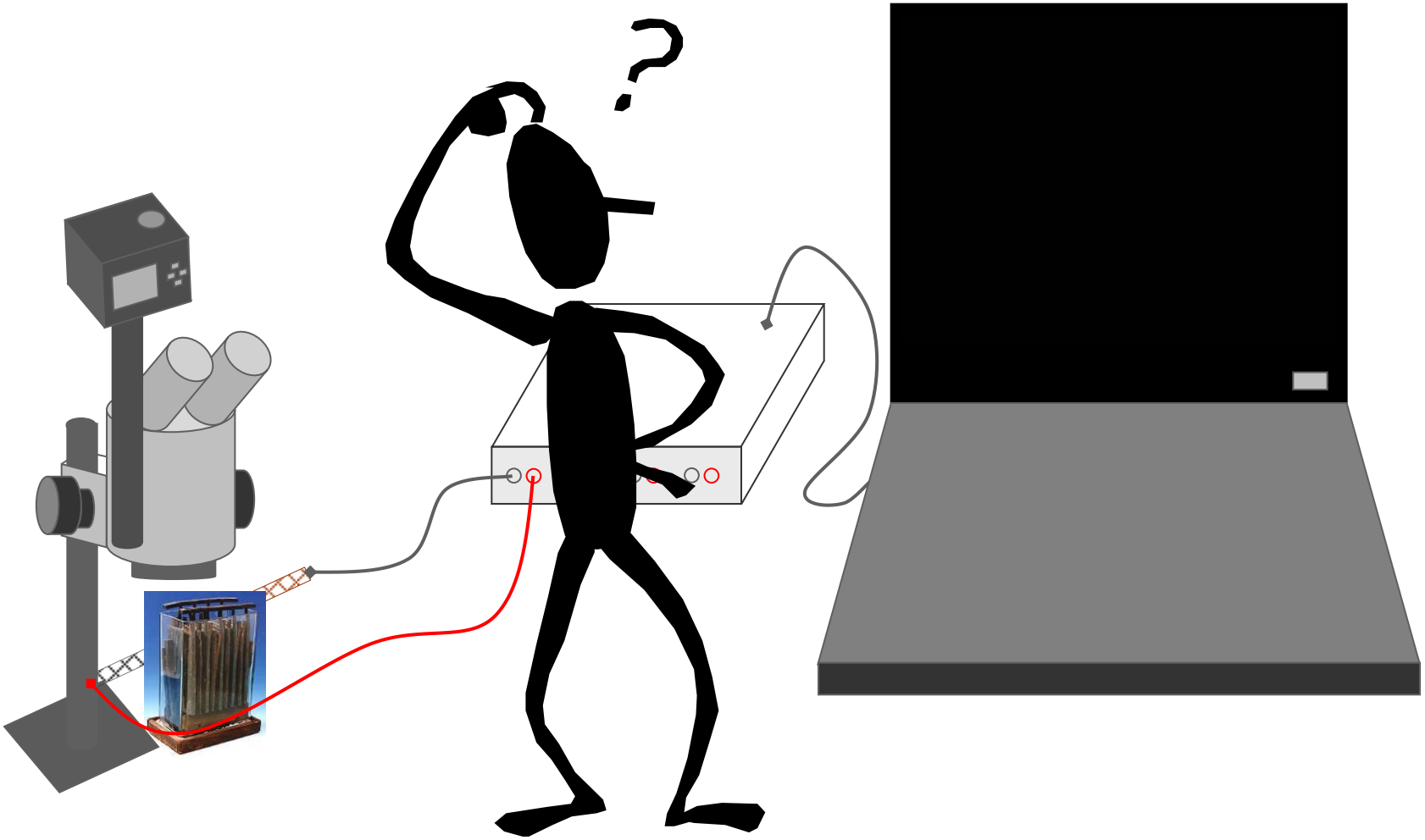
Inhomogenitäten in Elektroden:
Von der Entwicklung von Lithiumionen-Batterien zur Grundlagenforschung (und umgekehrt…)

Prof. Dr. Petr Novák und Dr. Pascal Maire

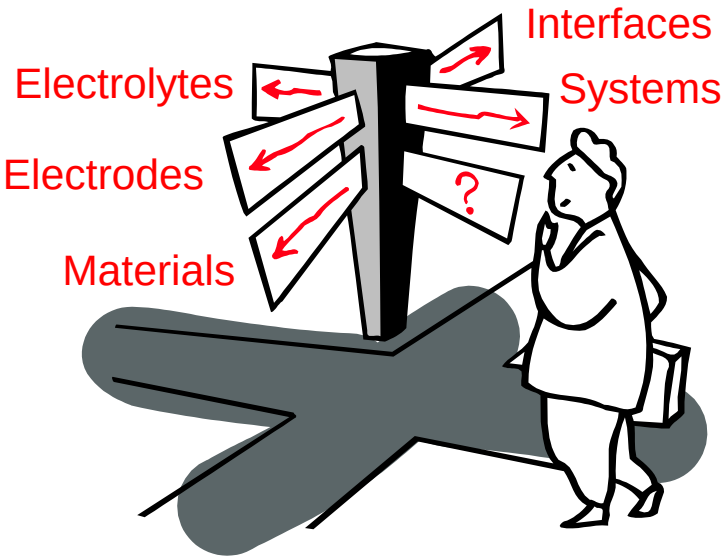
Sektion Elektrochemische Speicher
Forschungsbereich Allgemeine Energie, Labor für Elektrochemie
Paul Scherrer Institut
CH-5232 Villigen PSI
Schweiz

Scientific Look at Batteries

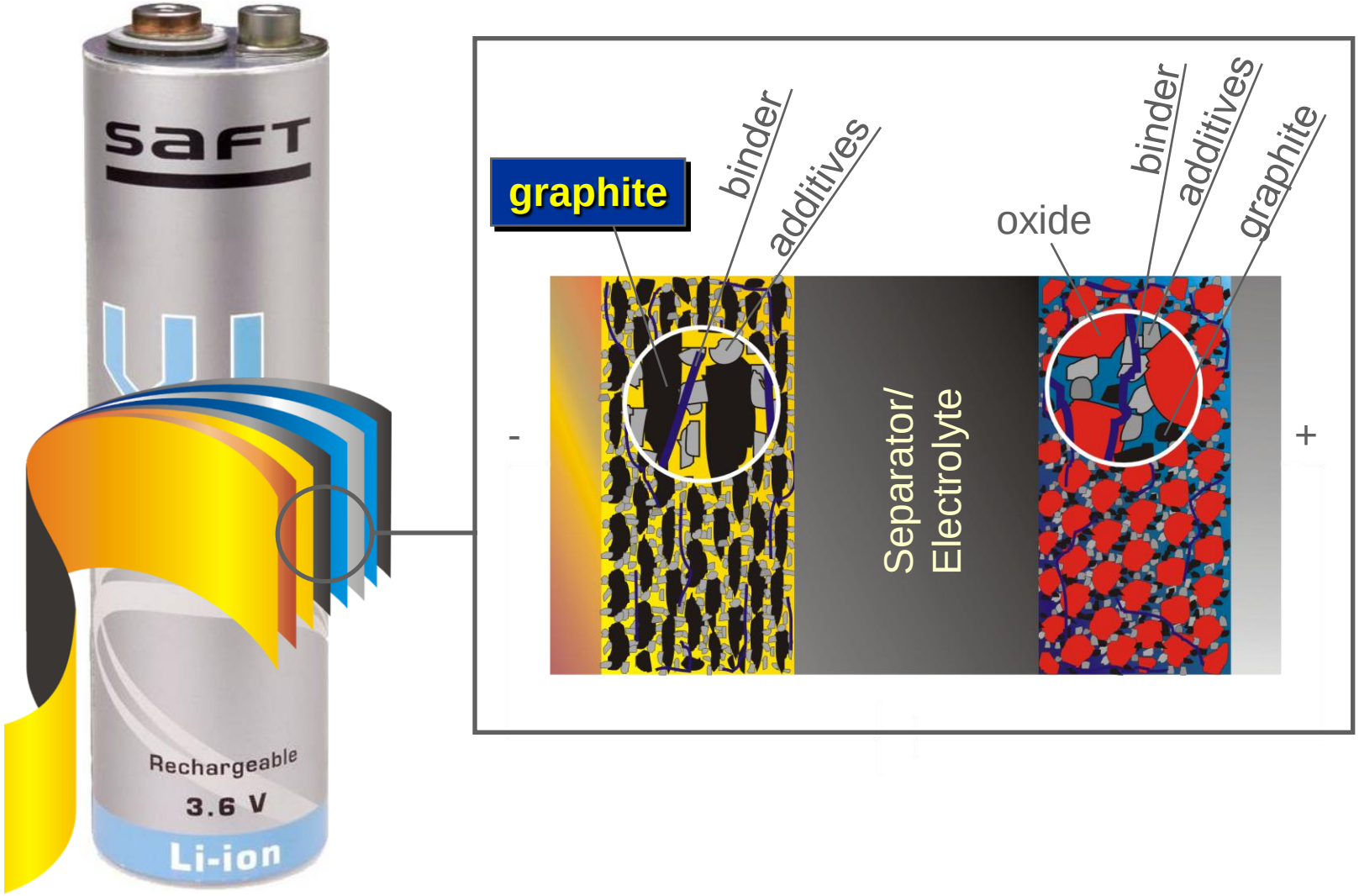


Outline of the Talk

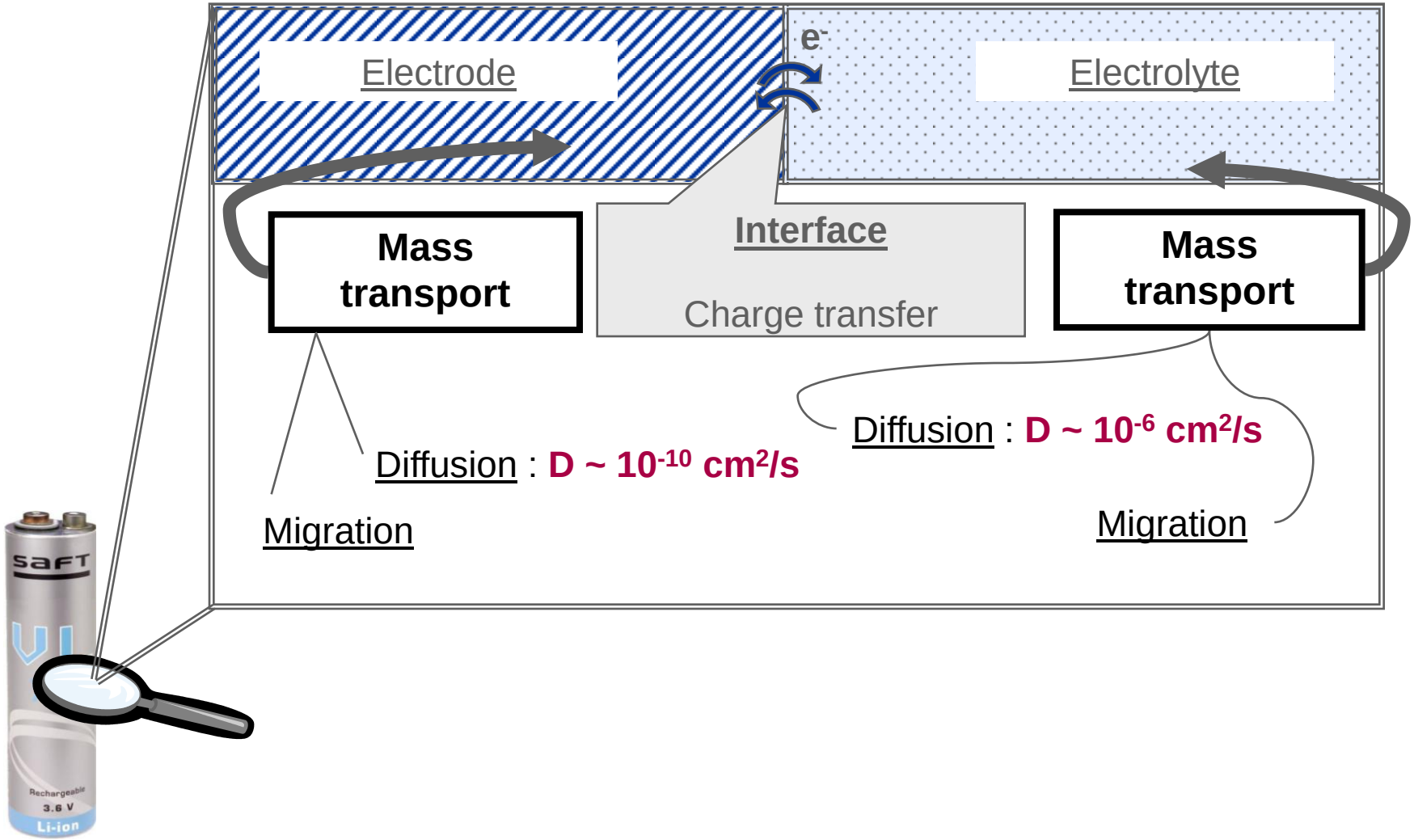
- *Mass Transport in Batteries*
- *Example: The Graphite Electrode*
- *Macroscopic Inhomogeneities*
- *Microscopic Inhomogeneities*
- *Conclusion*



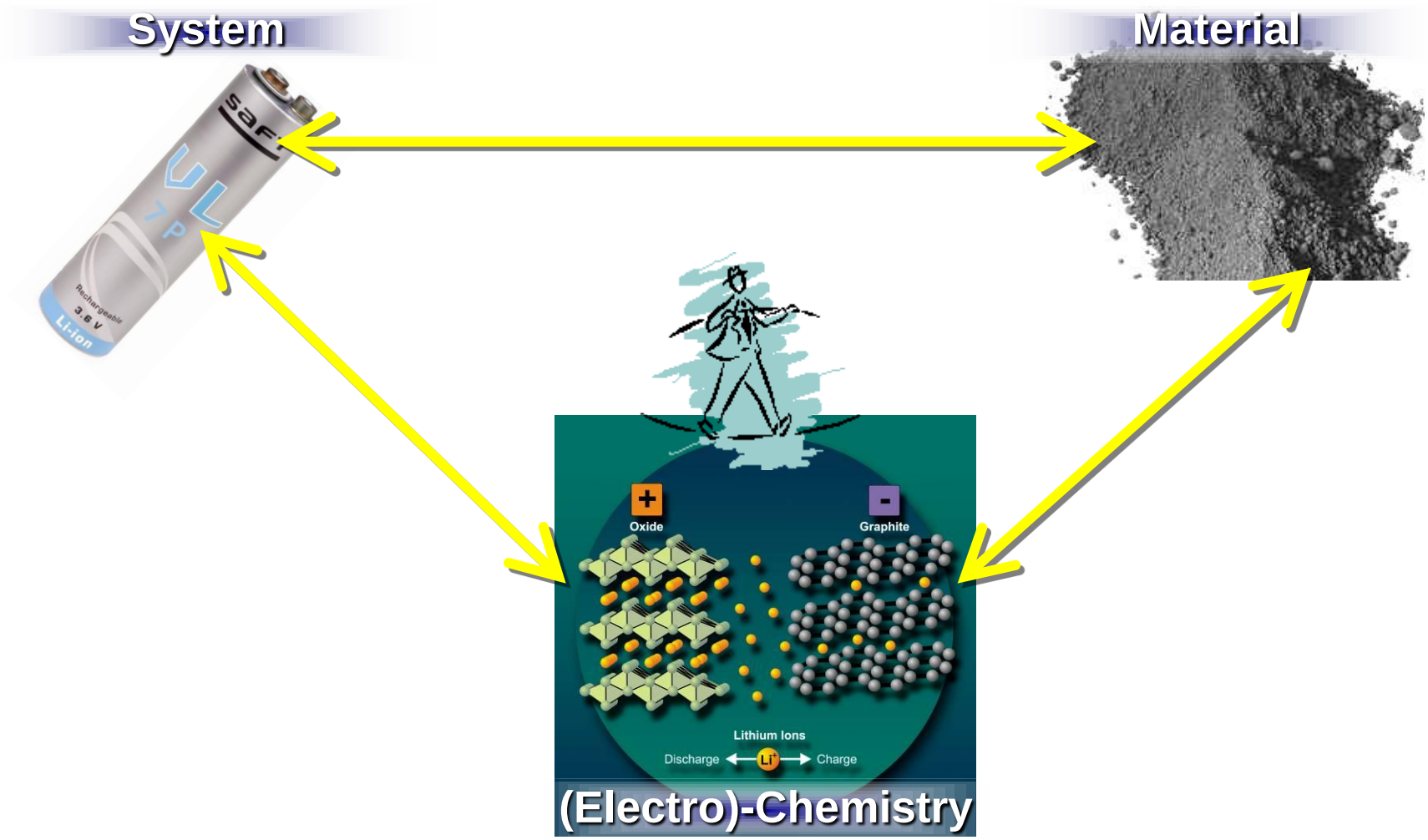
A Representative Lithium-Ion Battery



Processes Inside the Battery

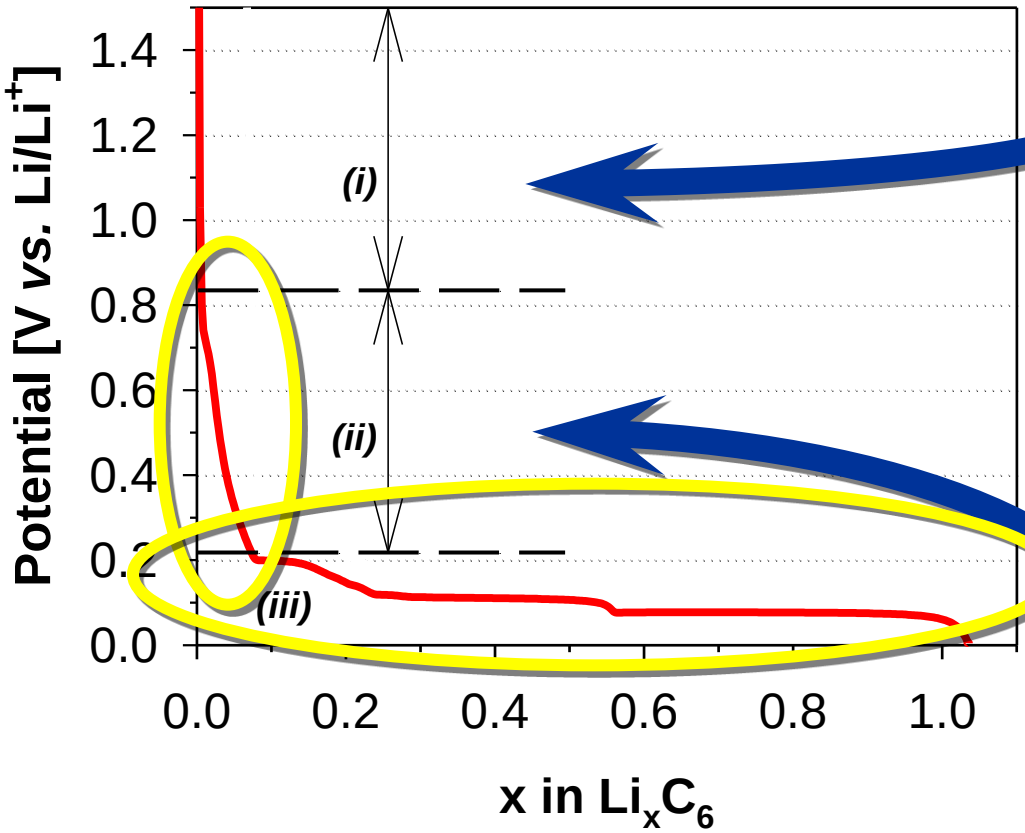


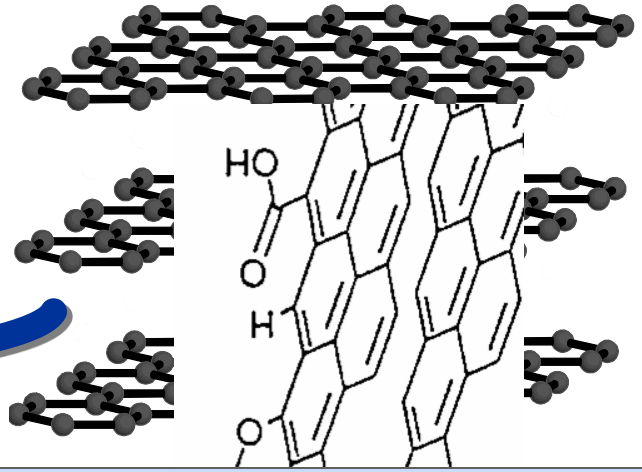
Lithium-Ion Battery



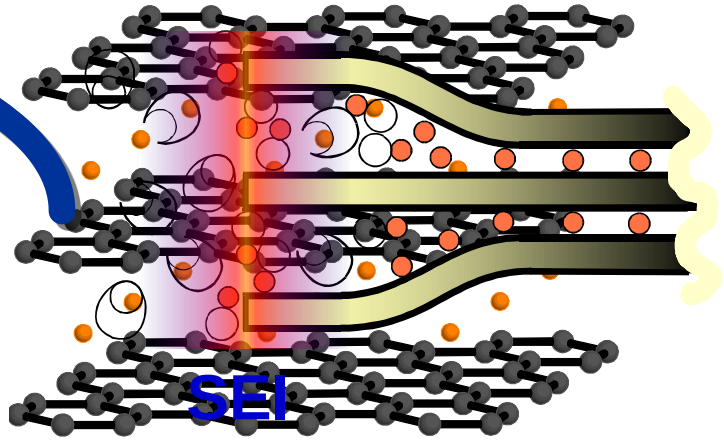
The Graphite Electrode

EC:DMC=1:1, 1*M* $LiPF_6$



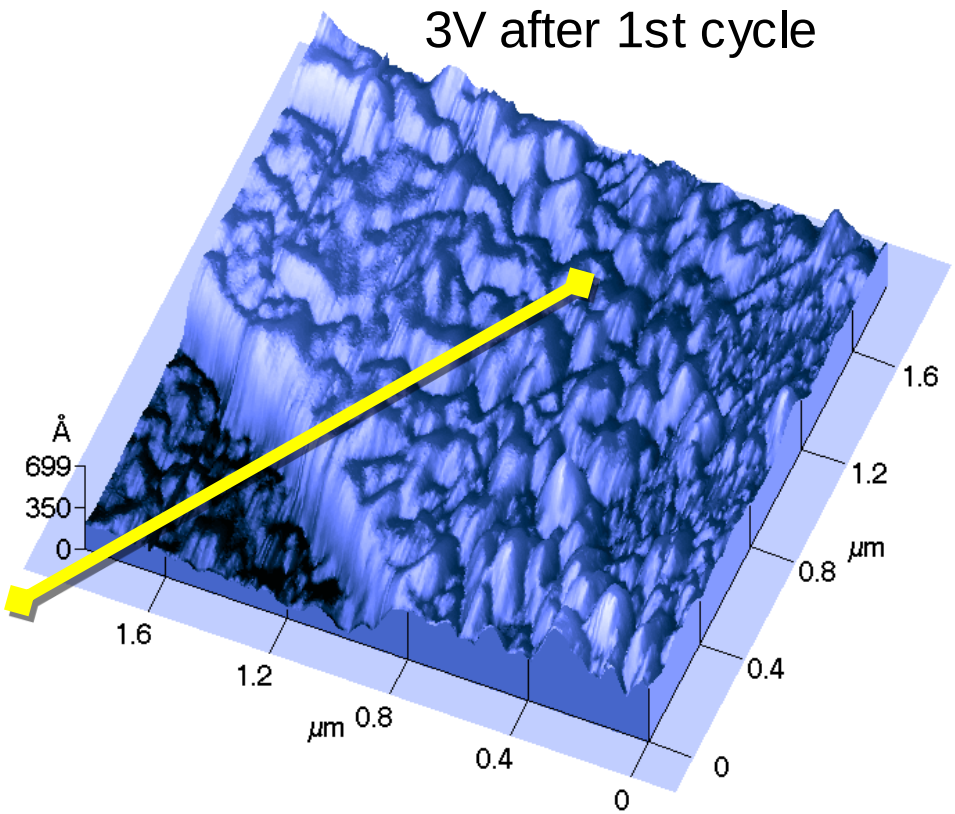


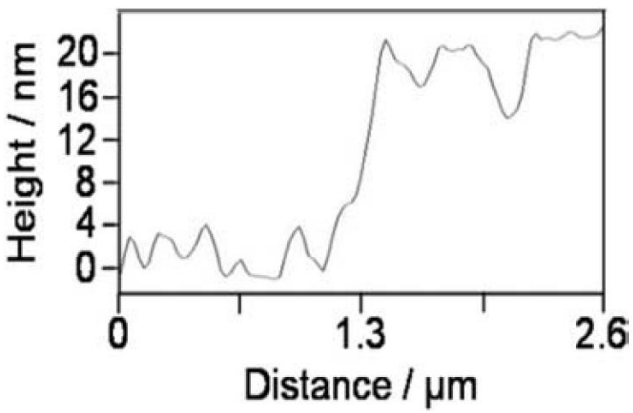
$$Li^+ + e^- + 6C \rightleftarrows LiC_6$$

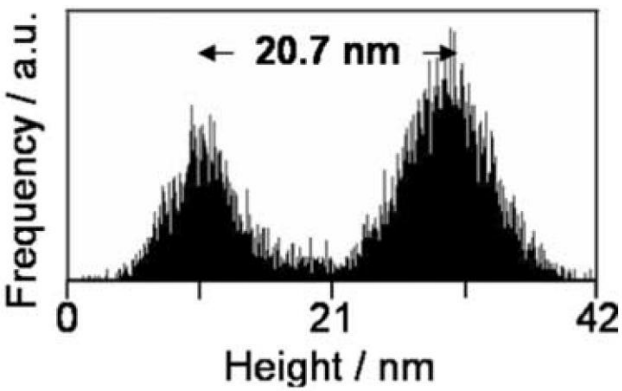


In Situ AFM Investigations: SEI Formation

3V after 1st cycle



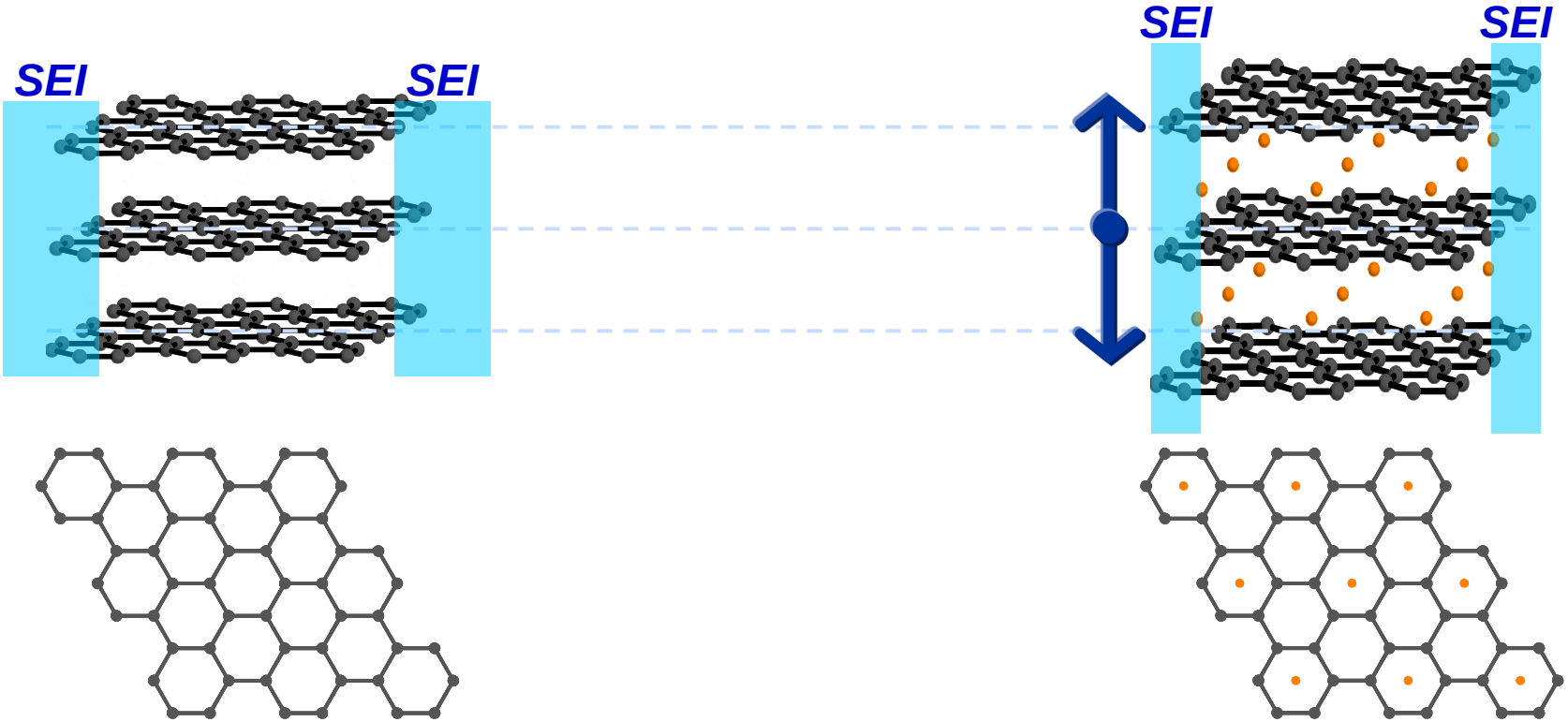




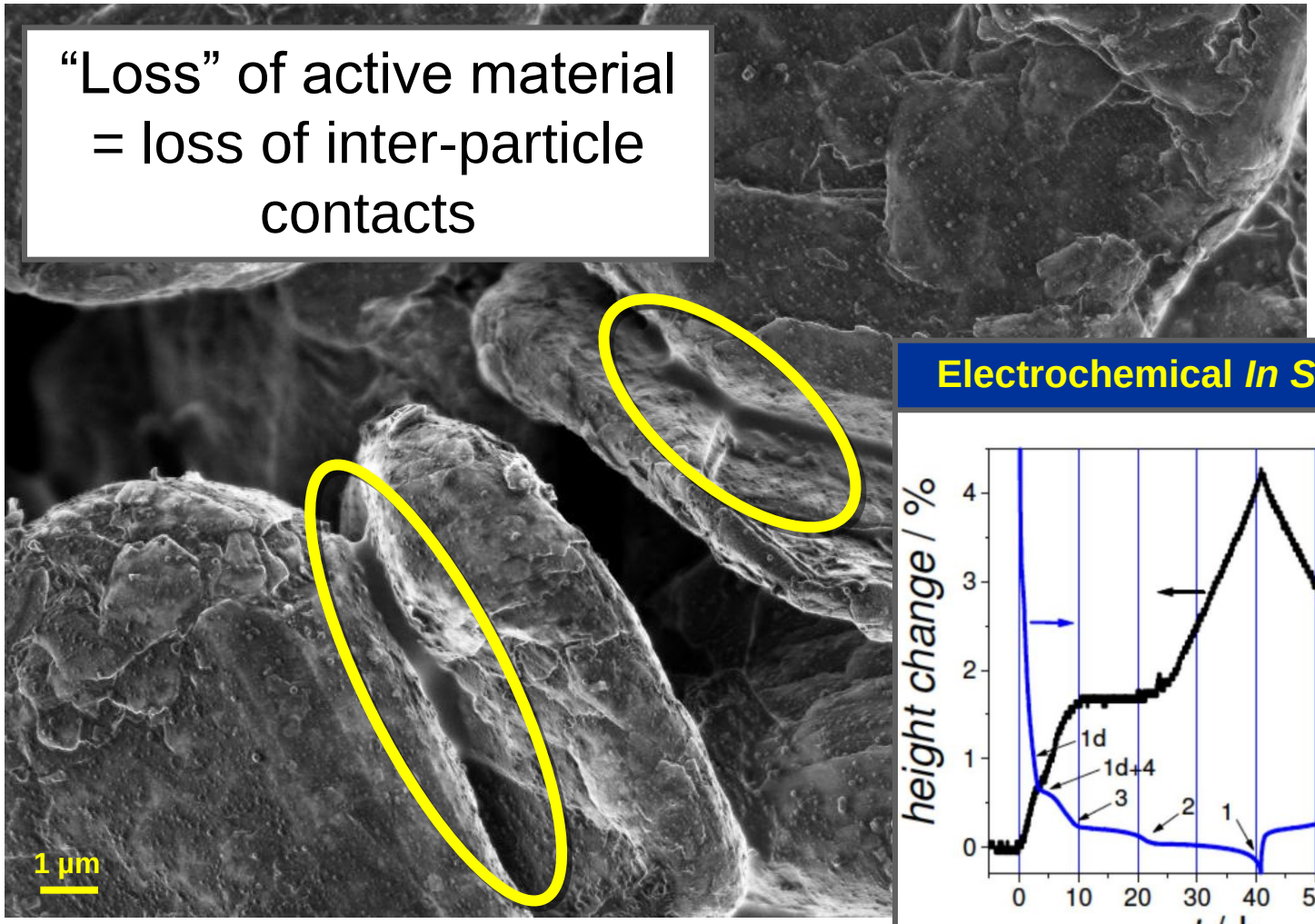
- *HOPG*
- *EC:DMC=1:1, 1M $LiClO_4$*
- *5 mV/s*

Cycling of Graphite

$$6C + Li^+ + e^- \rightleftarrows LiC_6$$

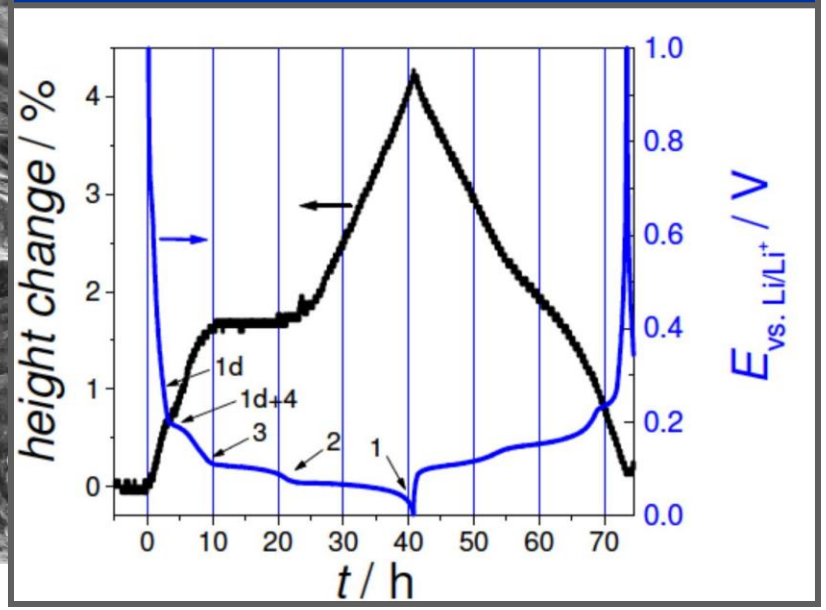


SEI on Graphite

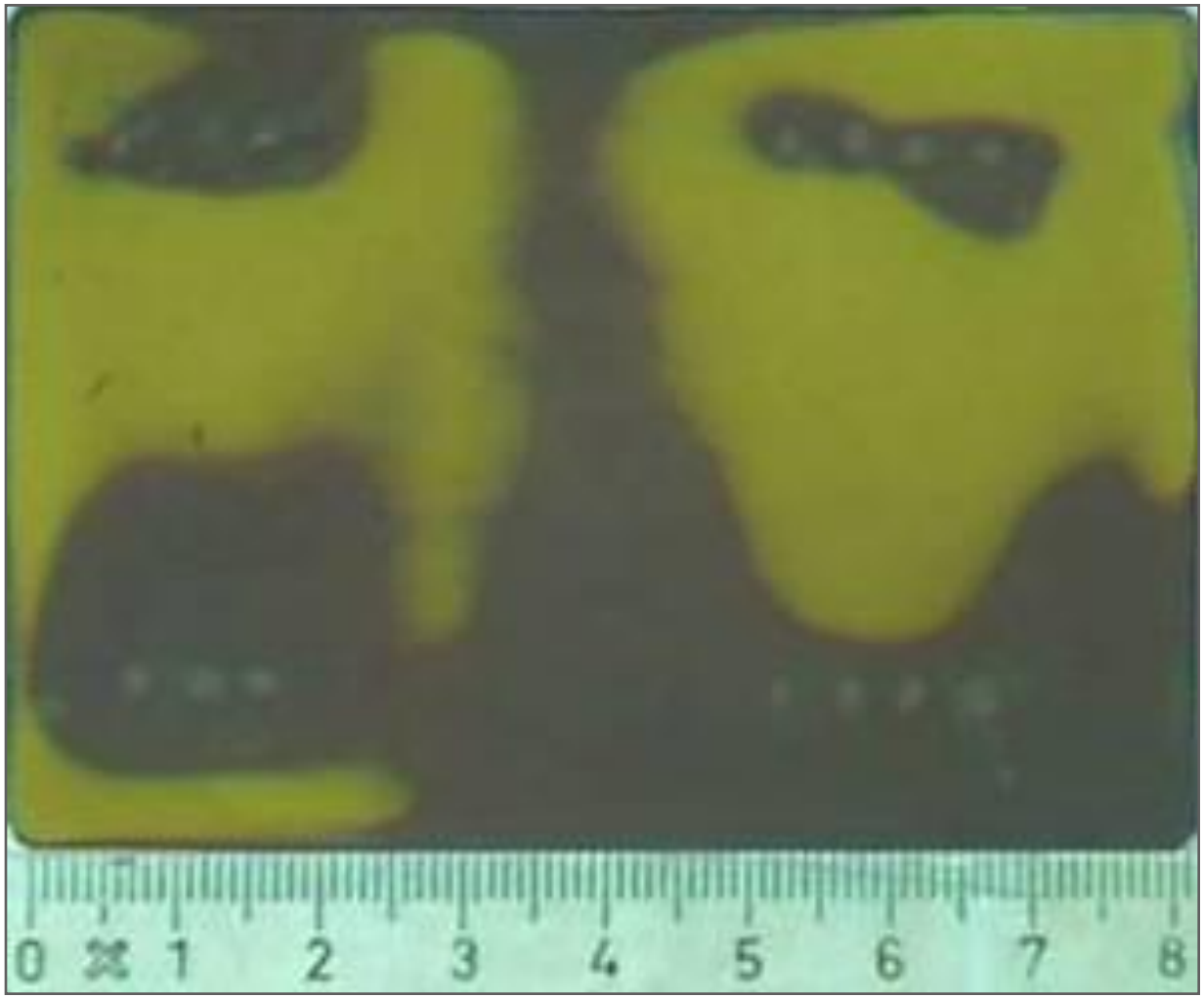


"Loss" of active material = loss of inter-particle contacts

Electrochemical *In Situ* Dilatometry



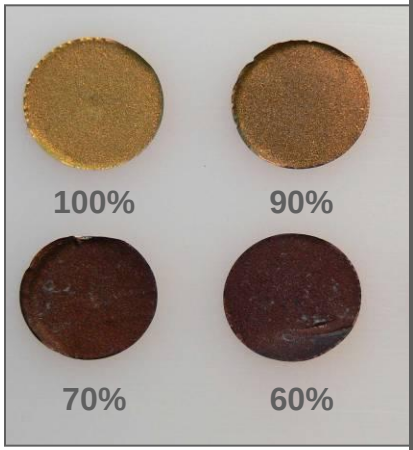
A Charged Graphite Negative Electrode



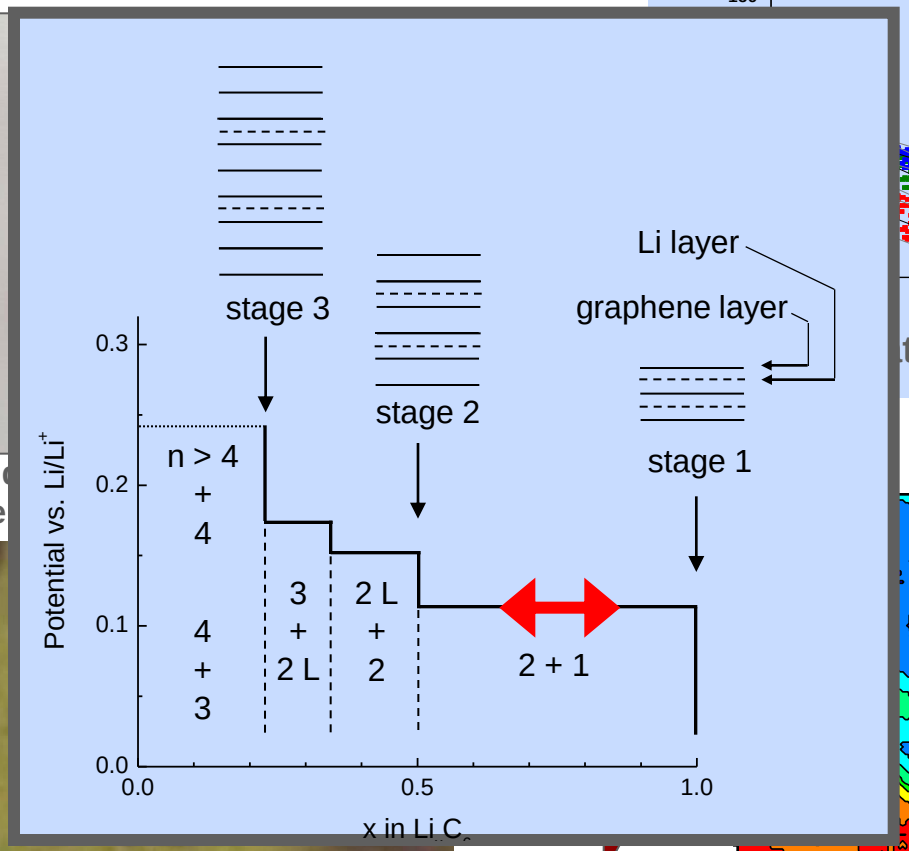
?

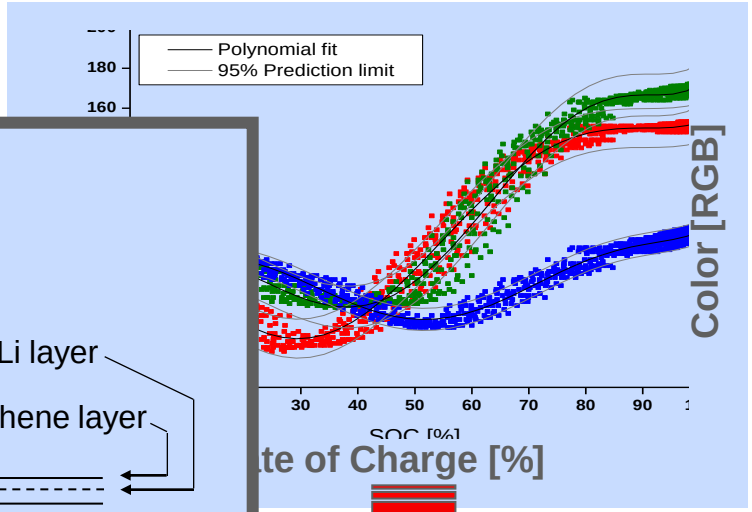
Commercial lithium-ion cell aged by long-term cycling (800 full charge and discharge cycles)

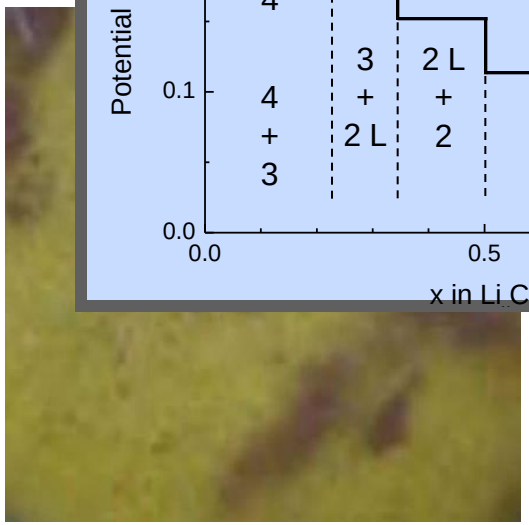
Cycling of Graphite



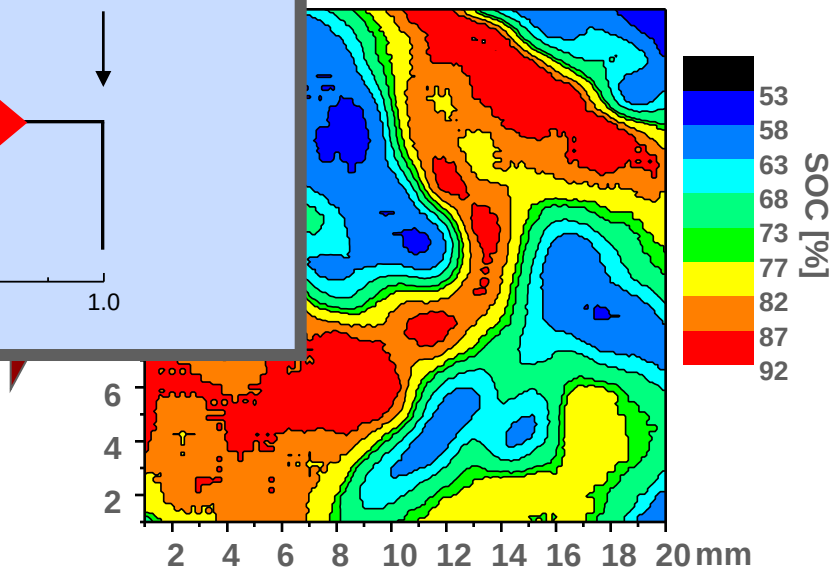
Graphite electrodes at
state of charge



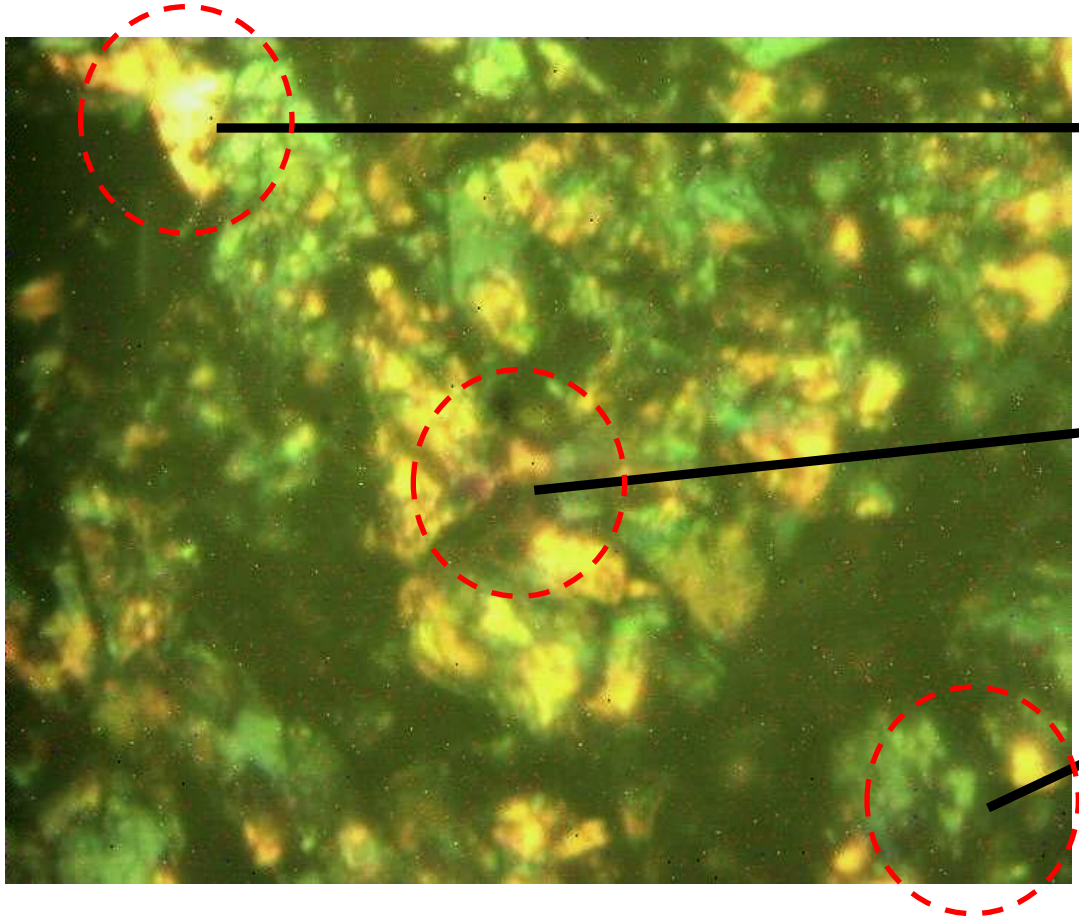




Li-ion battery anode
(graphite) after cycling



Single Graphite Particles



Golden Particles:

Li_xC_6: x = 1

Red Particles:

Li_xC_6: x = 0.5

Blue Particles:

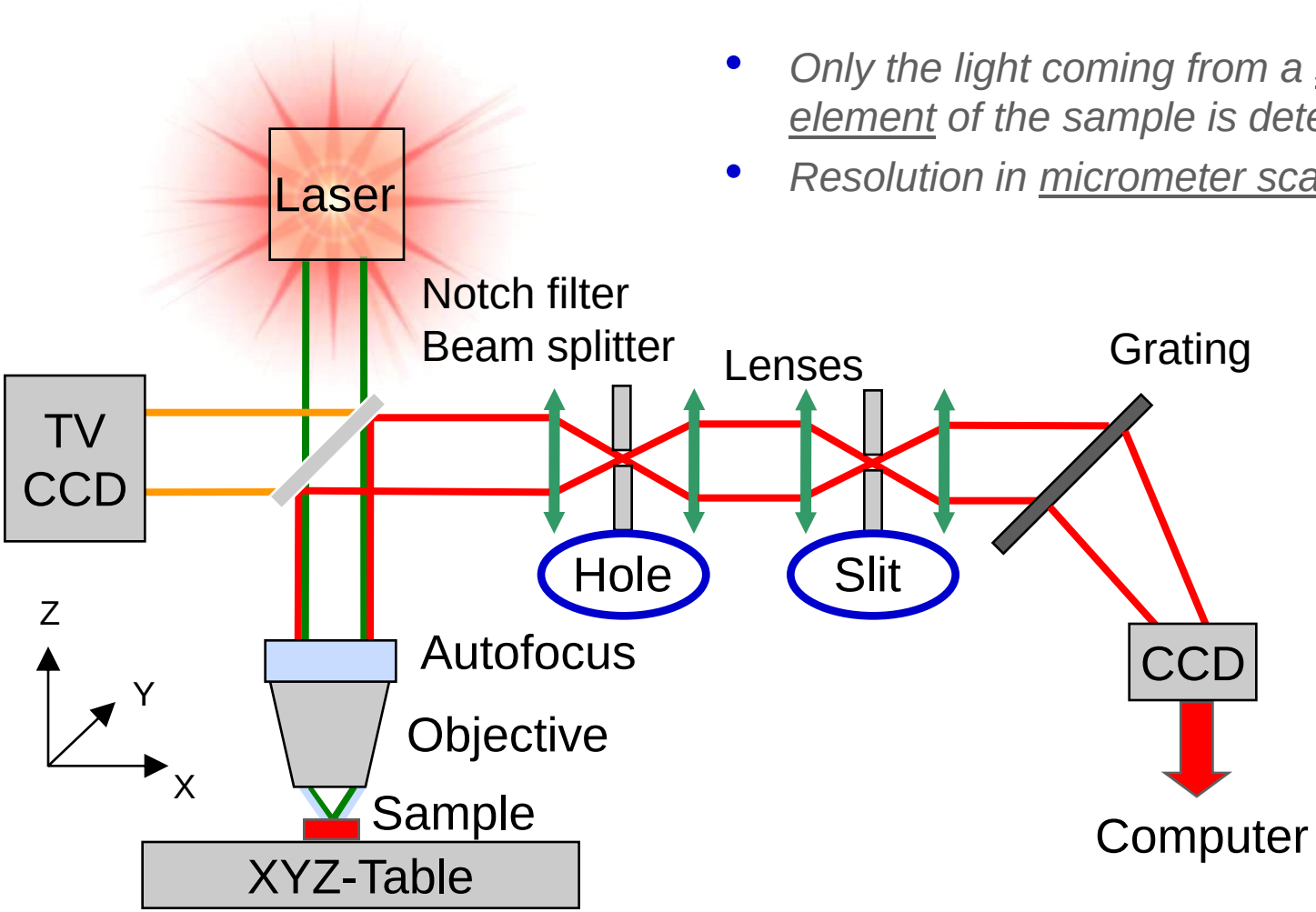
Li_xC_6: x < 0.5

In Situ Video Microscopy: Graphite Electrode

TIMREX® SFG44, 120 mV vs. Li/Li^+, C/5

Confocal Raman Microscopy

- *Only the light coming from a small volume element of the sample is detected*
- *Resolution in micrometer scale*

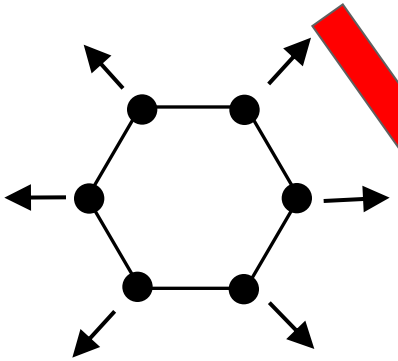


Raman Spectrum of Graphite

A_{1g}

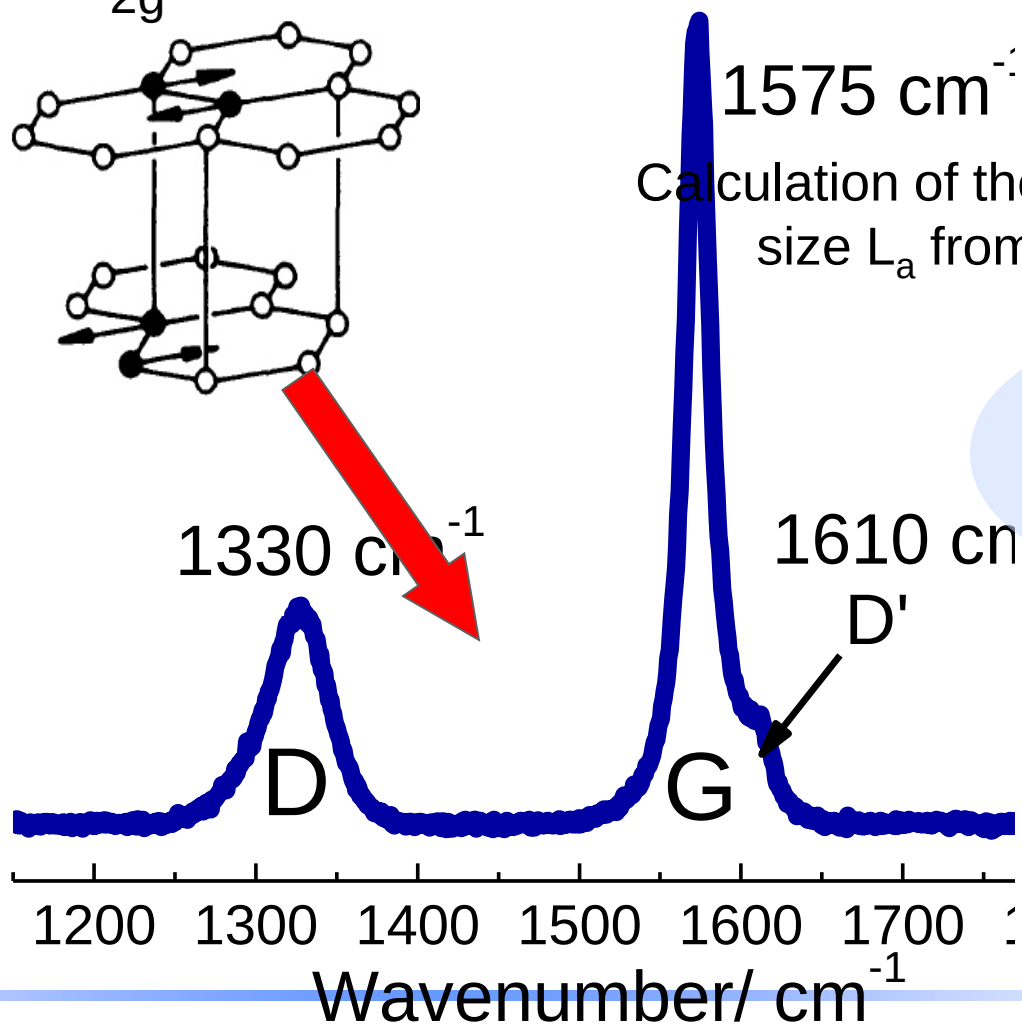
Disorder Band

Defects, holes, crystallite edge planes



Ring Breathing

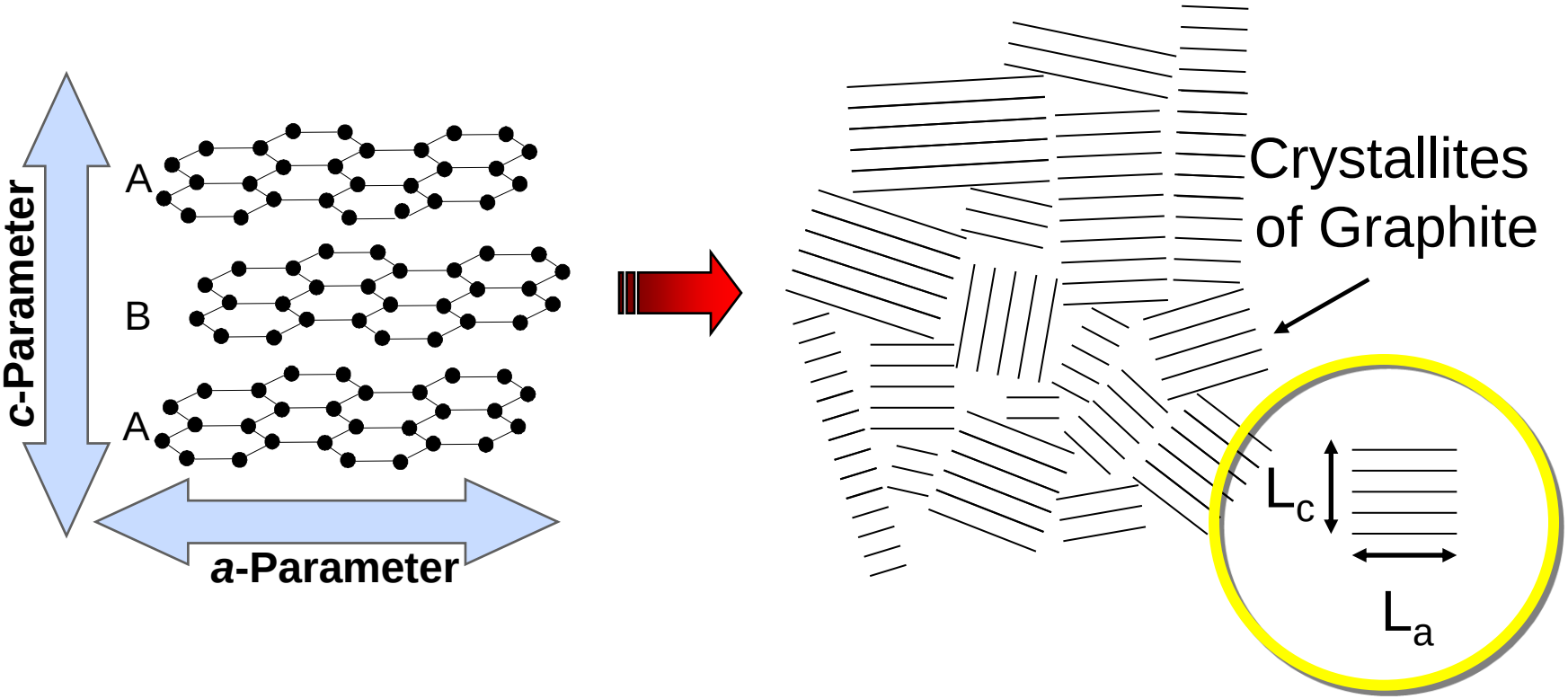
E_{2g}



Calculation of the crystallite size L_a from I_D / I_G

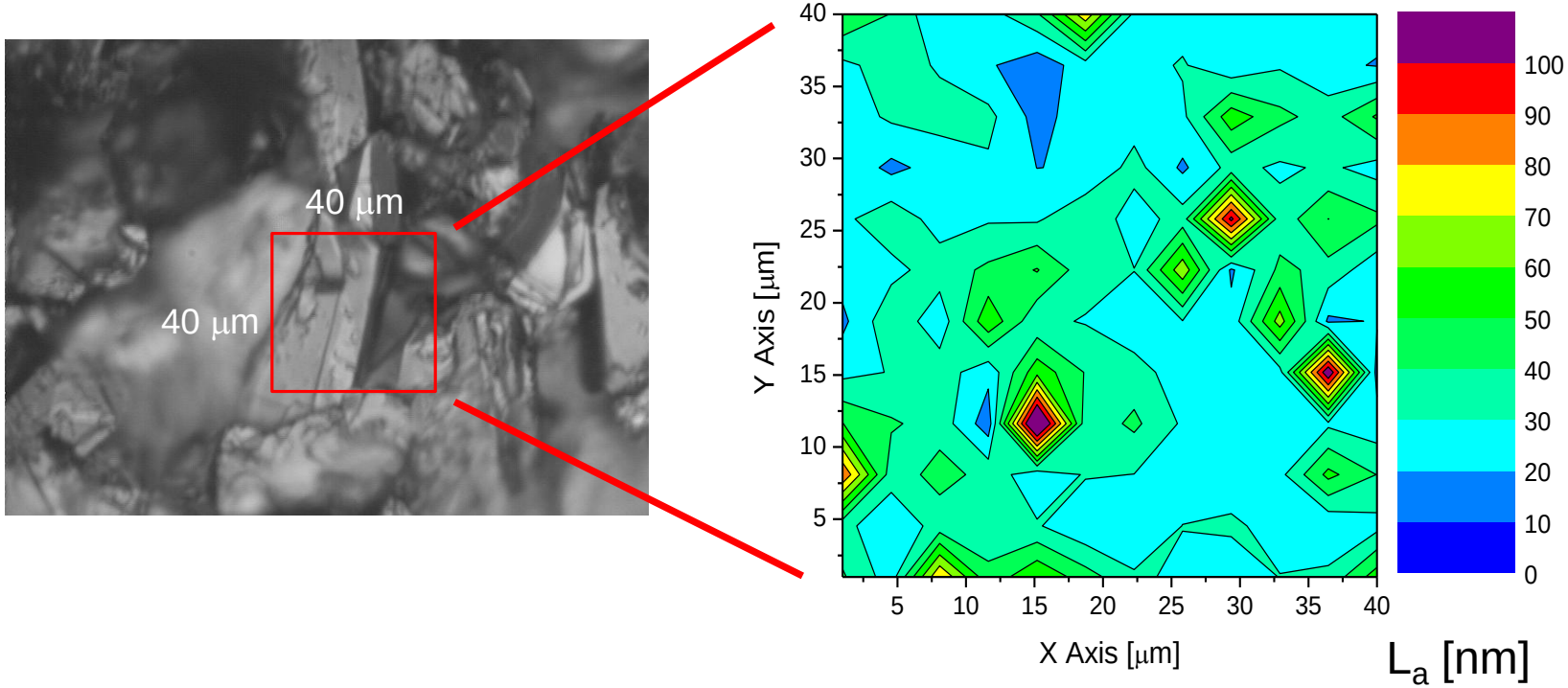
$$\frac{I(D)}{I(G)} = \frac{C(\lambda)}{L_a}$$

What Is the L_a Value?



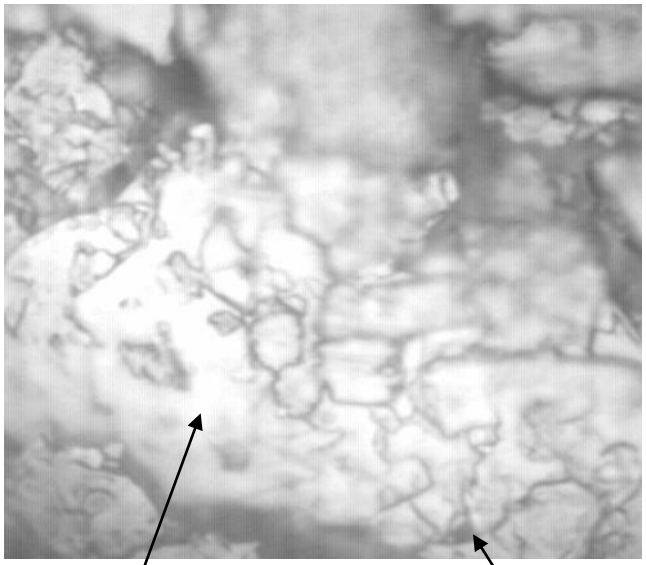
- *The L_a parameter is the length of the graphene sheets*
- *The length is in the nanometer scale*
- *L_a provides a measure of disorder within the graphite structure*

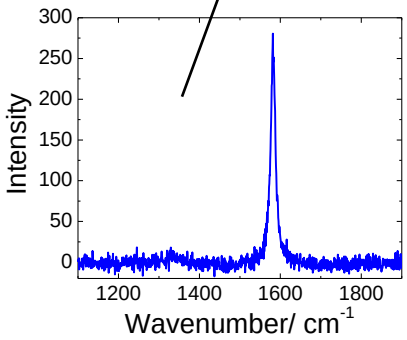
Raman Mapping of L_a

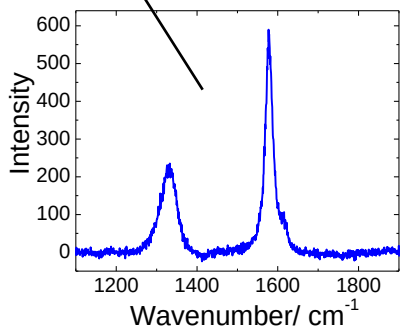


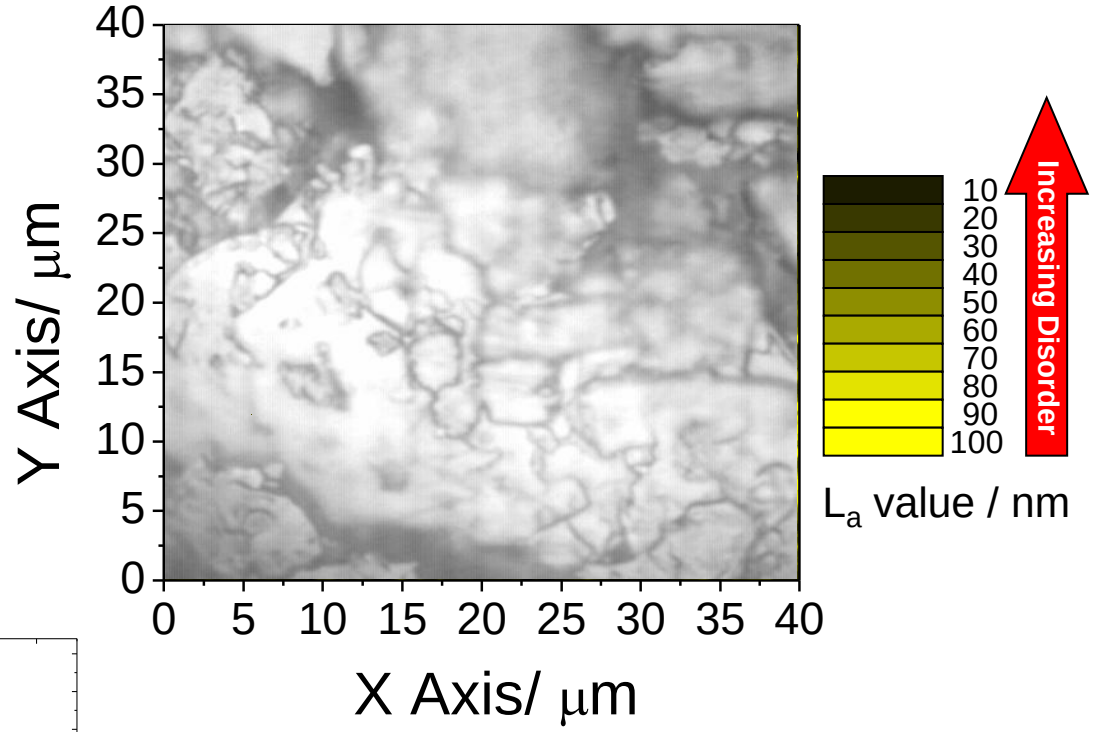
- *Graphite TIMREX® SLX50*
- *L_a mostly between 20-40 nm*
- *Map: 12 x 12 points; 144 spectra*
- *Small islands with higher values of L_a*

Raman Microscopy: L_a Map of Graphite









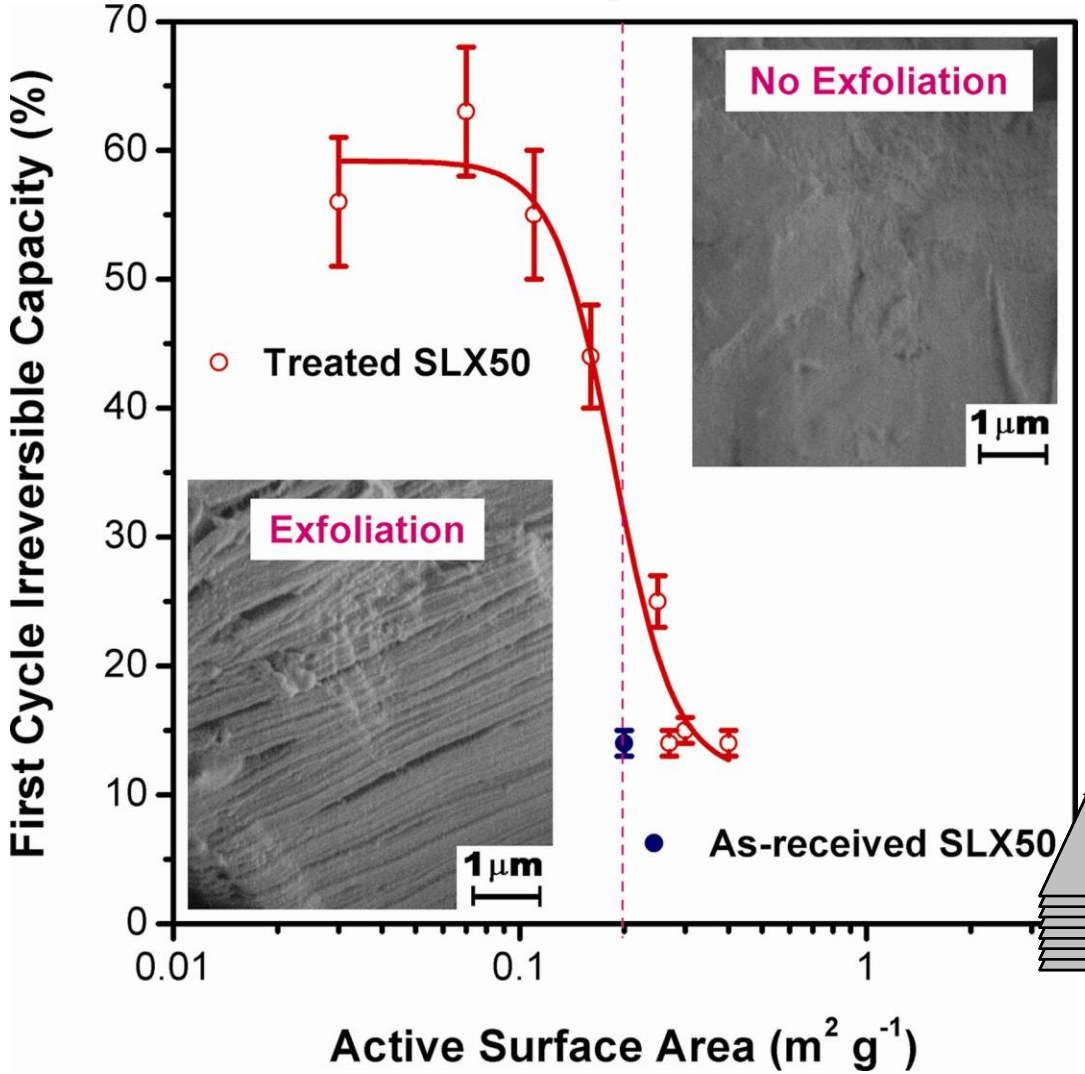
100 x 100 mapping
10,000 spectra
40 µm x 40 µm measurement square
resolution approaching (1µm)³

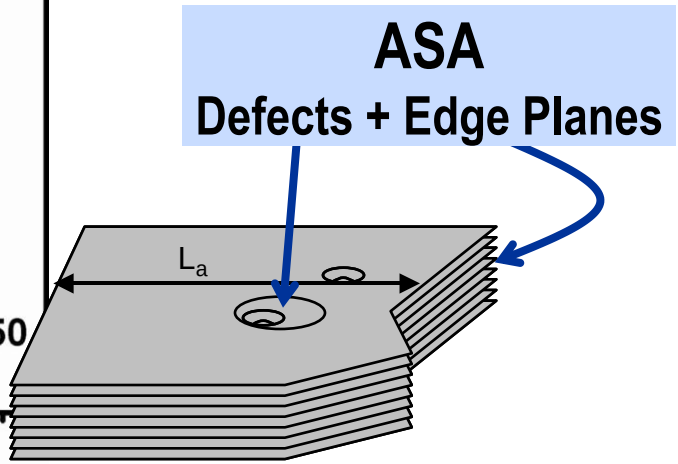
Exfoliation of Graphite

thanks to F. Krumeich, ETH Zurich

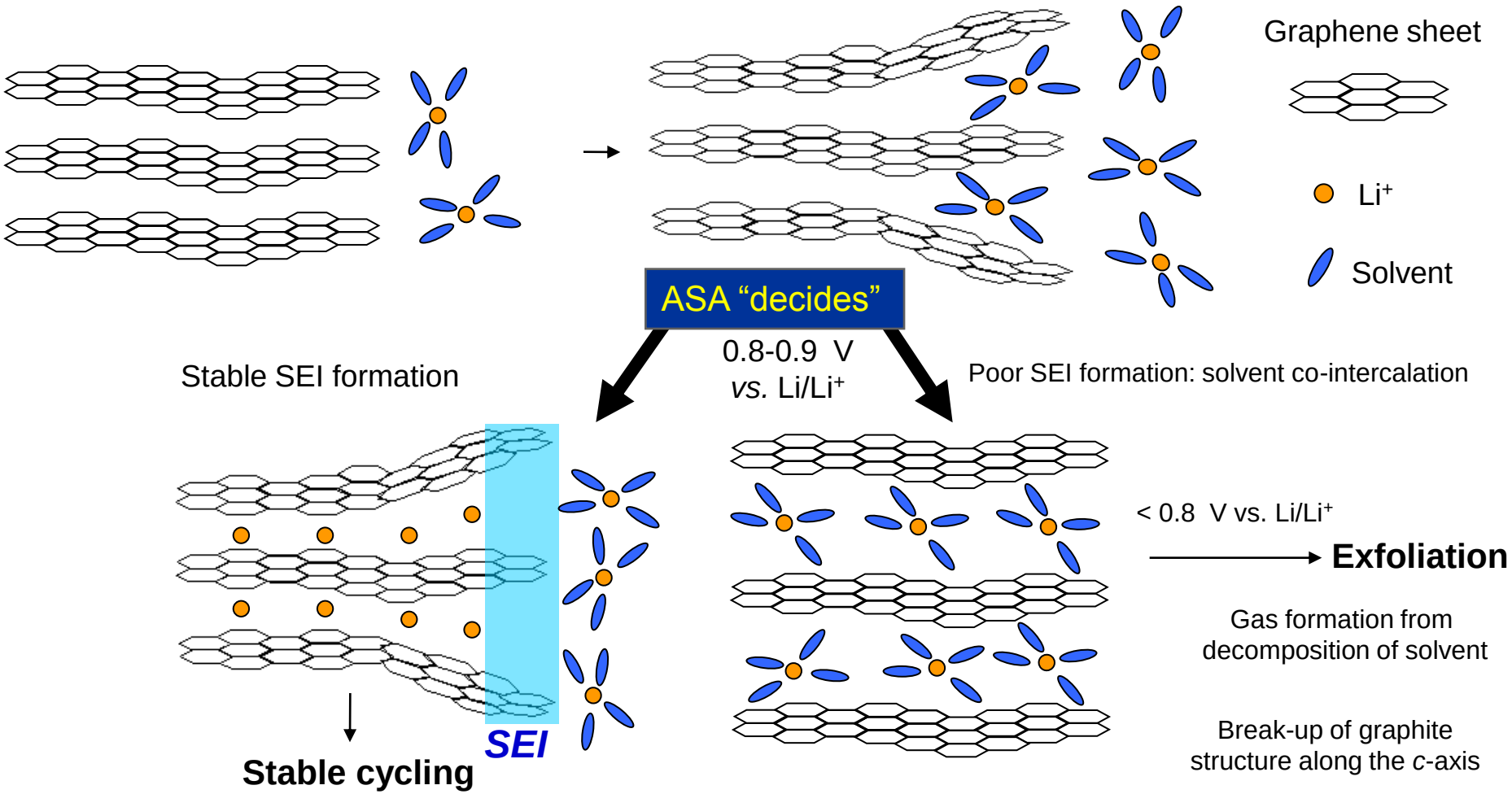
TIMREX® SFG44 in EC/PC 1:1, 1M $LiPF_6$

Exfoliation of Graphite

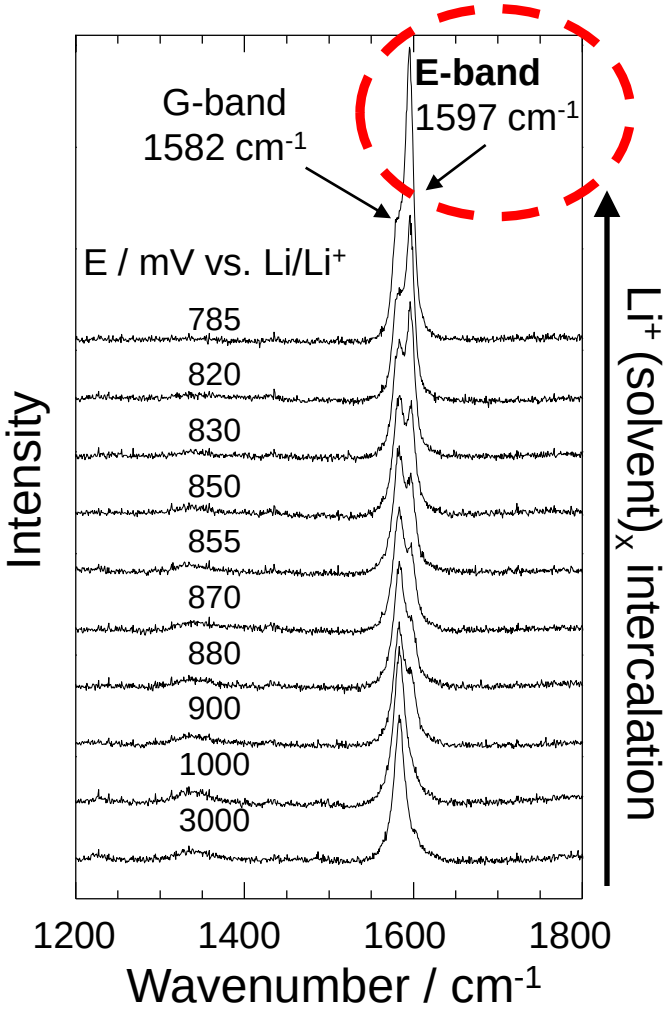


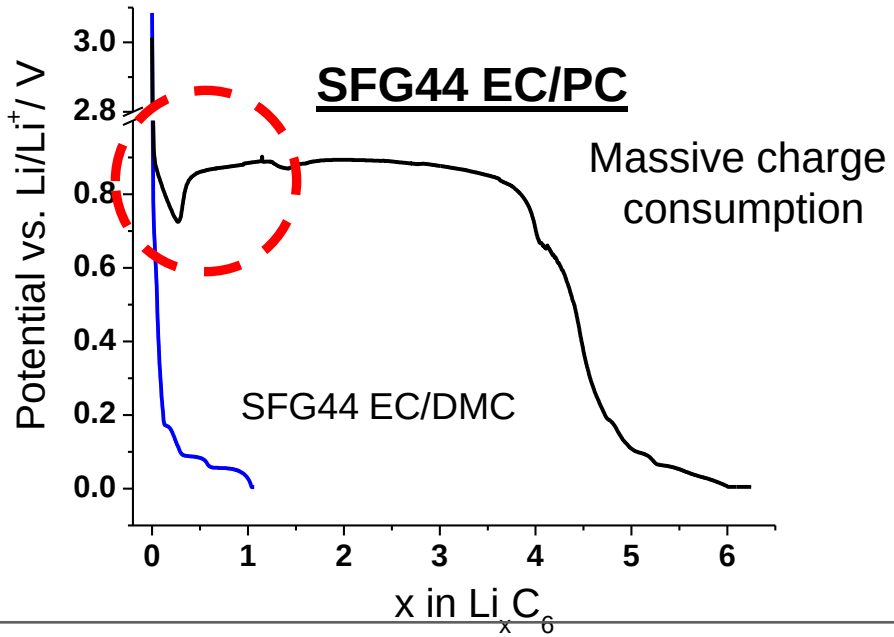


Exfoliation of Graphite: Besenhard's Model

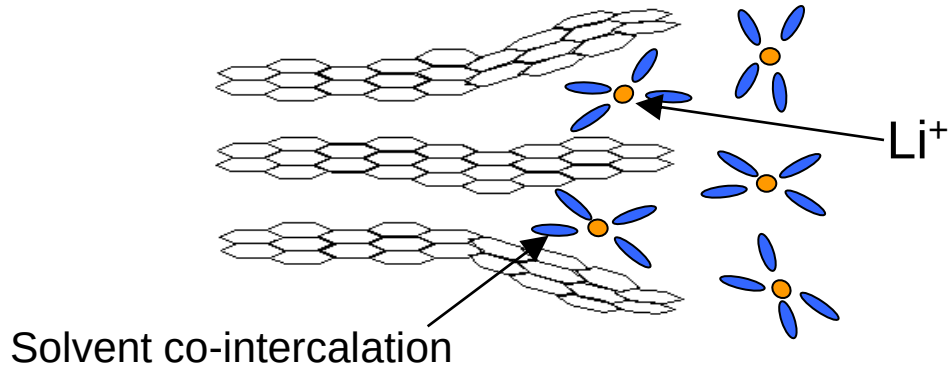


Exfoliation of Graphite

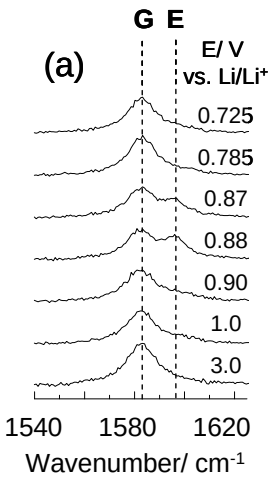


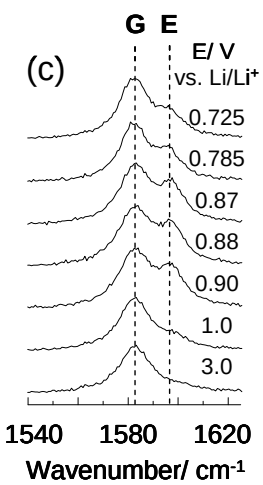


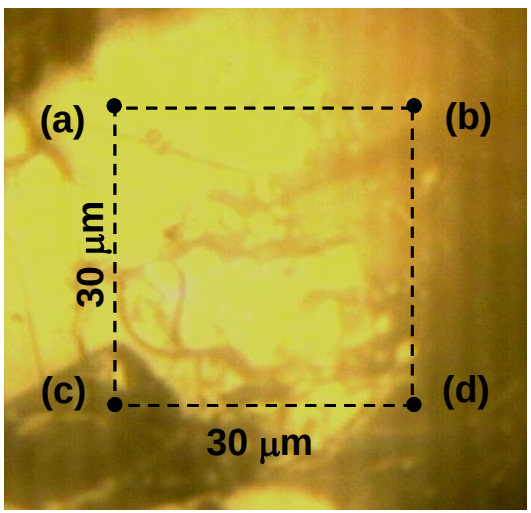
E-band: Graphene layers on which solvated Li^+ is bound

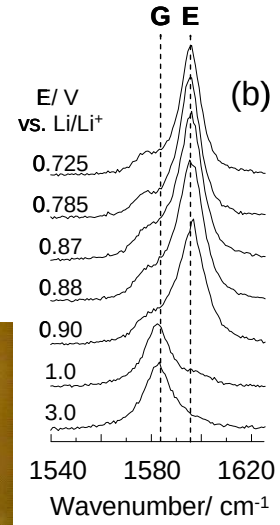


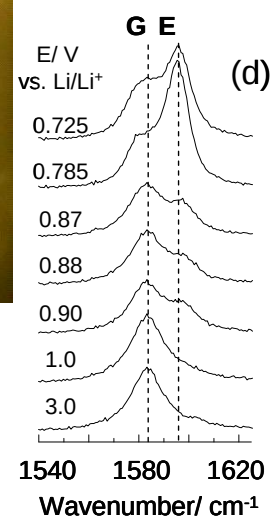
Multipoint Raman on Exfoliating Graphite



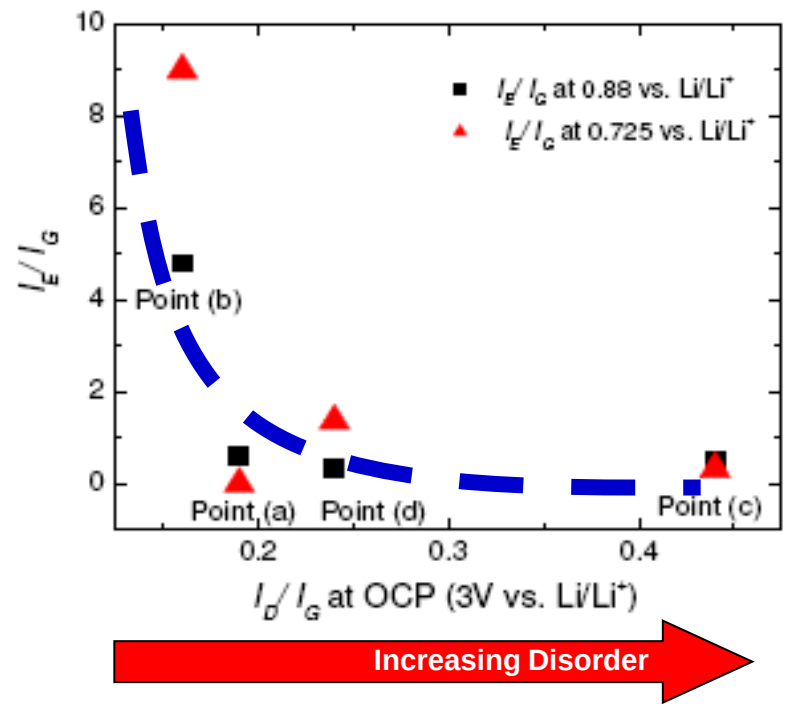






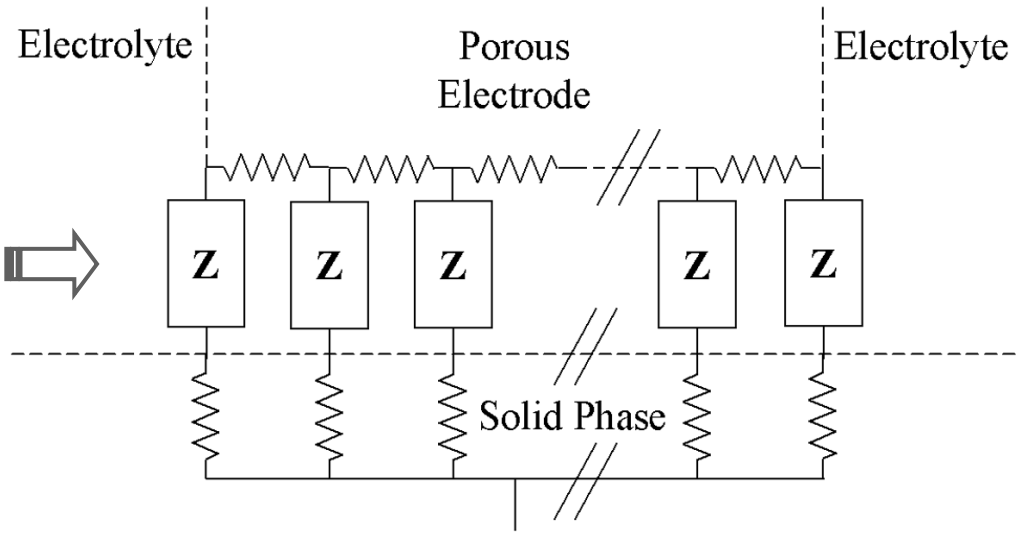


Link between point disorder and exfoliation!



The Practical Graphite Electrode

$$6C + Li^+ + e^- \rightleftarrows LiC_6$$



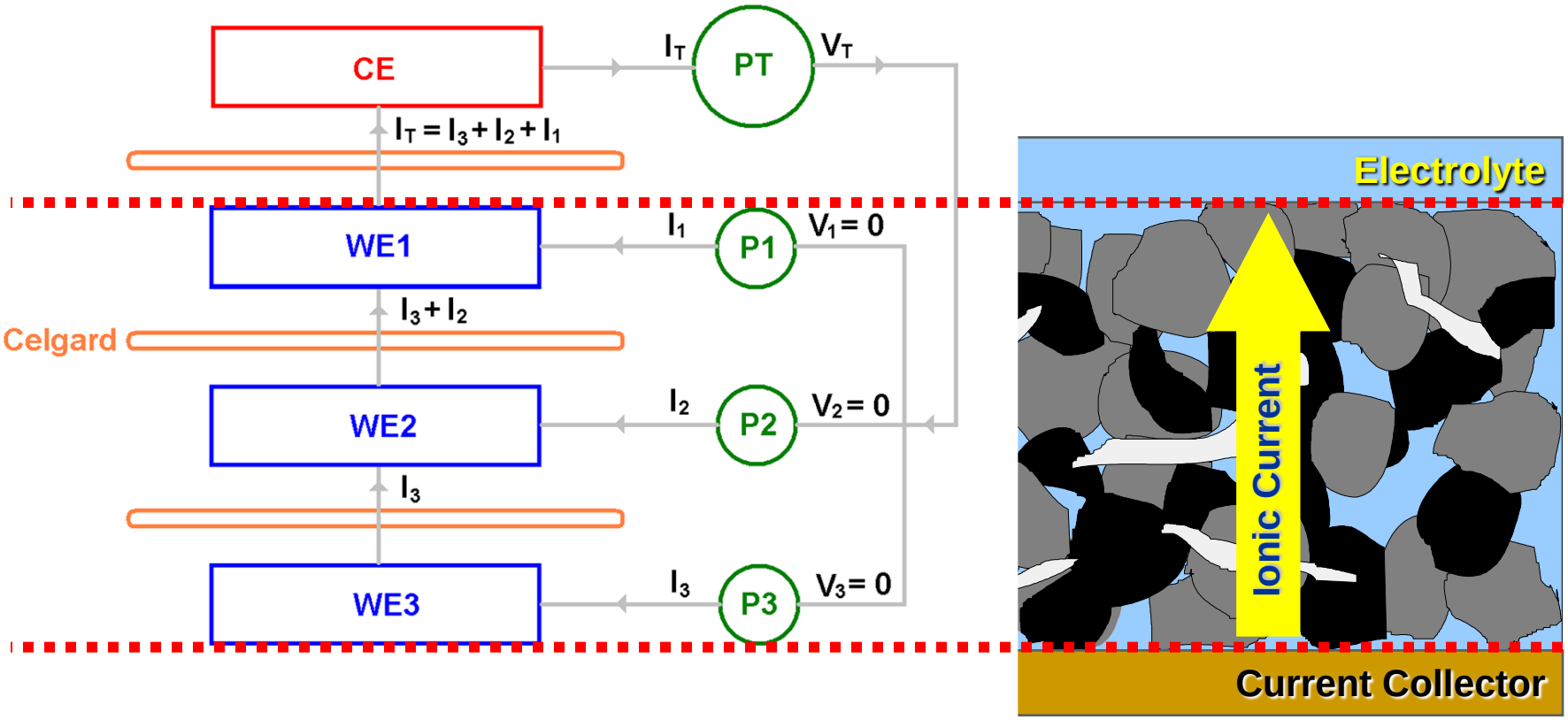
Lithium ions <u>in the pores</u> of the graphite electrode are consumed

⇒ the Li^+ concentration in the pores changes

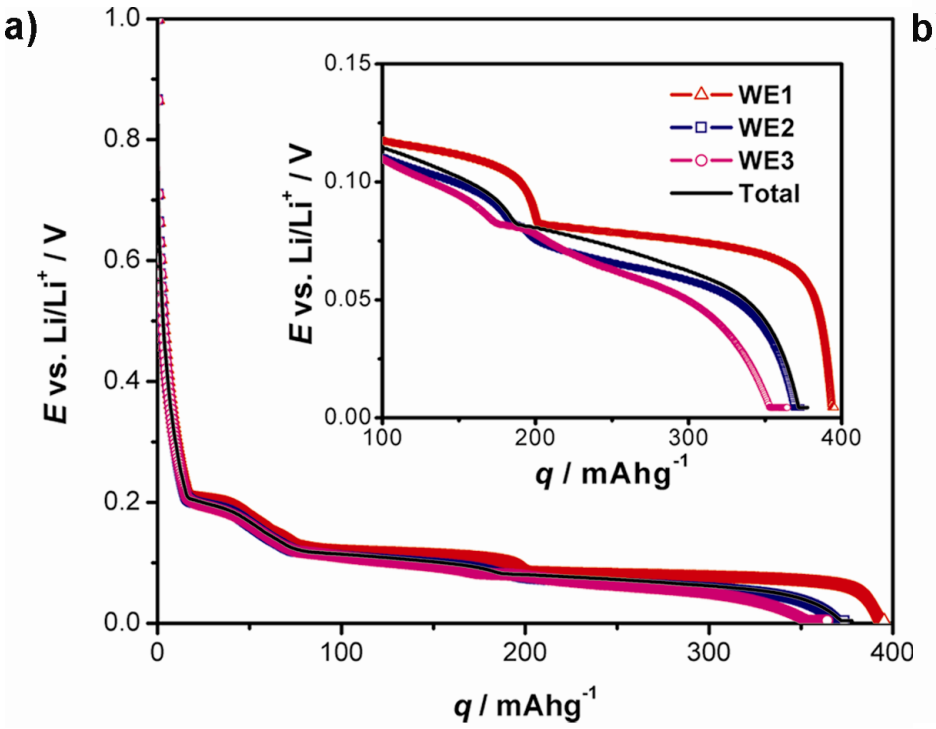
⇒ the overpotentials across the electrode change

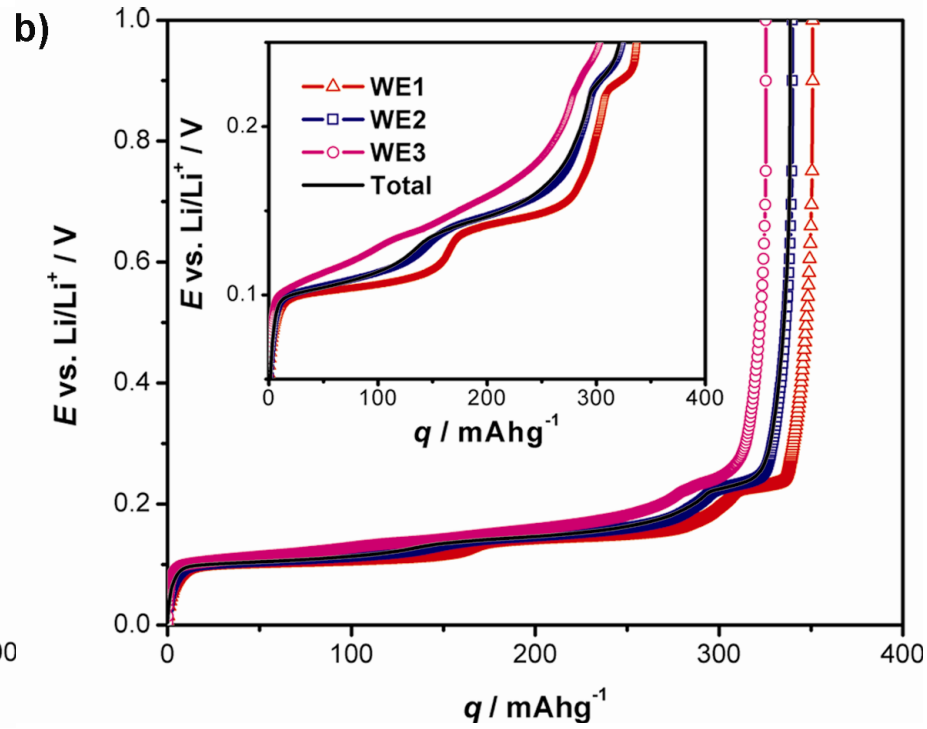
⇒ measure the current density distribution <u>across the electrode thickness</u>

How to Measure the Current Density Distribution?

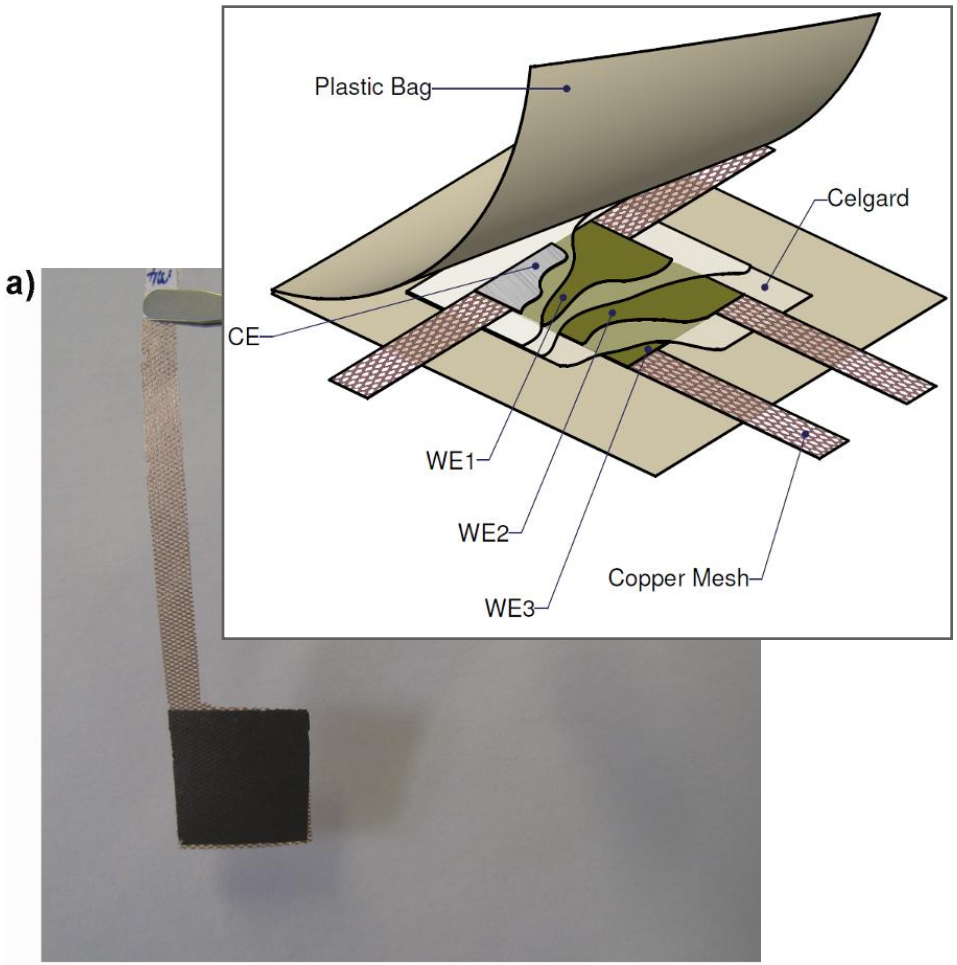


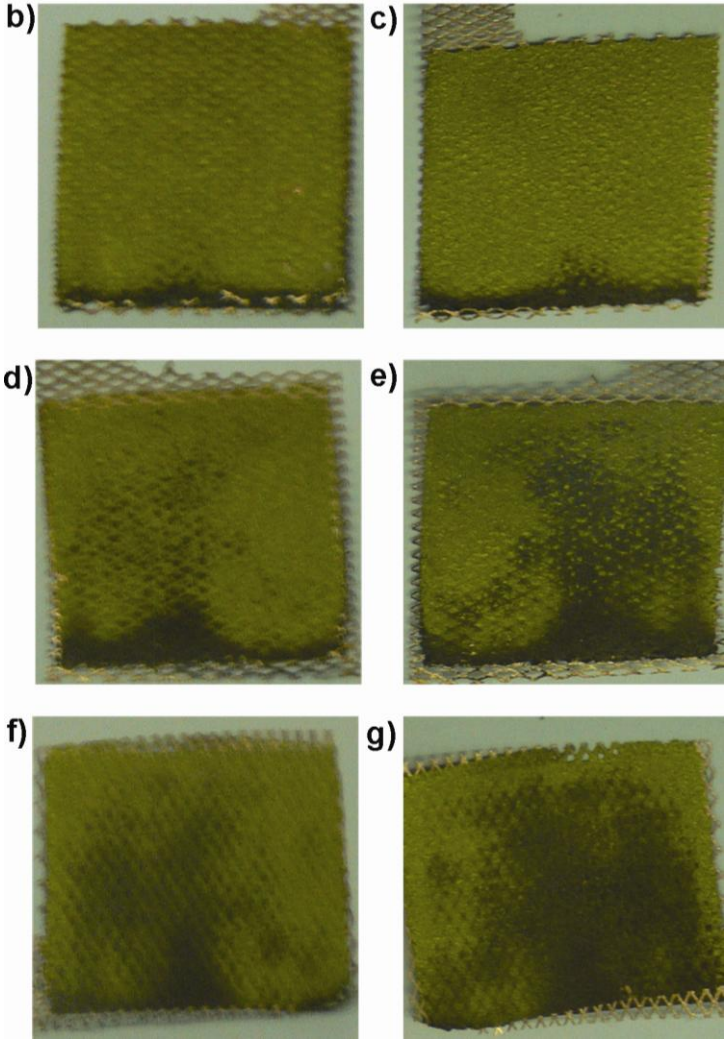
Current Density Across the Graphite Electrode



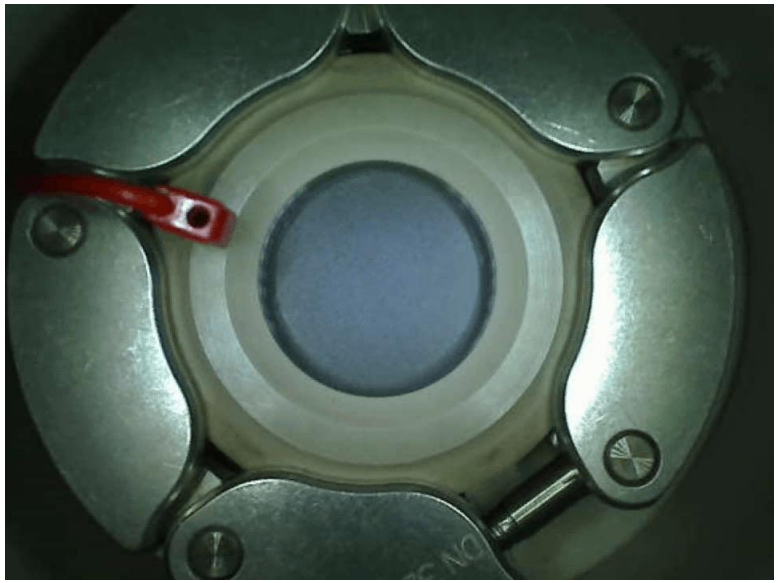


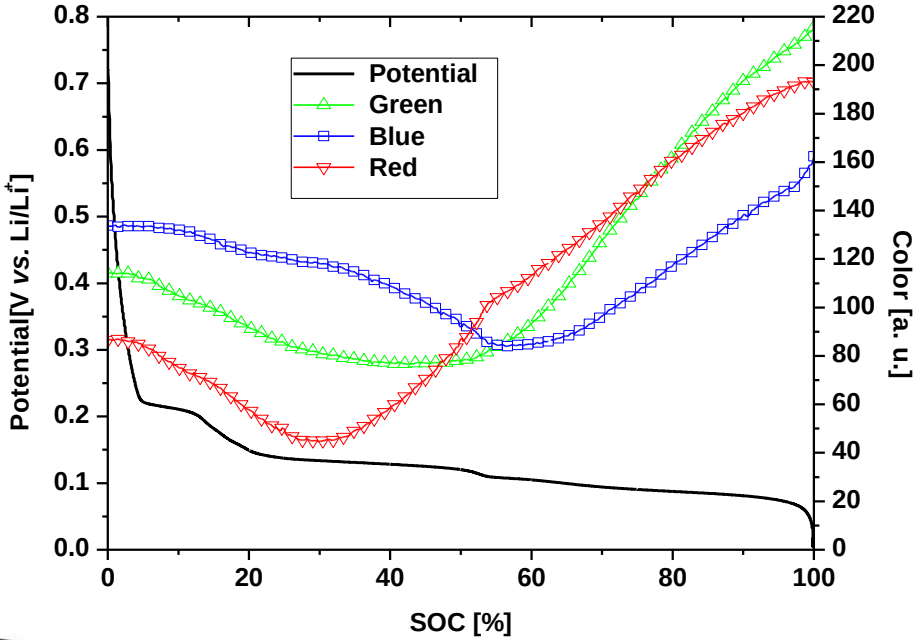
Color Changes Across the Graphite Electrode

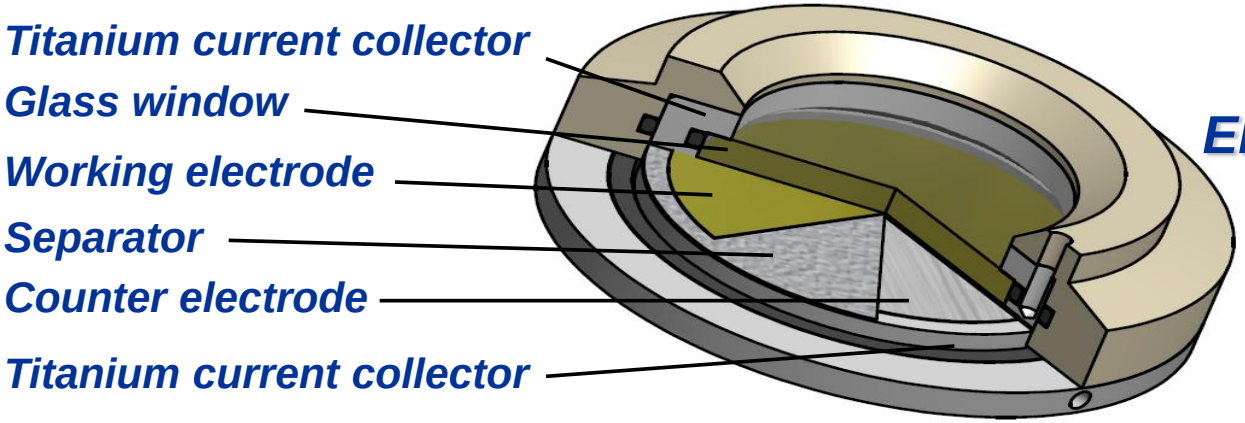




In Situ Look at the Working Graphite Electrode



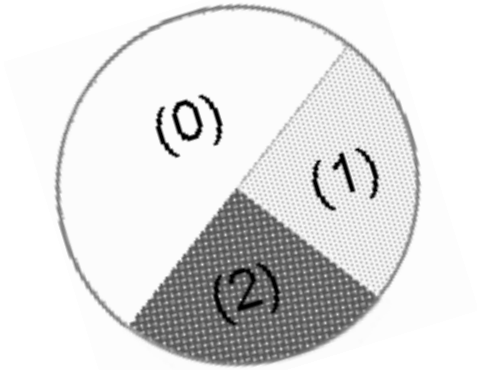


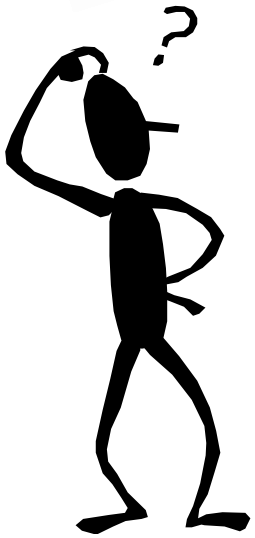


Electrode colors indicate the state of charge

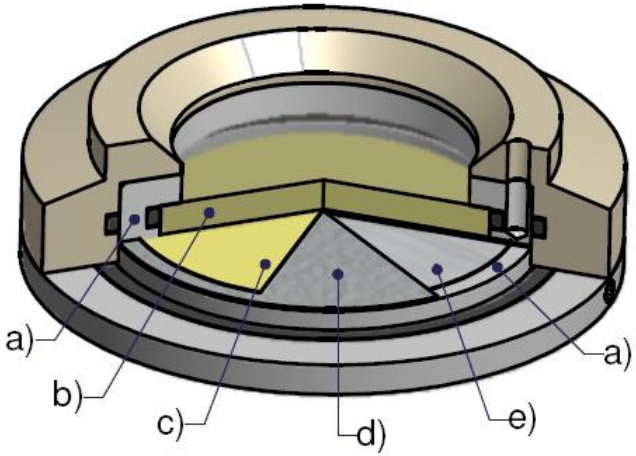
Graphite Electrode with Artificial Heterogeneities

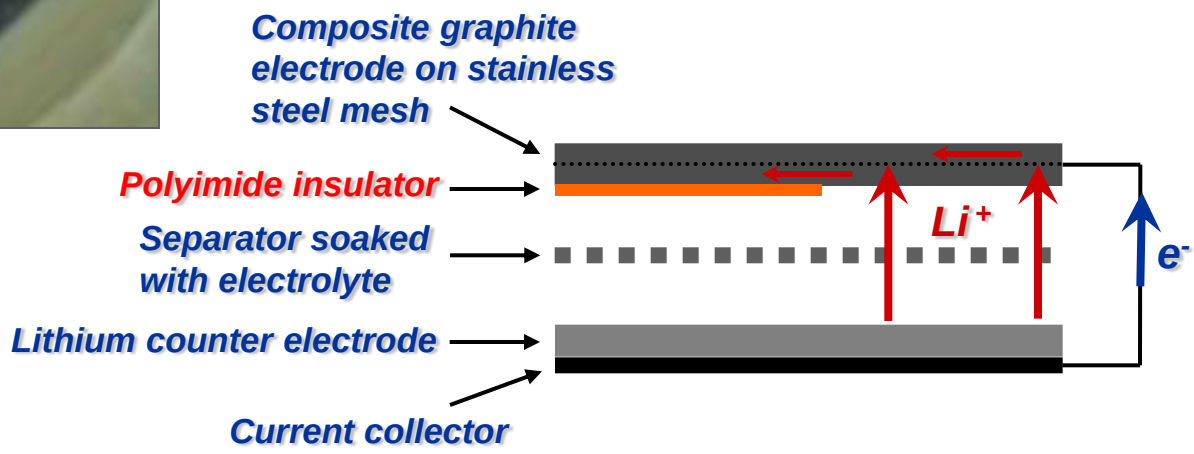
Additional separators:



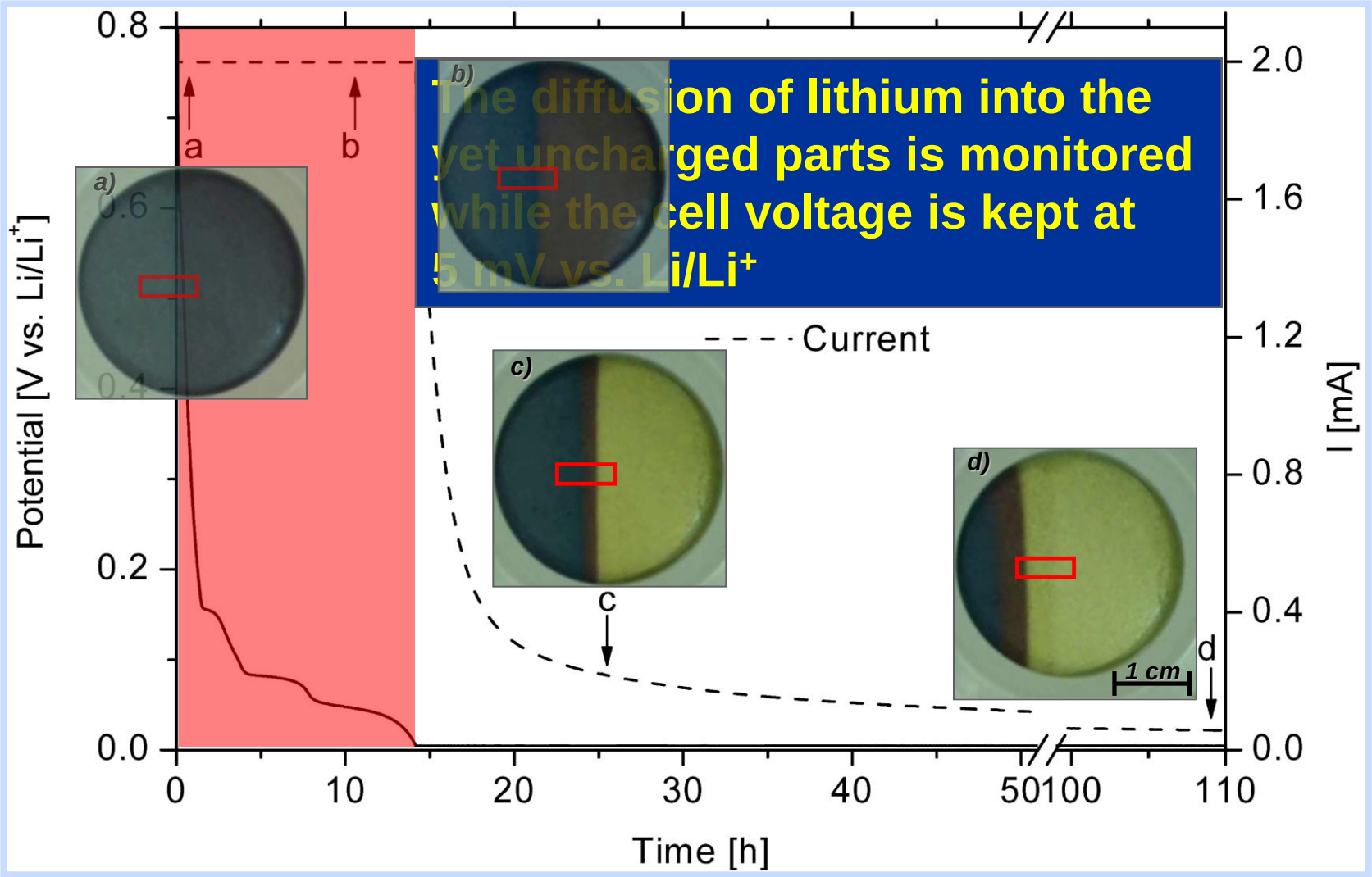


Graphite Electrode with an Artificial Heterogeneity

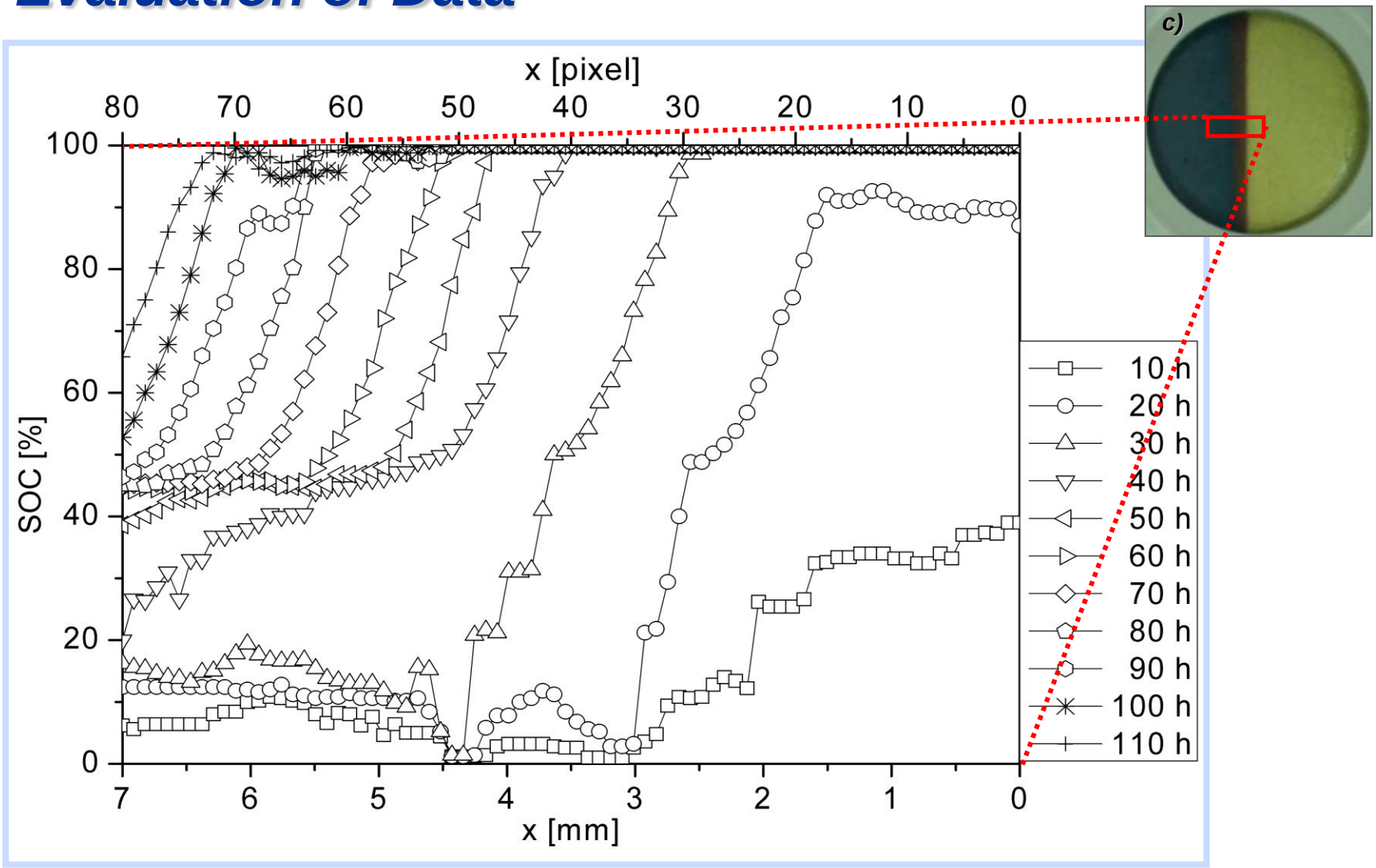




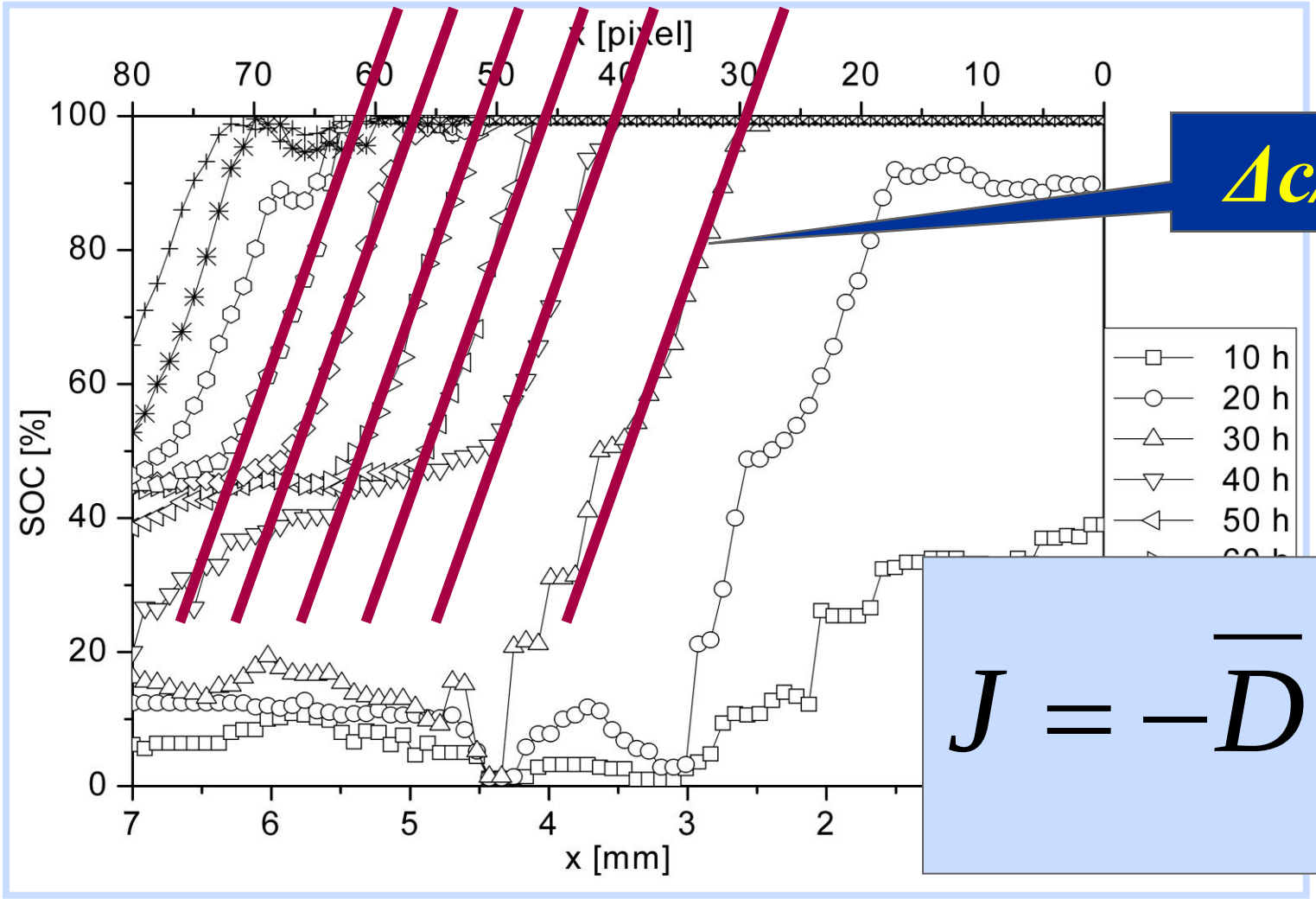
Graphite Electrode with an Artificial Heterogeneity



Evaluation of Data



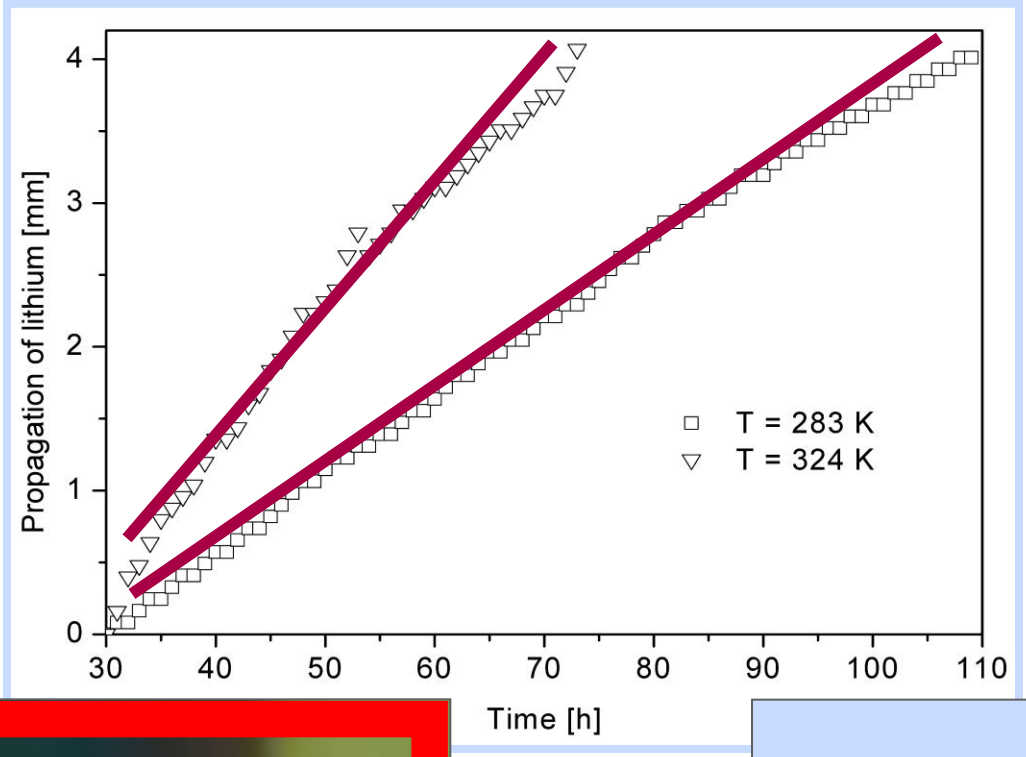
Evaluation of Data: Fick's Law

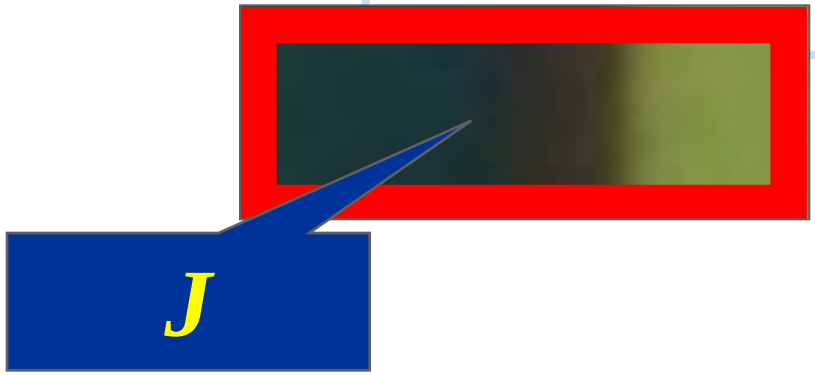


$\Delta c/\Delta x$

$$J = -\overline{D}\frac{dc}{dx}$$

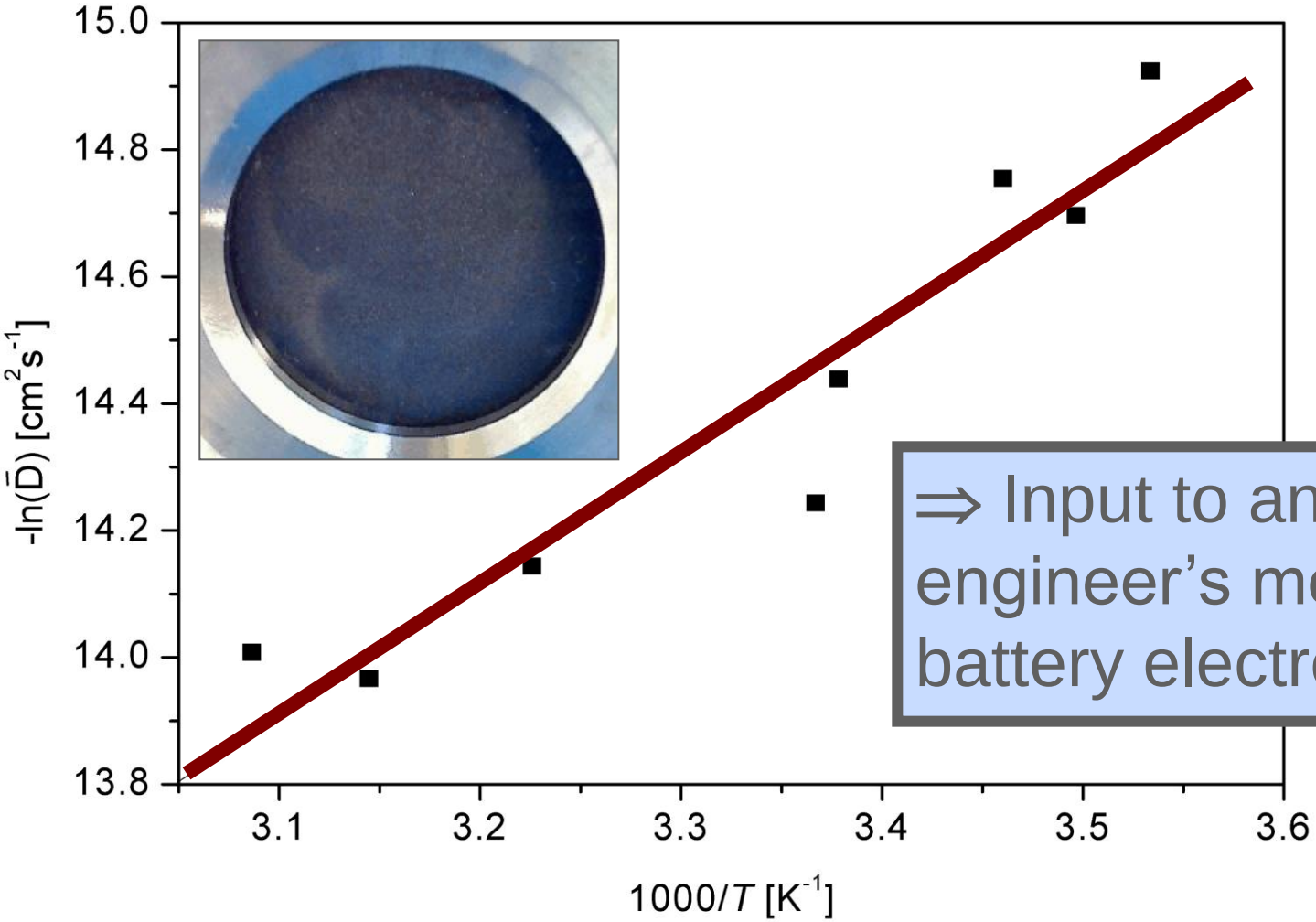
Evaluation of Data: Fick's Law





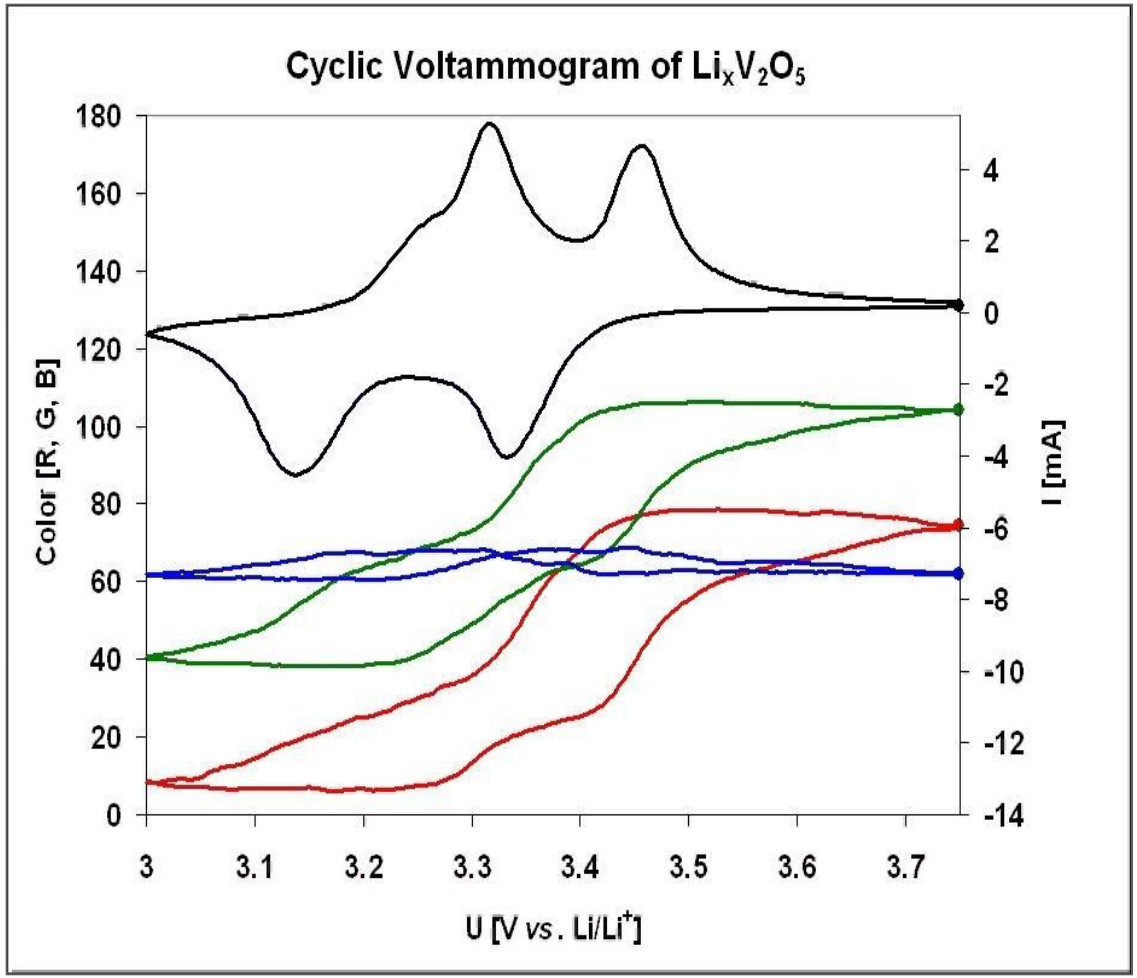
$$J = -\overline{D}\frac{dc}{dx}$$

The Result



⇒ Input to an engineer's model of battery electrodes

Finally… Electrochemical Lithiation of V_2O_5



Working Electrode: V_2O_5 (87%), VGCF (3%), PVDF (10%)

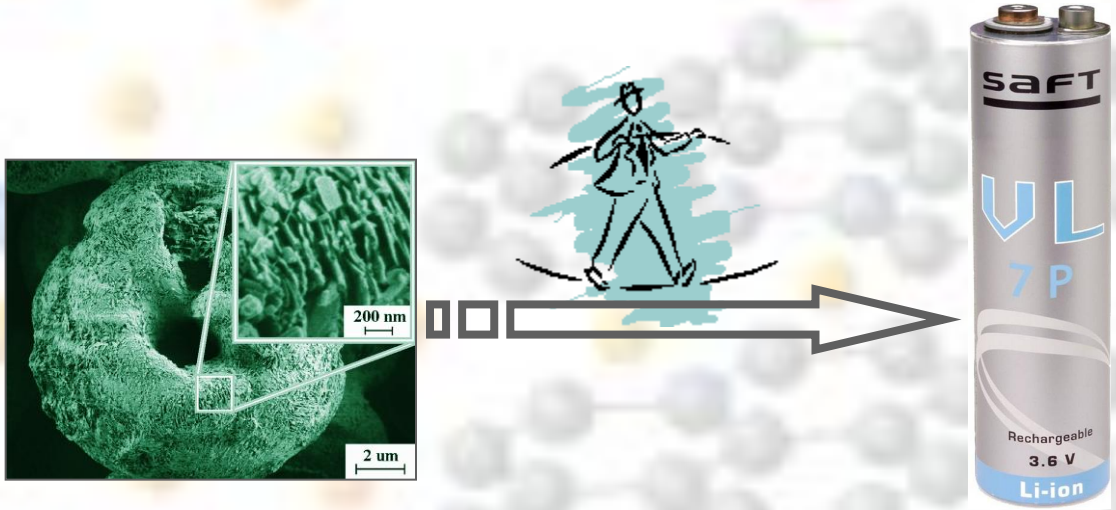
Counter Electrode: Lithium

Electrolyte: EC/DMC 1/1; 1M $LiPF_6$

Scan Rate 20 µV s^{-1}

Conclusion

- *Simple and cheap electrochemical methods provide important results needed on the long way from materials to industrial products.*



Acknowledgments

- *Swiss National Science Foundation*
- *Swiss State Secretariat for Education and Research*
- *European Community (CAMELiA, LiBERAL, and ALiSTORE projects)*
- *TIMCAL Ltd., Bodio, Switzerland*

- *my current group*

Contributors:
Hilmi Buqa
Flavio Campana
Anna Evans
Dietrich Goers
Laurence Hardwick
Hermann Kaiser
Fabio La Mantia
Pascal Maire
Desmond Ng
Werner Scheifele
Cathie Vix-Guterl

- ***and numerous former group members, other colleagues, and friends!***