

Graphite Revisited: New Insights into Lithium Intercalation

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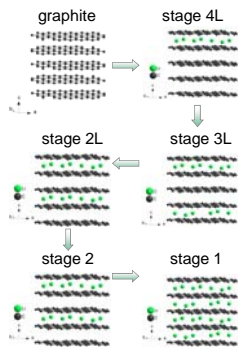
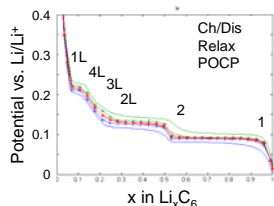
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1. Stage Transitions in Graphite

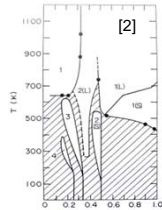
Motivation:

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

Investigate phases by *in situ* XRD/NPD



Li-C phase diagram

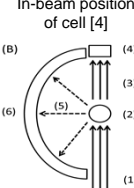
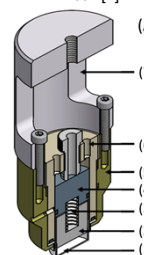


Working hypothesis:
Graphite has distinct phases, also at low state-of-charge

2. In Situ Cell

- 1) XRD: Pouch cell (polyimide and polypropylene window)
- 2) NPD: Cell with Ti/Al container with deuterated electrolyte LP30-D (1M LPF₆ in 1:1 EC:DMC)

New circular *in situ* NPD cell [4]

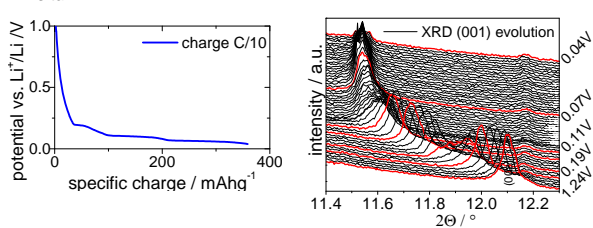


A: *in situ* cell
(1) Al/Ti electrode container (only part in beam), (2) Ti plunger for Li counter electrode, (3) spring, (4) Ti current collector, (5) Al cell body part, (6) PEEK cell, (7) polymeric attachment for D20 beamline.

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

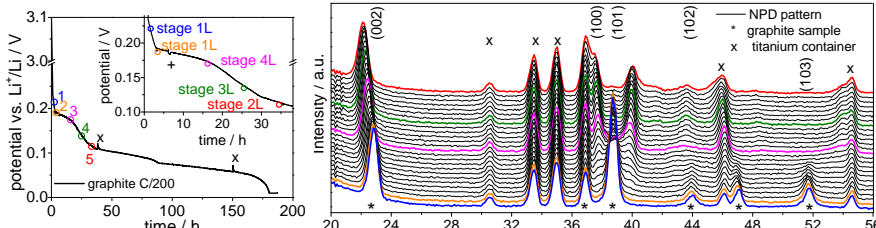
3. First Cycle: In Situ X-Ray (XRD) and Neutron (NPD) Powder Diffraction

In situ XRD:



- ➔ Good electrochemistry
- ➔ Refinement problematic

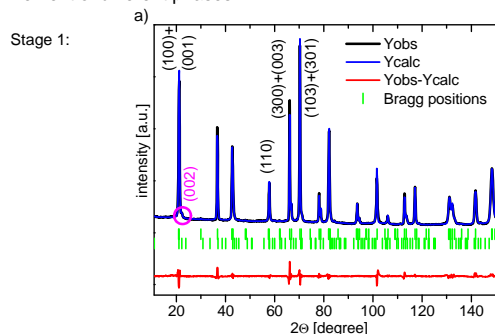
In situ NPD:



- ➔ Only graphite and titanium in beam
- ➔ Very good signal/noise ratio in LP30-D

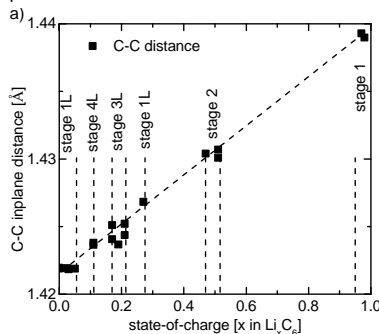
4. Results

Refinement of different phases:

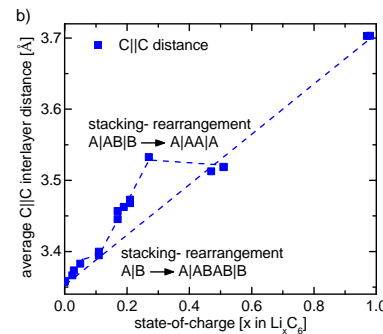


- ➔ refinement of NPD data with good fit
- ➔ phase identification possible

Lattice parameter evolution:



- ➔ C-C distance follows Vegard's law
- ➔ Graphene interlayer distance non-linear



Summary: **In situ XRD:**

- 1) Less suitable 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; neutron source needed

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

Lattice parameters:

	ch/dis, voltage	space group	a-axis	c-axis	FWHM	fraction [%]	Rwp/zero shift
	Na ₂ Ca ₃ Al ₂ F ₁₄ standard	I213	10.25	0.32	100	8 / -0.31	
a) Stage 1	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	P63/mmc	2.46	6.72	0.32	72	8 / -0.27
d) Graphite	-3V	R-3m	2.46	10.07	0.37	28	
Graphite	dis 3V	P63/mmc	2.46	6.72	0.4	100	7 / -0.27

[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)

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