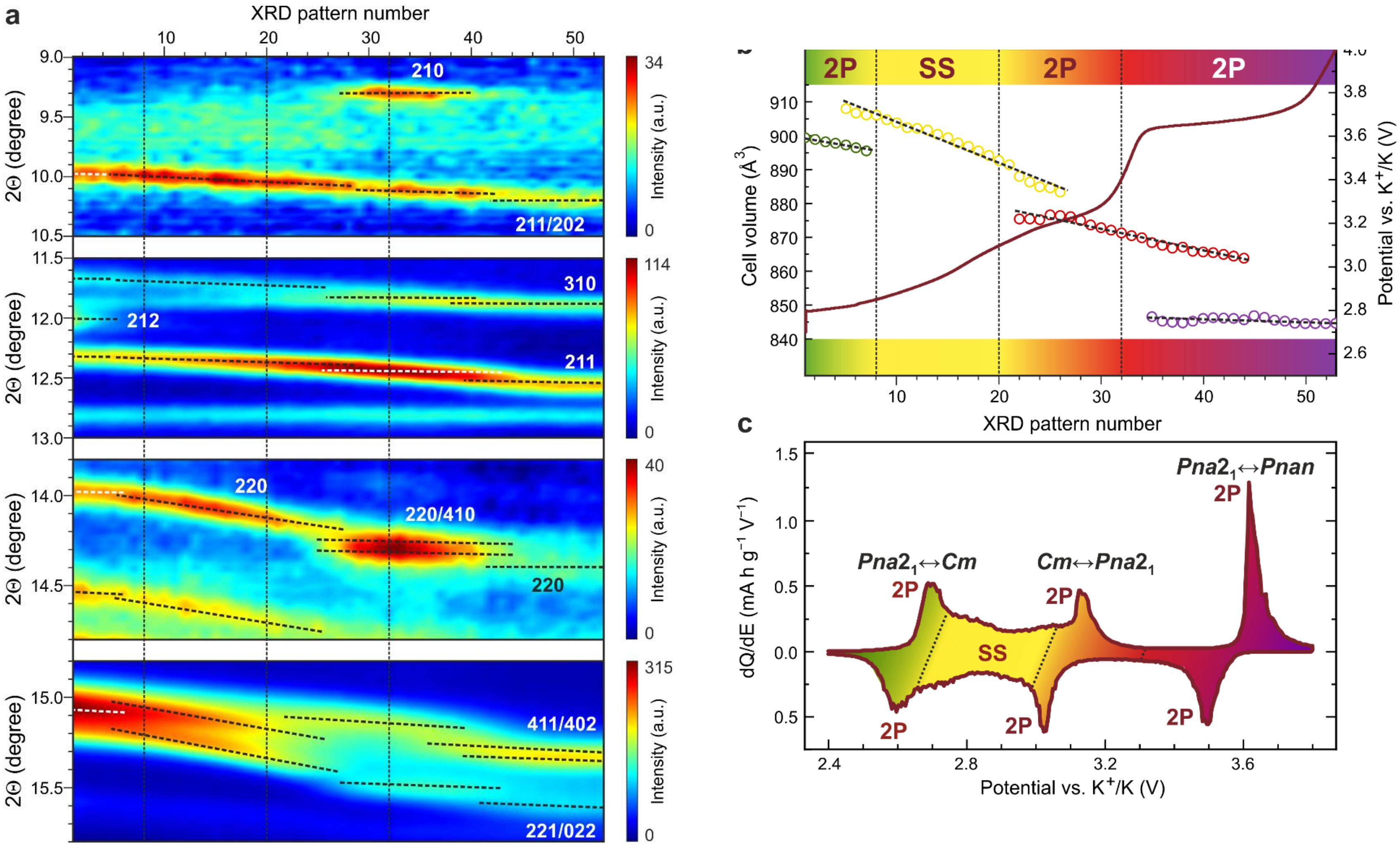


$KTiPO_4F$



S. S. Fedotov et al. Nature Comm. 2020, 11, 1484.

$KTiPO_4F$



S. S. Fedotov et al. Nature Comm. 2020, 11, 1484.

Thank you for your attention!

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