Forschungsneutronenquelle
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NESESS – Neutron Scattering Studies on Energy Storage Systems

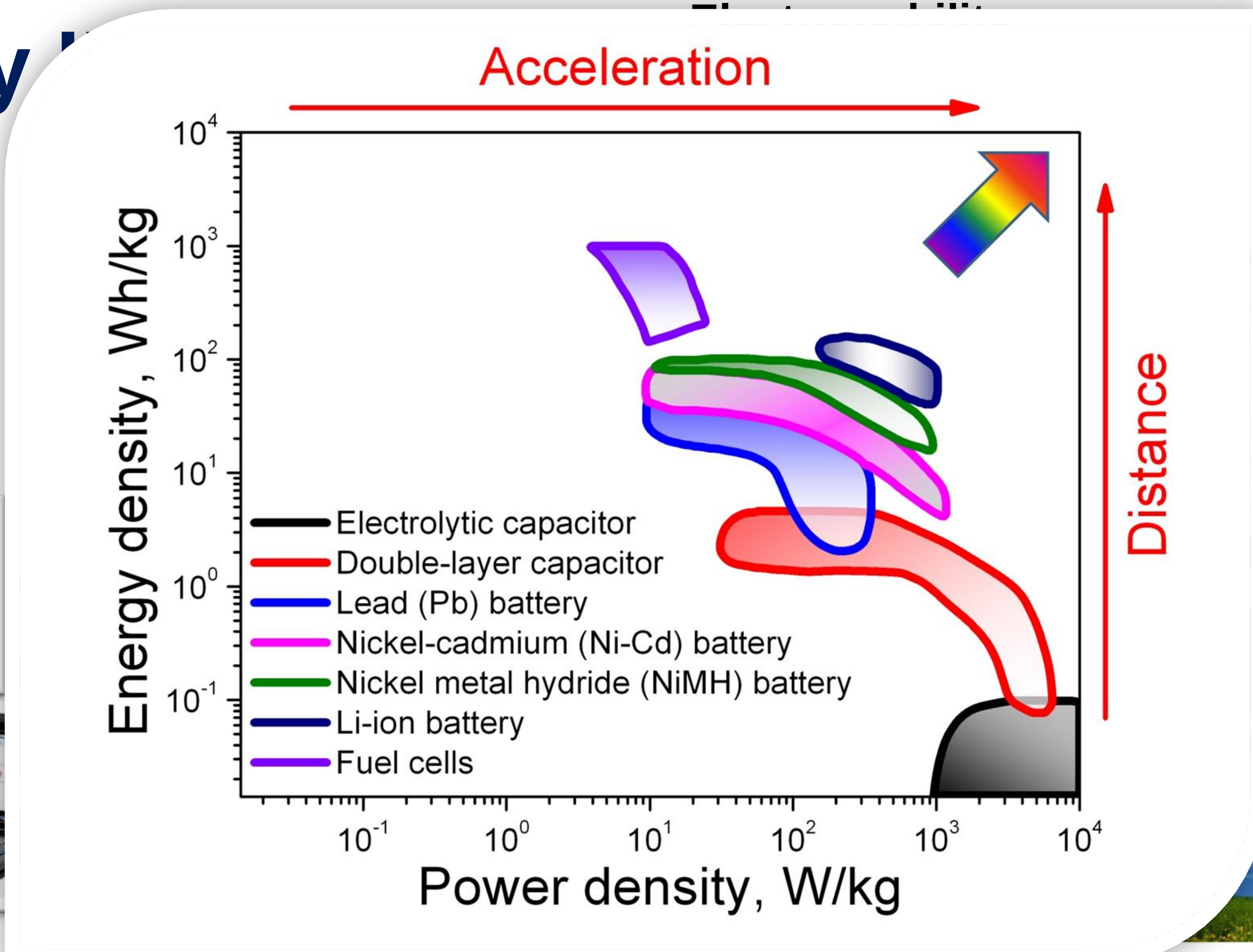
Technische Universität München

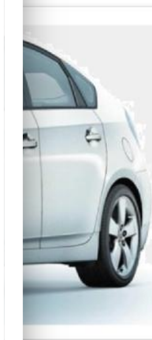
SFB 595
Deutsche Forschungsgemeinschaft
DFG

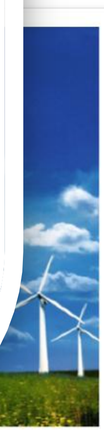
"In-operando" neutron scattering studies on commercial Li-ion batteries

A. Senyshyn, M.J. Mühlbauer, O. Dolotko, H. Ehrenberg

Why


Acceleration
Distance
Energy density, Wh/kg
Power density, W/kg
10^{-1}
10^{0}
10^{1}
10^{2}
10^{3}
10^{4}
Electrolytic capacitor
Double-layer capacitor
Lead (Pb) battery
Nickel-cadmium (Ni-Cd) battery
Nickel metal hydride (NiMH) battery
Li-ion battery
Fuel cells



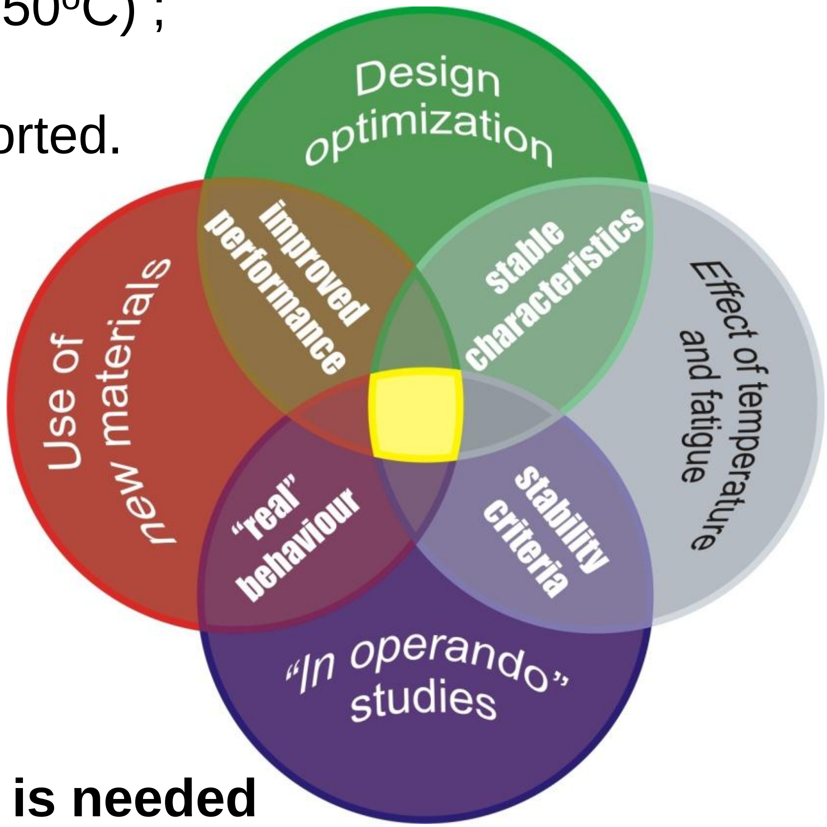


Major challenges of Li-ion battery technology

1. Specific energy – amount of energy per unit mass (C/3, 150Wh/kg);
2. Energy density – amount of energy per unit volume (C/3, 230Wh/l);
2. Calender life – (10 ÷ 15 years);
3. Operating temperature range – (-40ºC ÷ 50ºC) ;
4. Selling price – (150$/kWh);
5. Safety – serious hazards have been reported.

Ways to improve:

1. Use of new materials;
2. Optimisation of the battery design and processing;
3. Understanding of the fatigue processes;
4. Enhancement of thermal stability;



Studies of the battery „in-operando“.
New non-destructive technique of studies is needed

Advantages of neutron scattering

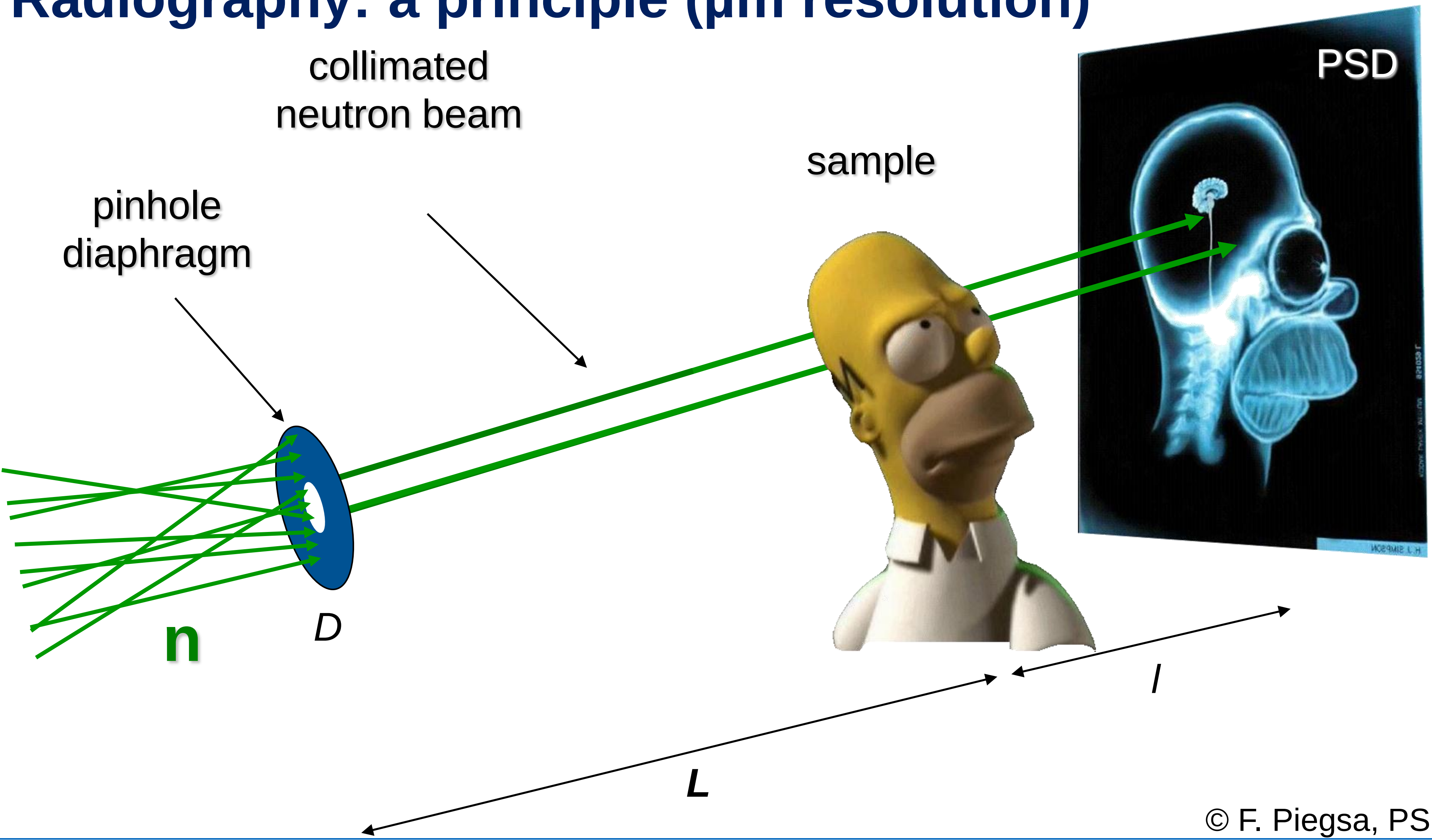
The energy of thermal neutrons is in range of meV → Neutrons weakly perturb the experimental system, i.e. non-destructive.

Neutrons are highly penetrating into the matter → Studies of bulk processes under realistic conditions (in complex environments).

Neutrons interact with nucleous. → Neutrons can localize light atoms (e.g. hydrogen, lithium) in the presence of heavier ones and to distinguish neighboring elements from Periodic Table and isotopes.

The wavelength of thermal neutrons is similar to interatomic spacings. → Details of the crystal structure.

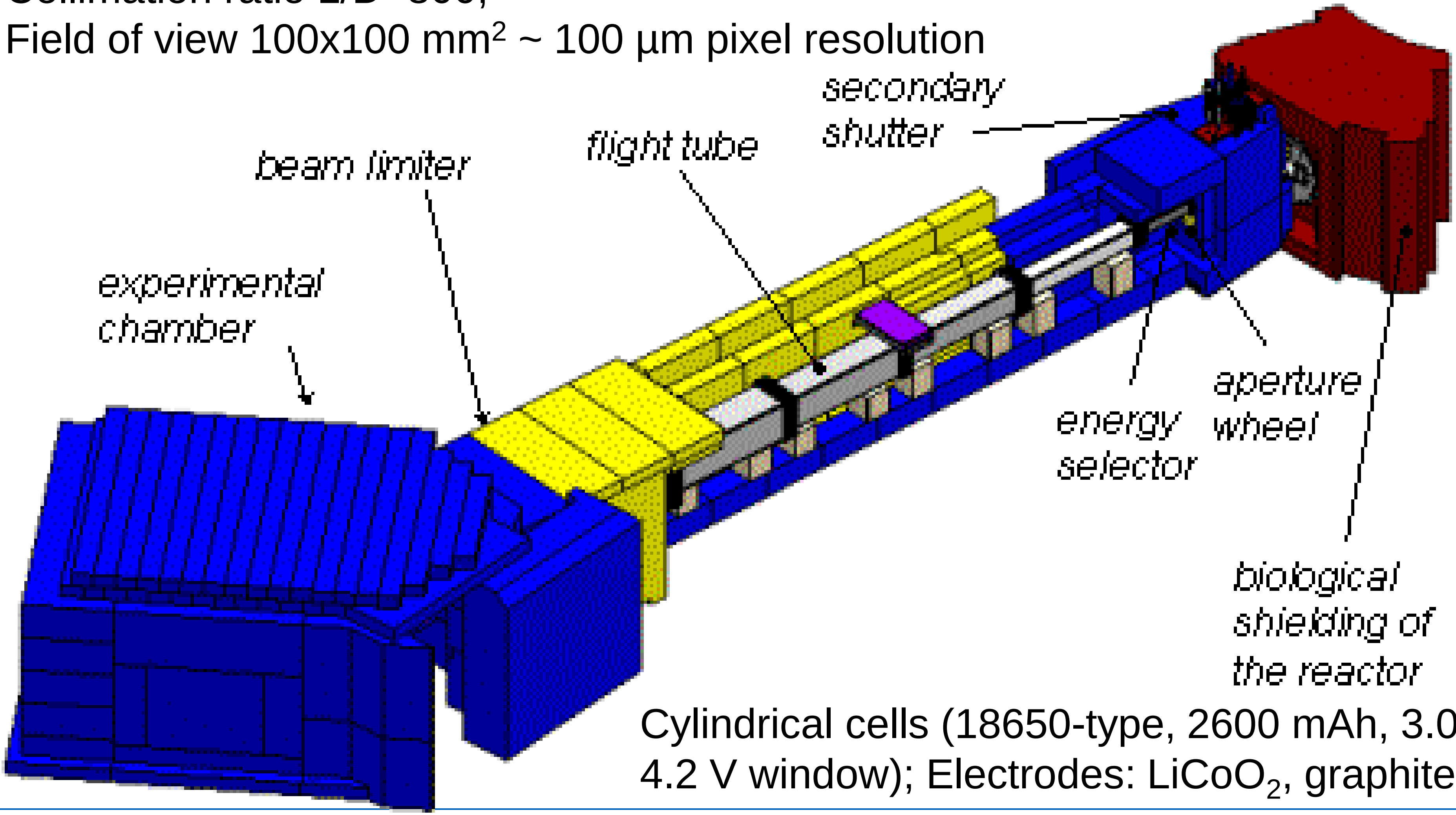
Radiography: a principle (μm resolution)



ANTARES - Neutron radiography and tomography

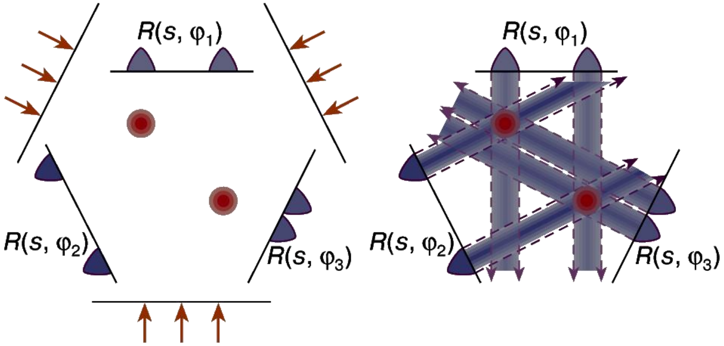
Collimation ratio L/D=800,

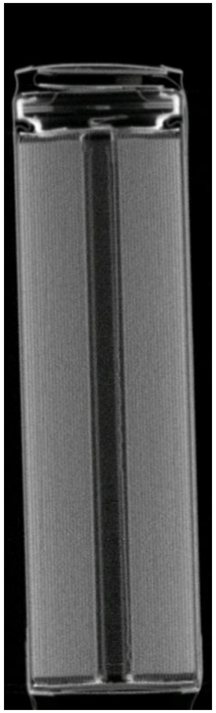
Field of view 100x100 mm^2 ~ 100 µm pixel resolution



Cylindrical cells (18650-type, 2600 mAh, 3.0-4.2 V window); Electrodes: $LiCoO_2$, graphite

Tomography: a principle



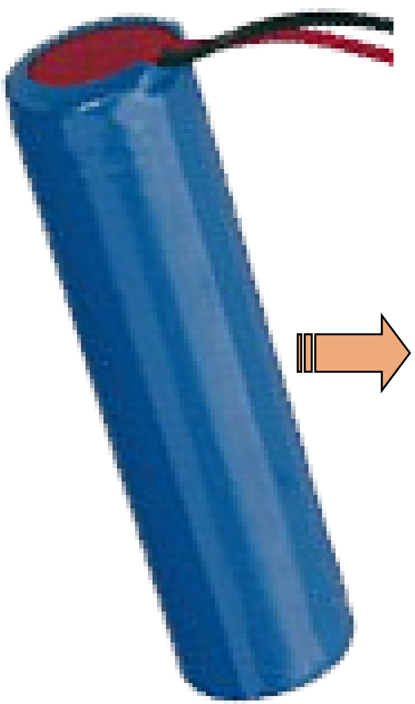


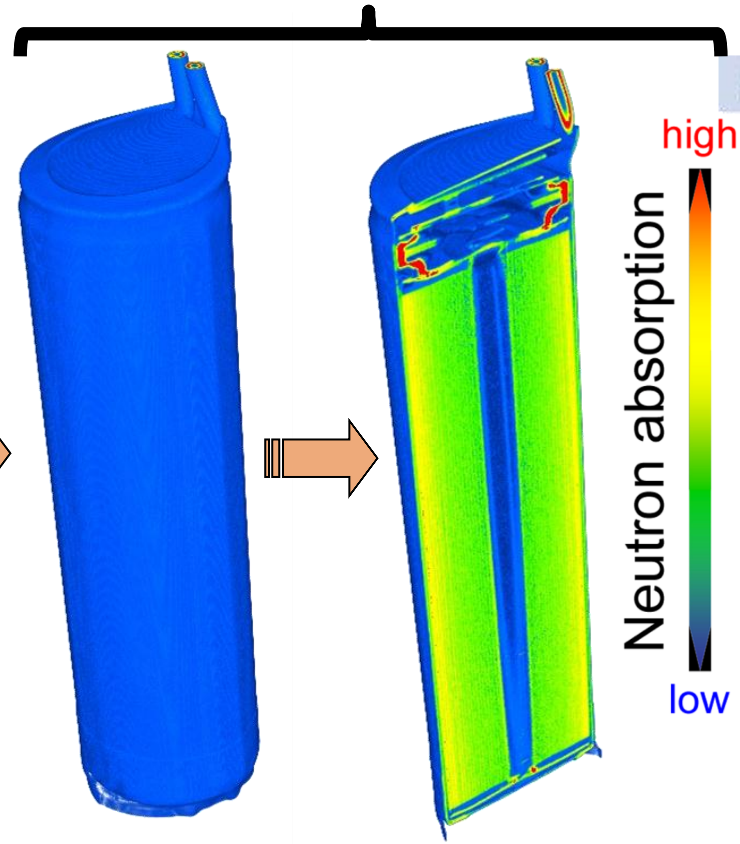
Inverse Radon transformation;
filtered back projection algorithm;
number of projections 600;

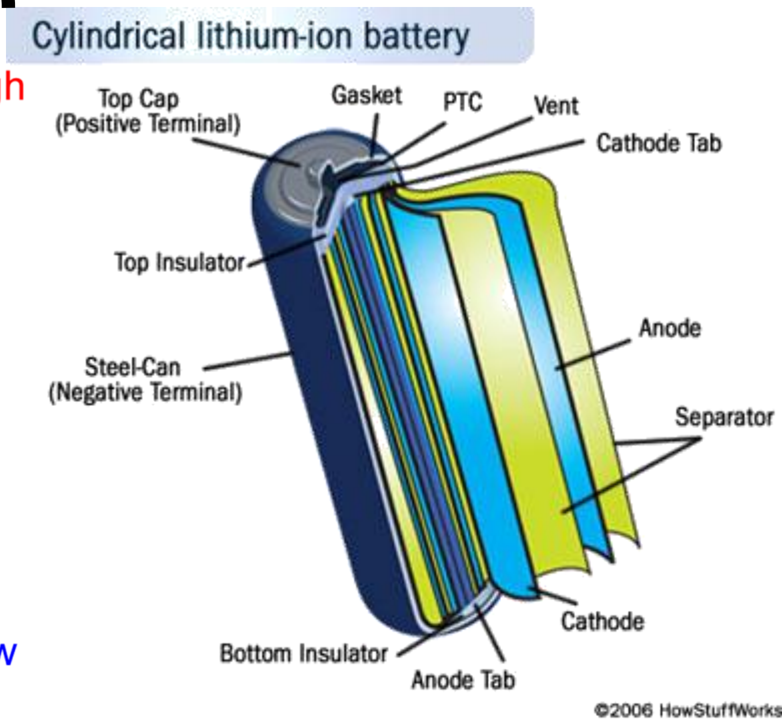
Assignment of Absorption Levels
to a chosen color scheme

Tomography reconstruction on 18650-type battery

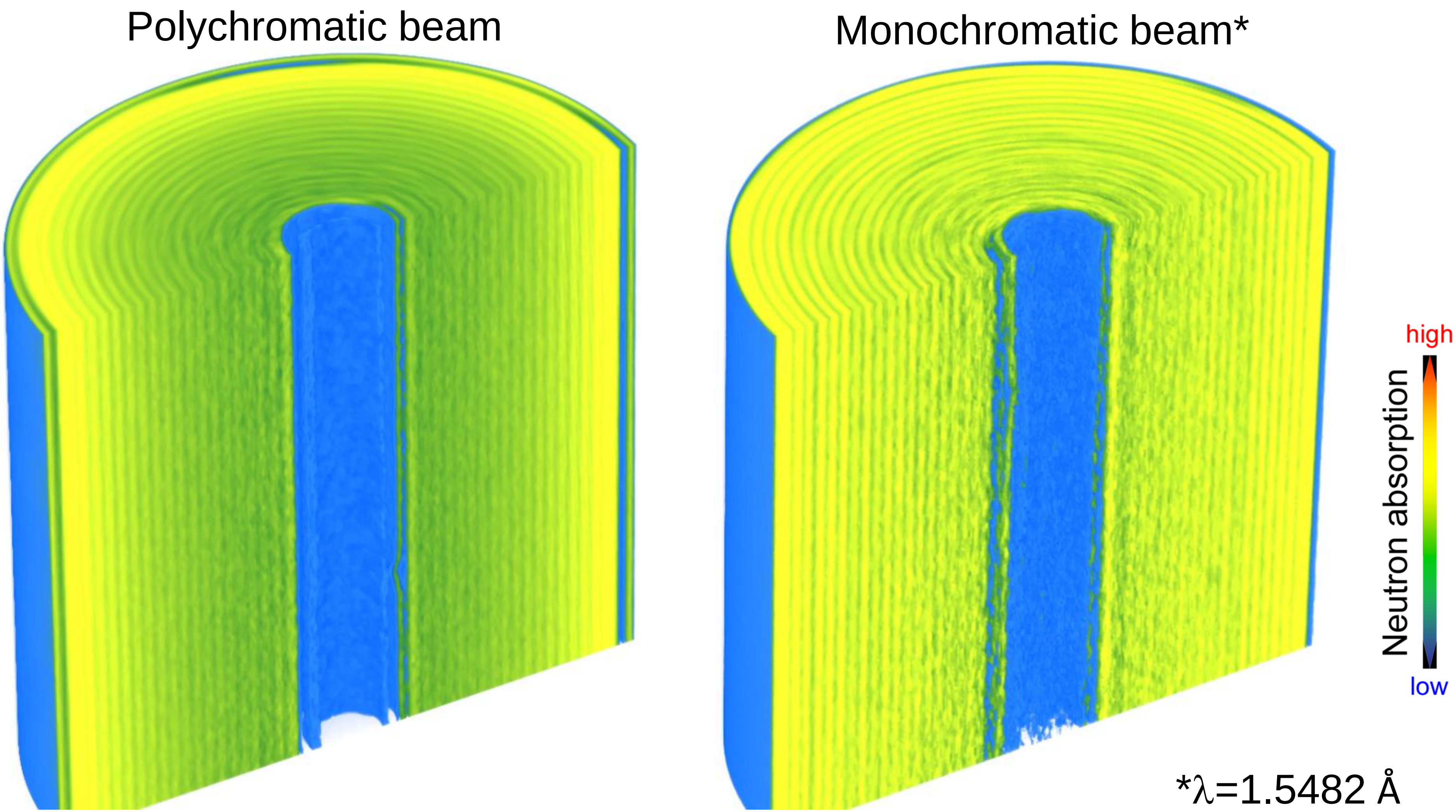
Photo | **3D model** | **Sketch**







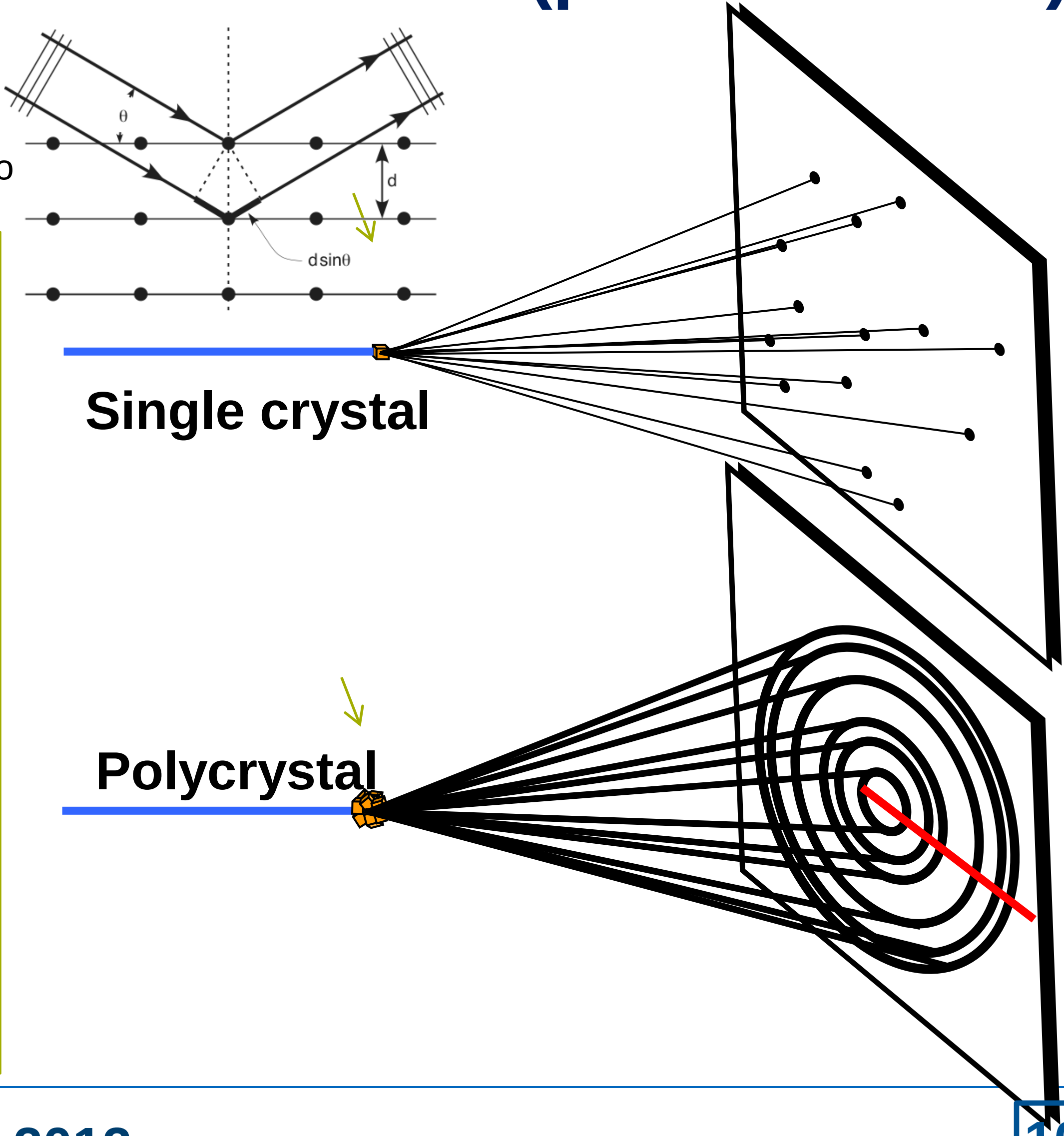
Tomography reconstruction on 18650-type battery



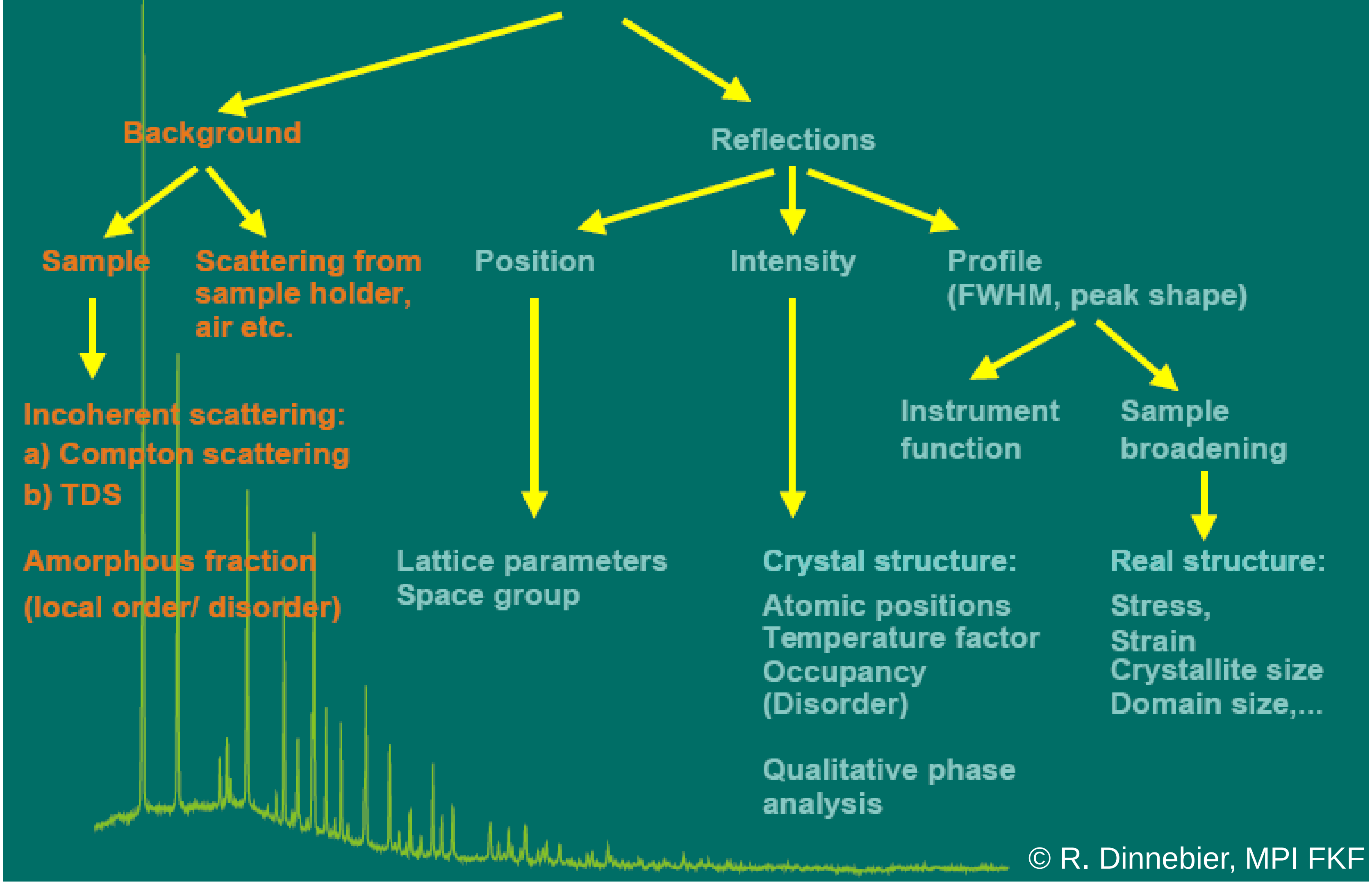
*λ=1.5482 Å

Diffraction from crystalline materials (pm resolution)

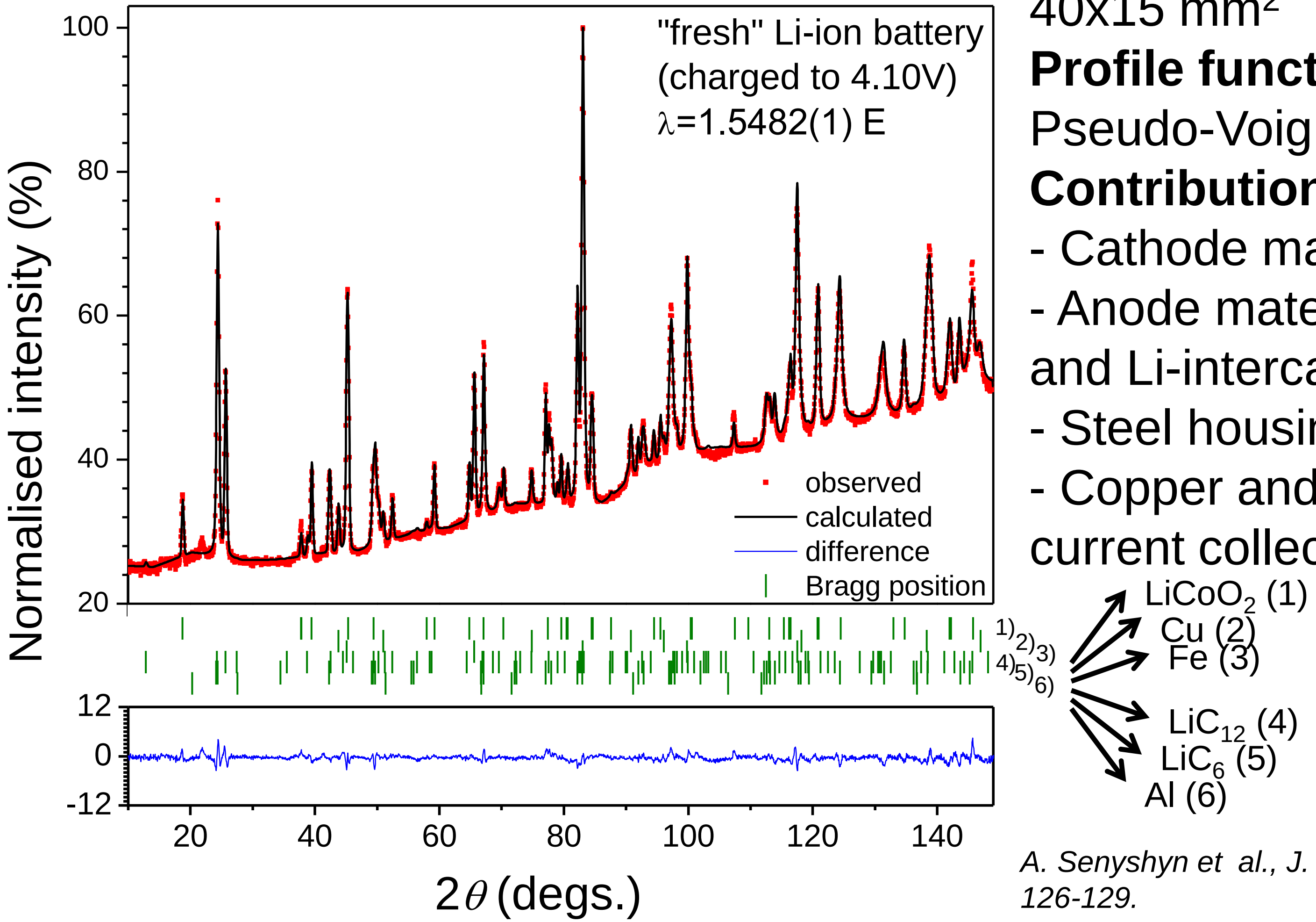
High resolution neutron powder diffractometer SPODI at FRM-II
Transmission mode, Take-off 155°



Information content of a powder pattern



Rietveld refinement of typical diffraction pattern for 18650 Li-ion battery

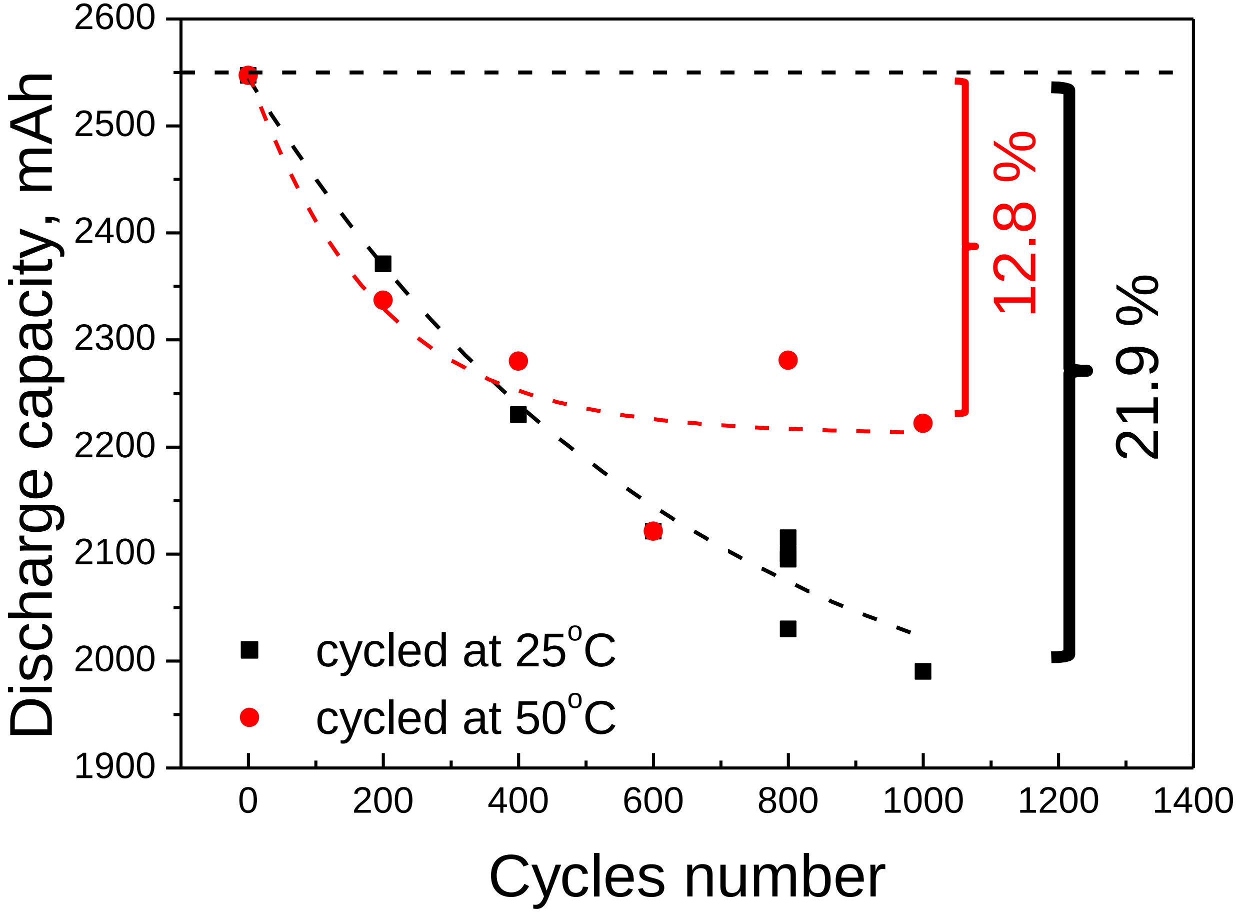


Beam dimensions:
40x15 mm^2
Profile function:
Pseudo-Voight (TCH)
Contributions
- Cathode material $LiCoO_2$;
- Anode material (graphite and Li-intercalated carbons);
- Steel housing + centre pin;
- Copper and aluminum current collectors;

A. Senyshyn et al., J. Power Sources 203 (2012) 126-129.

Fatigue of battery: introduction

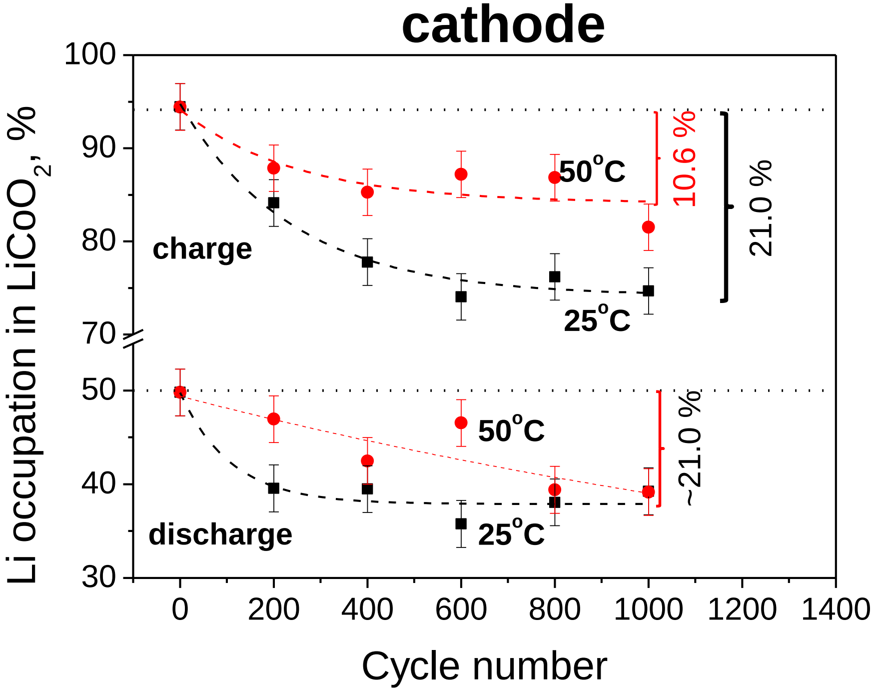
Two batches of Li-ion cells purposefully cycled (CCCV, 1C) at 25ºC and 50ºC for 200, 400, 600, 800 and 1000 times

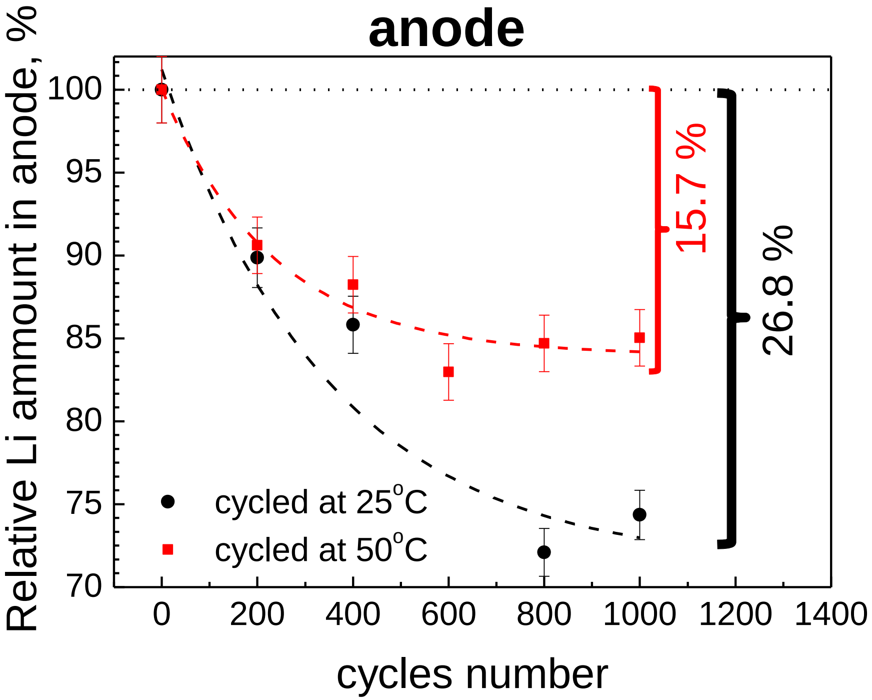


Fatigue of battery: crystal structure

Possible reasons: Li-plating (dendrite growth), microcracks formation in electrodes; oxidation processes and phase transformations; SEI growth/electrolyte decomposition

Effect on Li-concentration

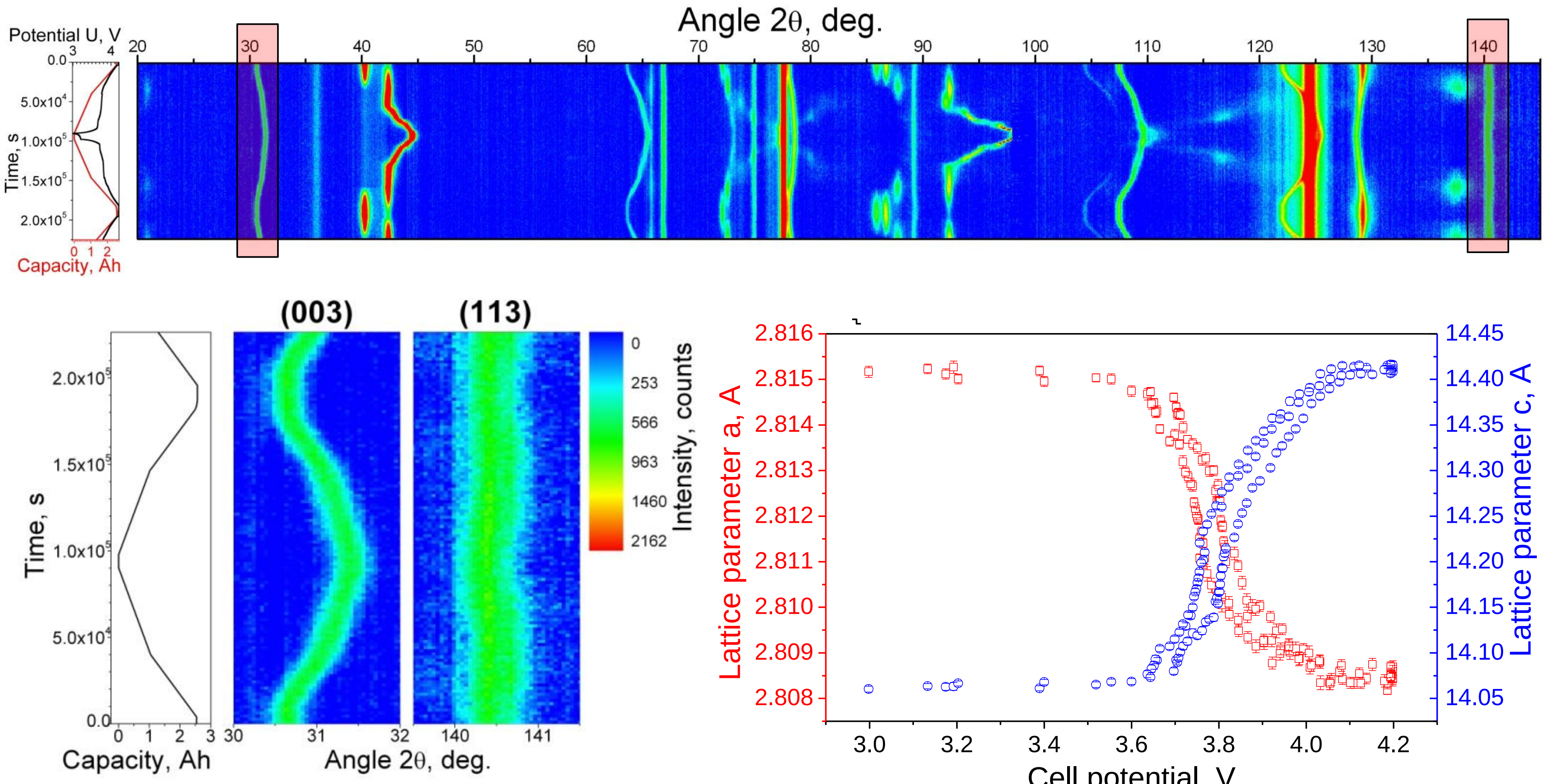




By the fatigue introduced the system looses free (transport) lithium;
Lithium loss correlate to the reduction of discharge capacity;

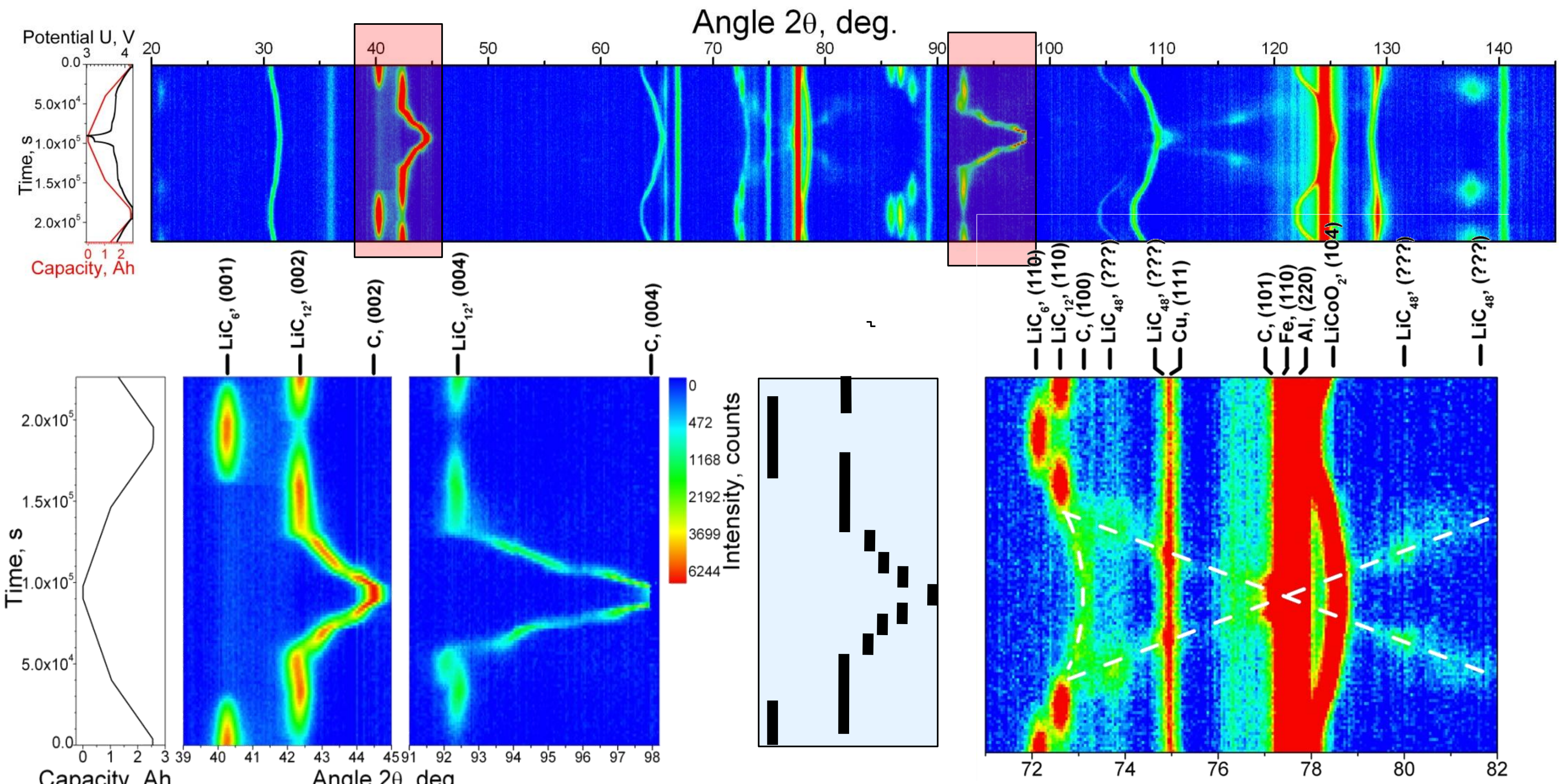
Evolution of diffraction data vs. Electrochemical treatment

(Cathode, SPODI, λ=2.536 Å)

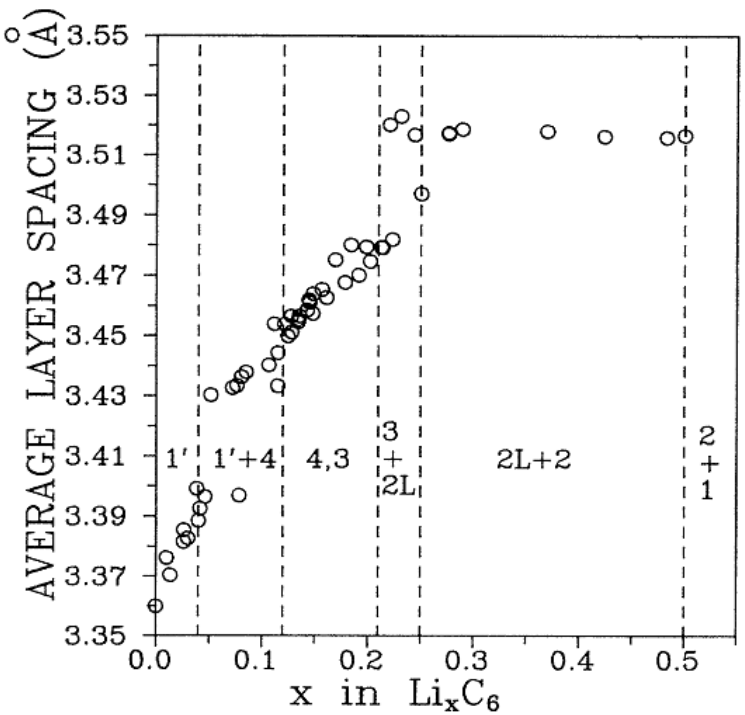


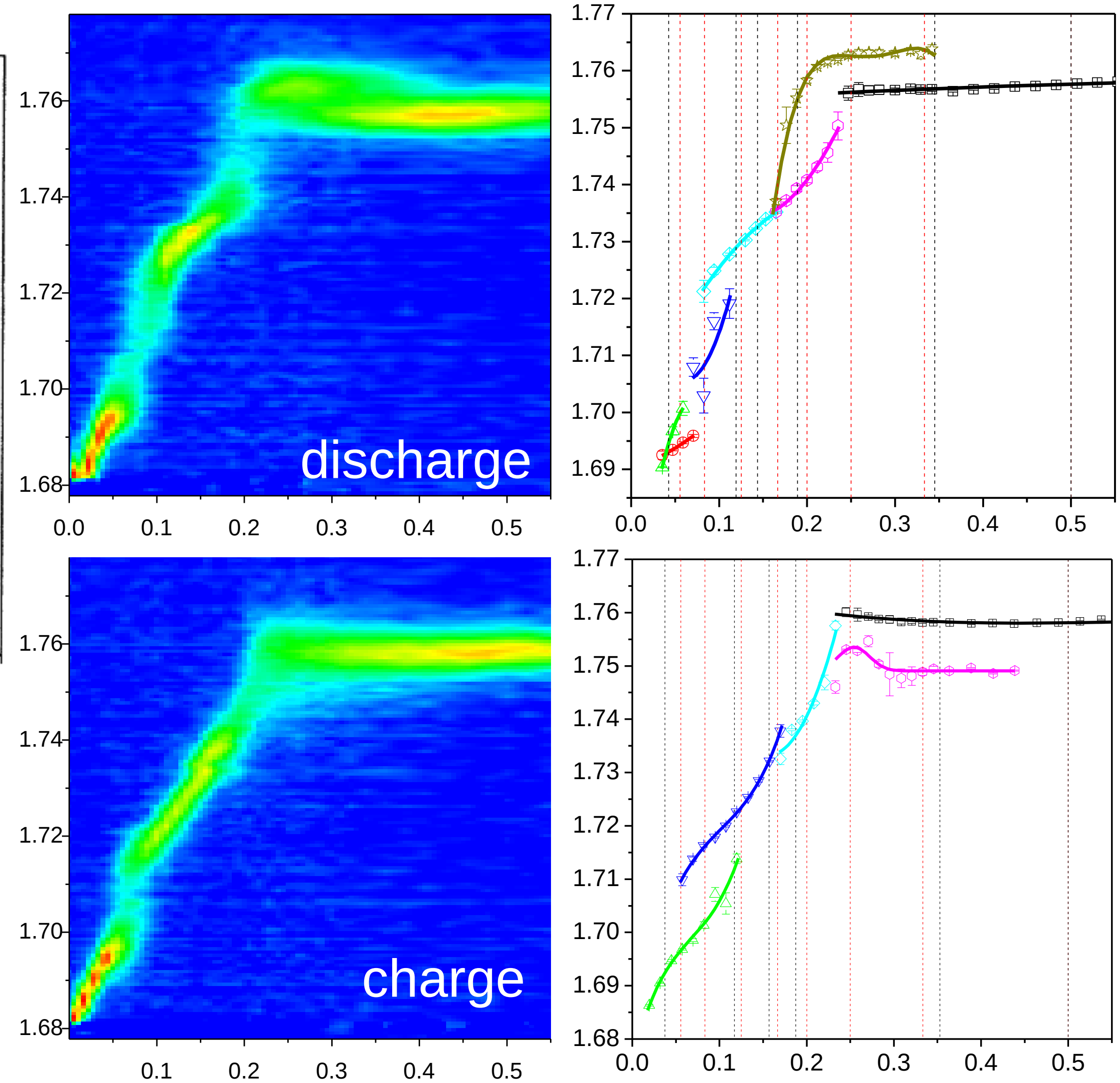
Evolution of diffraction data vs. Electrochemical treatment

(Anode, SPODI, λ=2.536 Å)



Phase diagram of Li-intercalated carbons





J.R. Dahn, Phase diagram of Li_xC_6, Phys. Rev. B 44(17) 9170-9177 (1991).
T. Ohzuku, Y. Iwakoshi, K. Sawai, Formation of Lithium-Graphite Intercalation Compounds in Nonaqueous Electrolytes and Their Application as a Negative Electrode for a Lithium Ion (Shuttlecock) Cell , J. Electrochem. Soc., 140(9) 2490-2498 (1993).