BATTERIES

ELECTROCHEMISTRY LABORATORY

PAUL SCHERRER INSTITUT

Eidgenössische Technische Hochschule Zürich
Swiss Federal Institute of Technology Zurich

Investigating the phase transitions of graphite by in situ neutron diffraction

Michael Hess[a,b], Claire Villevieille[a], Reinhard Nesper[b], Petr Novák[a,b]

[a] *Paul Scherrer Institute, Electrochemical Energy Storage Section, CH-5232 Villigen PSI, Switzerland*

[b] *ETH Zurich, Laboratory of Inorganic Chemistry, CH-8096 Zurich, Switzerland,*

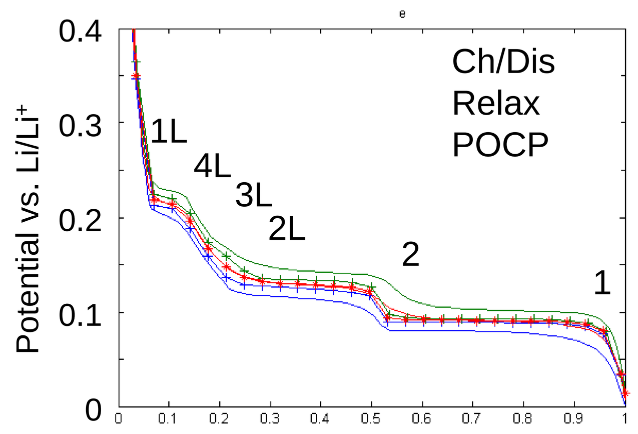
hessmi@inorg.chem.ethz.ch

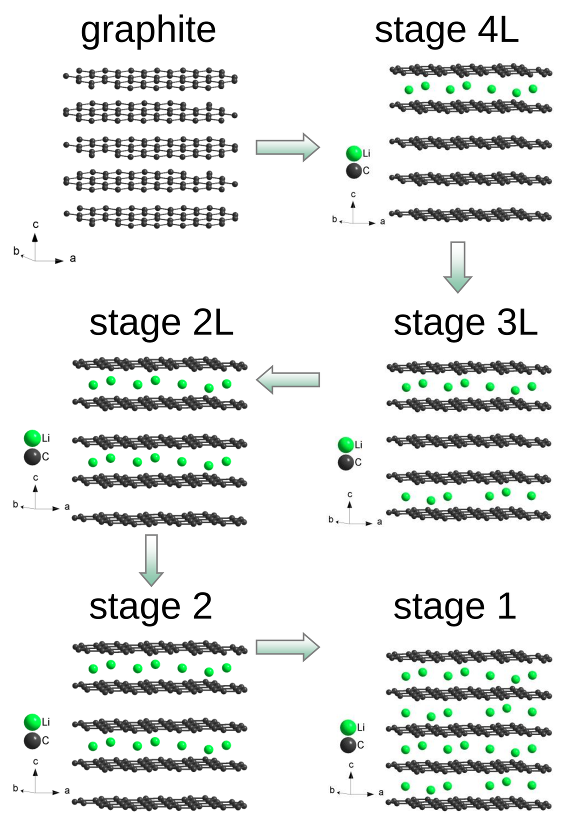
1. Stage transitions in graphite

Motivation:

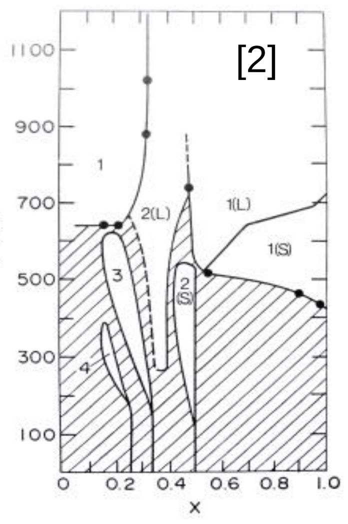
1) Graphite in 90% of today's batteries
2) Phase transitions show different C-rates [1]

Investigate phases by in situ XRD/NPD





Li-C phase diagram

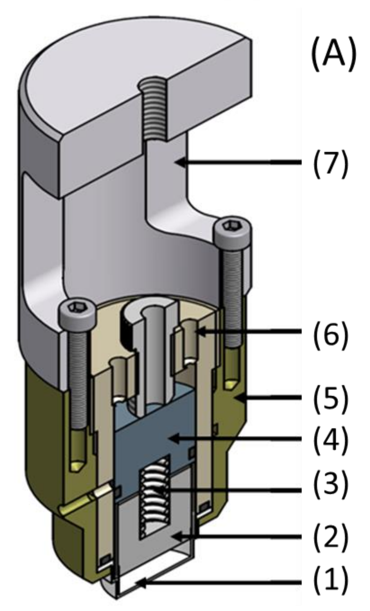


Working hypothesis:
Graphite has distinct phases also at low state-of-charge

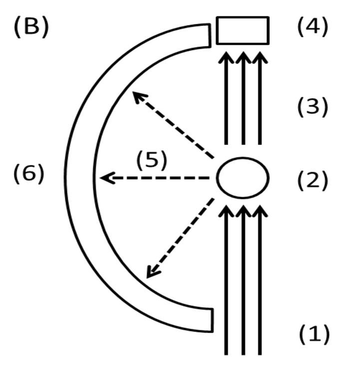
2. In situ cell

1) XRD: Pouch cell (polyimide and polypropylene window)
2) NPD: Cell with Ti/Al container with deuterated electrolyte LP30-D

new circular *in situ* NPD cell [4]



In-beam position of cell [4]

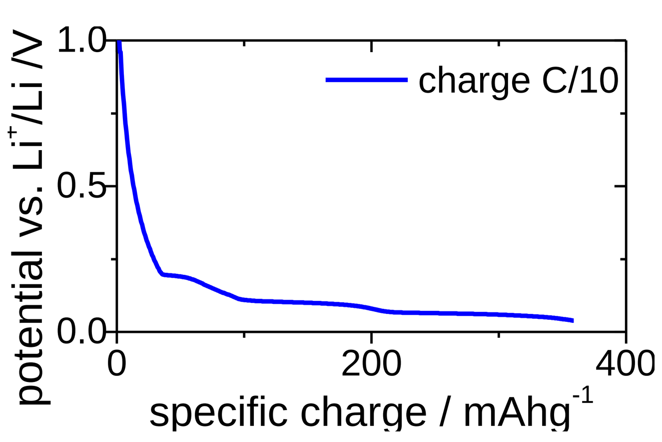


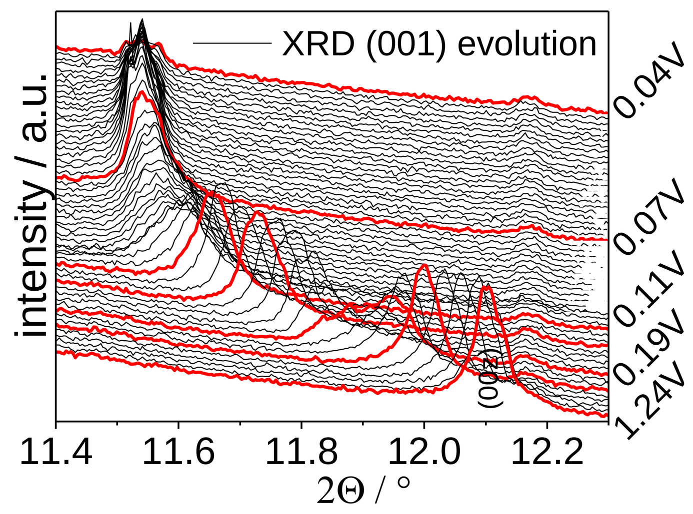
A: in situ cell
(1) Al/Ti electrode container (only part in beam), (2) Ti plunger for Li counter electrode, (3) spring, (4) Ti current collector, (5) Al cell body part, (6) PEEK cell, (7) polymeric attachment for D20 beamline.

B: beam position
(1) Neutron beam, (2) in situ NPD cell (3) out-going beam, (4) beam stop, (5) diffracted beam, (6) detector

3. In situ x-ray and neutron powder diffraction

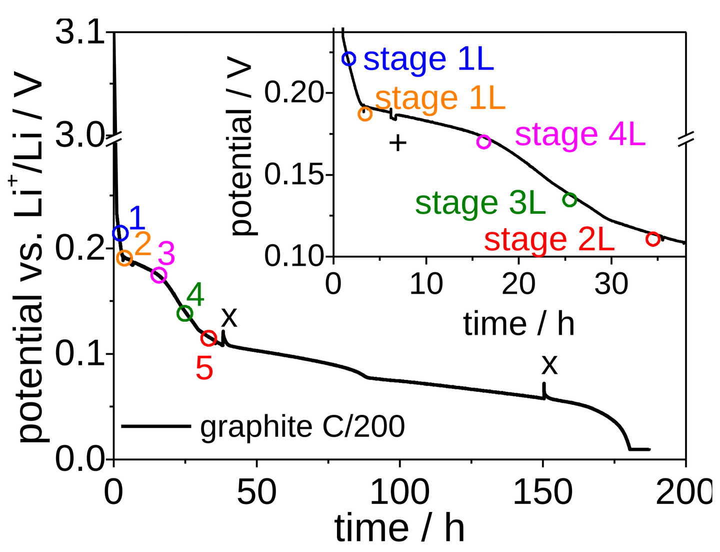
In situ XRD:

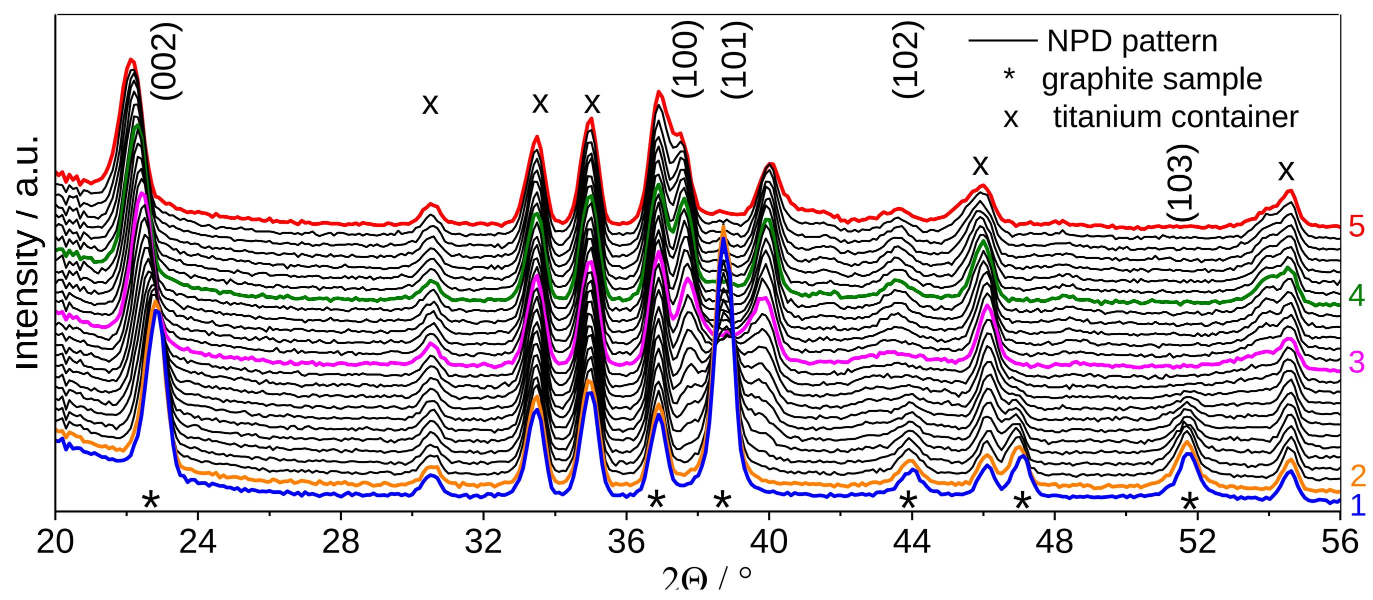




➡ good electrochemistry
➡ refinement problematic

In situ NPD:



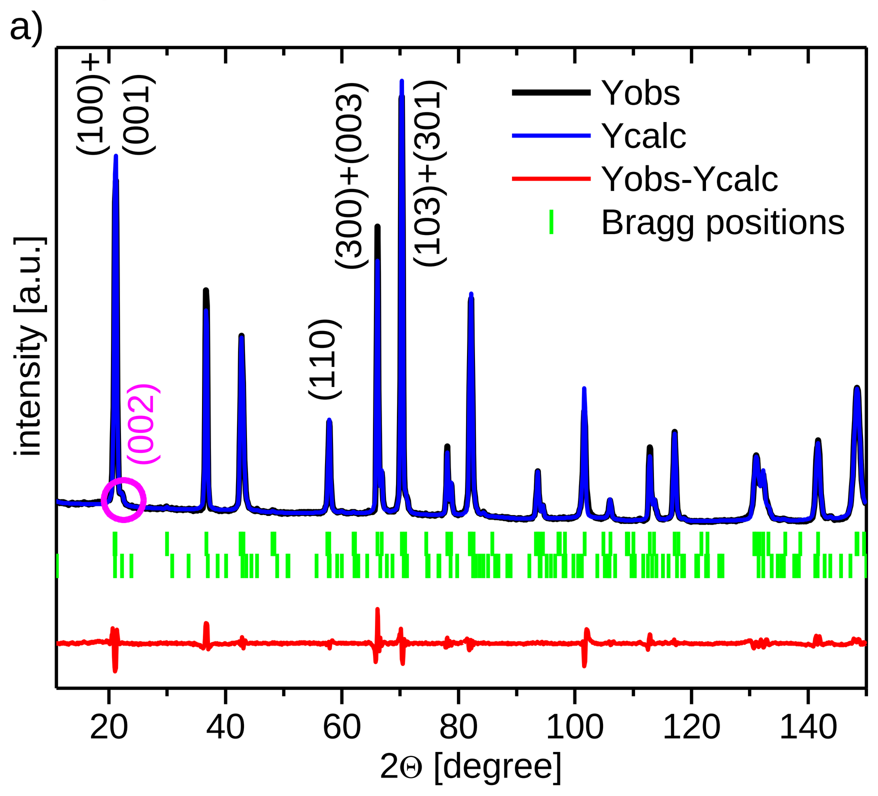


➡ Only graphite and titanium in beam
➡ very good signal/noise ratio in LP30-D

4. Results

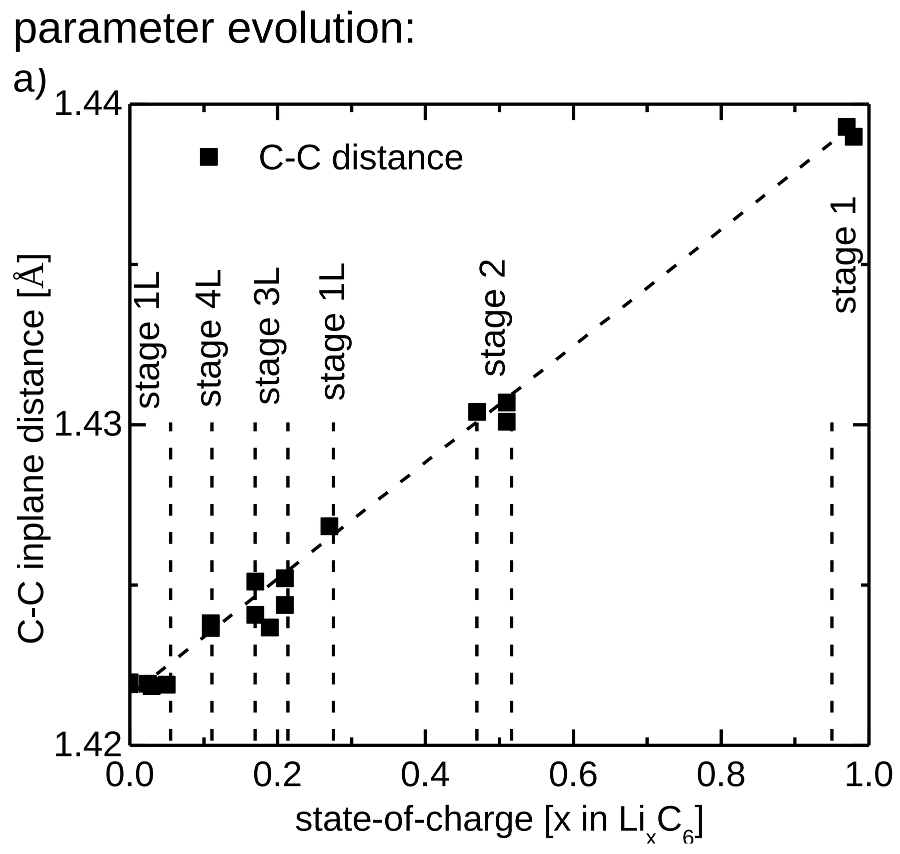
Refinement of different phases:

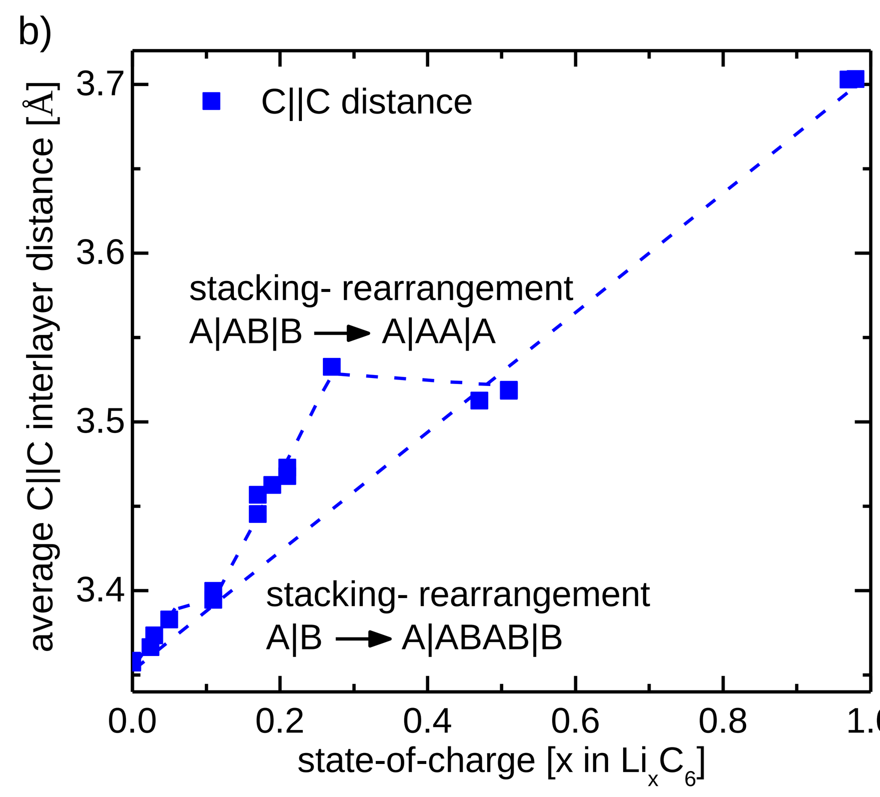
Stage 1:



➡ refinement of NPD data with good fit
➡ phase identification possible

Lattice parameter evolution:





➡ C-C distance follows Vegard's law
➡ graphene interlayer distance non-linear

Summary: In situ XRD:
1) less good method for Li-graphite system (low scattering of C, Li)
2) easy to redo at any synchrotron, very good electrochemistry in cell

In situ NPD:
1) very good results for Li-graphite diffraction
2) high overpotentials for 200 mg/cm² loading and neutron sources needed

Lattice parameter:

	ch/dis, voltage	Space group	a-axis	c-axis	FWHM	fraction [%]	Rwp/ zero shift
$Na_2Ca_3Al_2F_{14}$	standard	I213	10.25		0.32	100	8 /-0.31
a) Stage1	ch 0.01V	P6/mmm	4.32	3.70	0.37	94	5 /-0.28
a) Stage 2		P6/mmm	4.29	7.04	0.48	6	
c) Stage 2	ch 0.1V	P6/mmm	4.29	7.02	0.55	26	4.5 /-0.3
c) Stage 2L		P63/mmc	2.47	14.13	0.46	28	
f) Stage 3L	dis 0.16V	P6/mmm	2.47	10.37	0.44	44	4.5/-0.24
f) Stage 4L		P63/mmc	2.47	27.16	0.4	56	
d) Graphite	pristine ~3V	P63/mmc	2.46	6.72	0.32	72	8 /-0.27
d) Graphite		R-3m	2.46	10.07	0.37	28	
Graphite	dis 3V	P63/mmc	2.46	6.72	0.4	100	7 /-0.27

➡ Phase identification of stage 1, 2, 1L and graphite according to literature
➡ Phases 2L, 3L and 4L could be refined
➡ For the first time, proper determination of Li-in-plane concentration in disorder stages

[1] M. Hess, P. Novák, Electrochim Acta, 106, 149 (2013)
[2] K.C. Woo, H. Mertwoy, J.E. Fischer, W.A. Kamitakahara, D.S. Robinson, Phys. Rev. B, 27, 7831 (1983)
[3] G.K. Singh, G. Ceder, M.Z. Bazant, Electrochim Acta, 53, 7599 (2008)
[4] V.A. Godbole, M. Hess, C. Villevieille, H. Kaiser, J.-F. Colin, P. Novák, RSC Advances, 3, 757 (2013)

Acknowledgement: H. Kaiser, C. Junker, N. Casati, A. Cervellino for the support with equipment/beam.