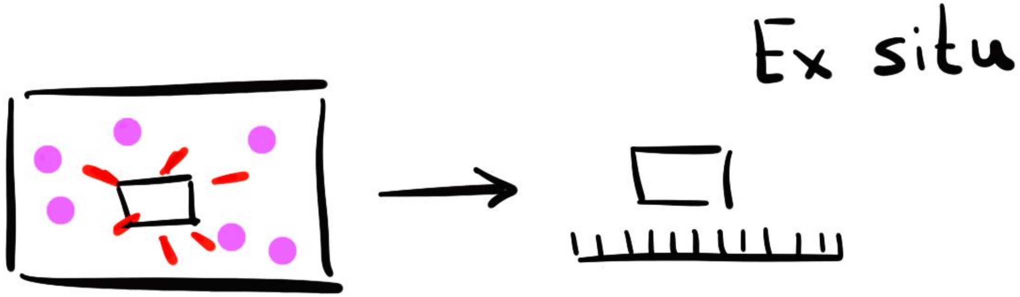
H2020-MSCA ITN
Grant n. 956099

NanED

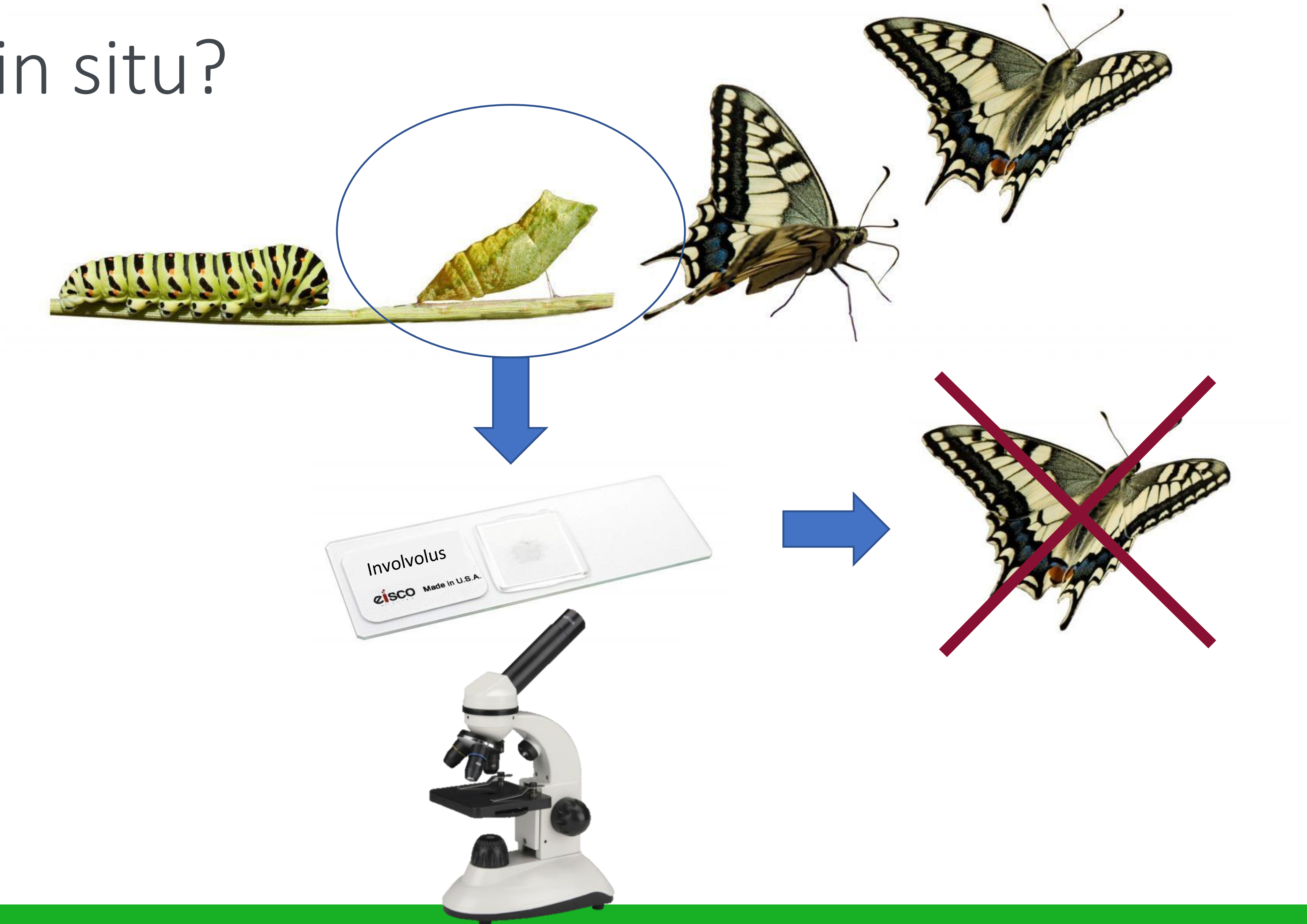
# In situ 3D electron diffraction for following reactions in gas and electrochemical environment

Joke Hadermann - University of Antwerp

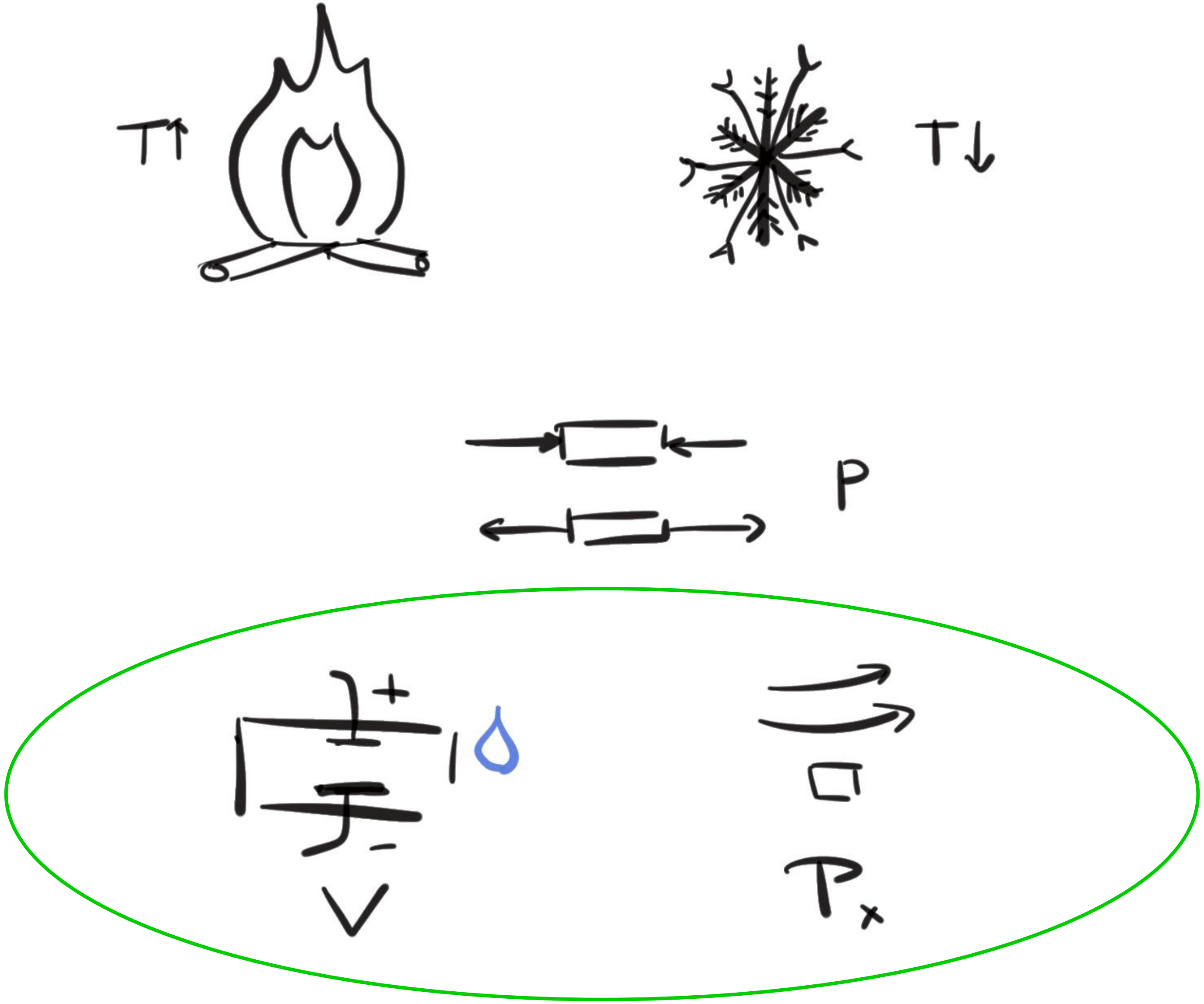
# Ex situ - in situ - operando



# Why in situ?

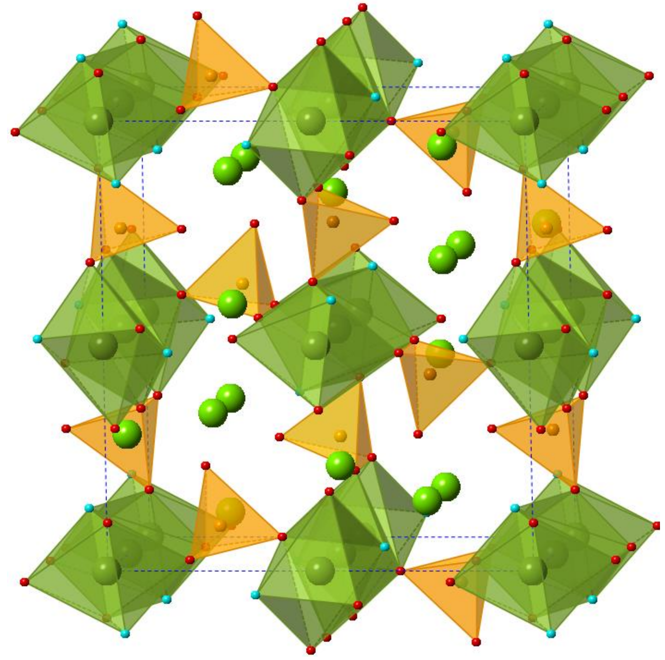


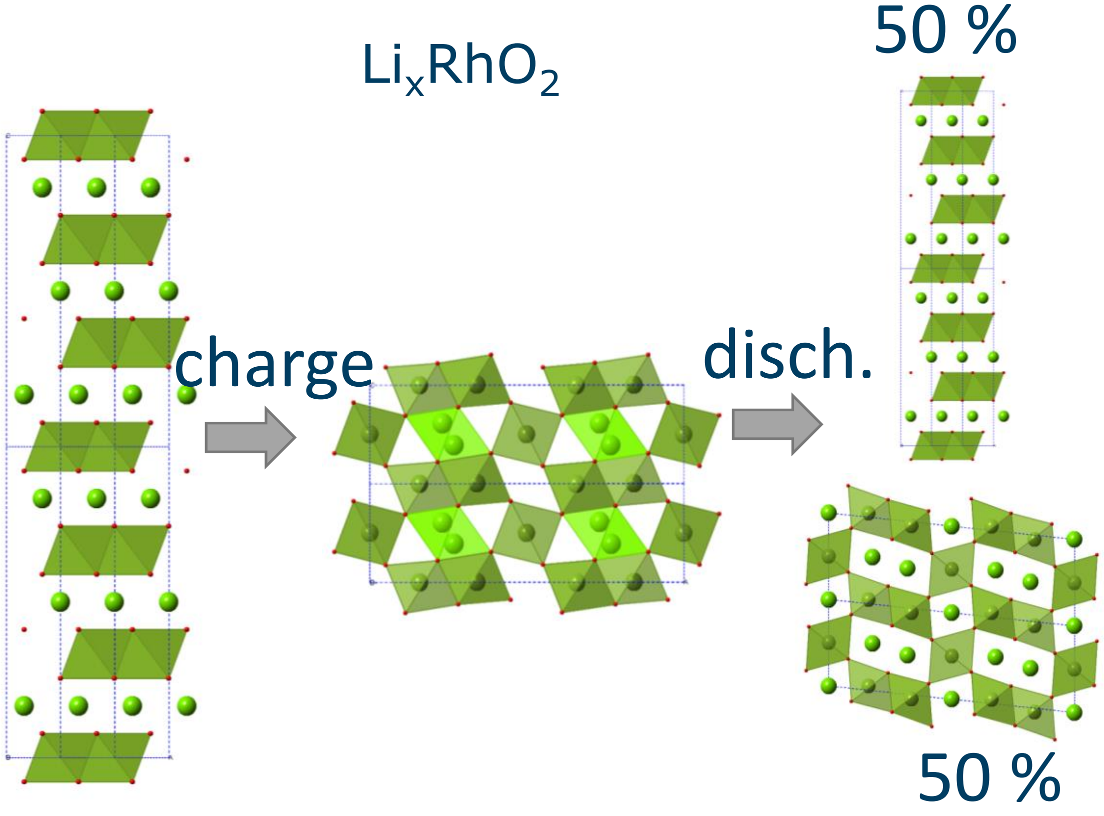
# Ex situ - in situ - operando



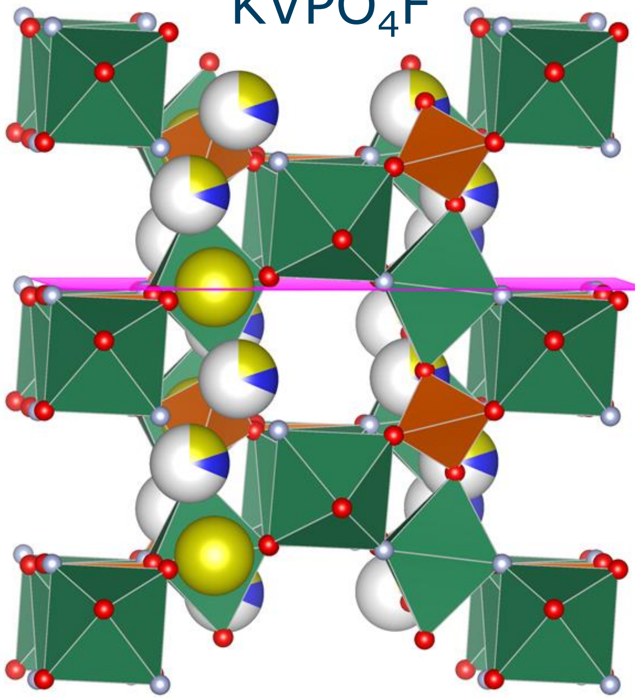
# Ex situ results asking for in situ...

$Li_2FePO_4F$






$KVPO_4F$



O.M. Karakulina et al. *Chem. Mater.* 2016, *28* (21), 7578–7581.

D. Mikhailova et al. *Inorg. Chem.* 2016, *55* (14), 7079–7089.

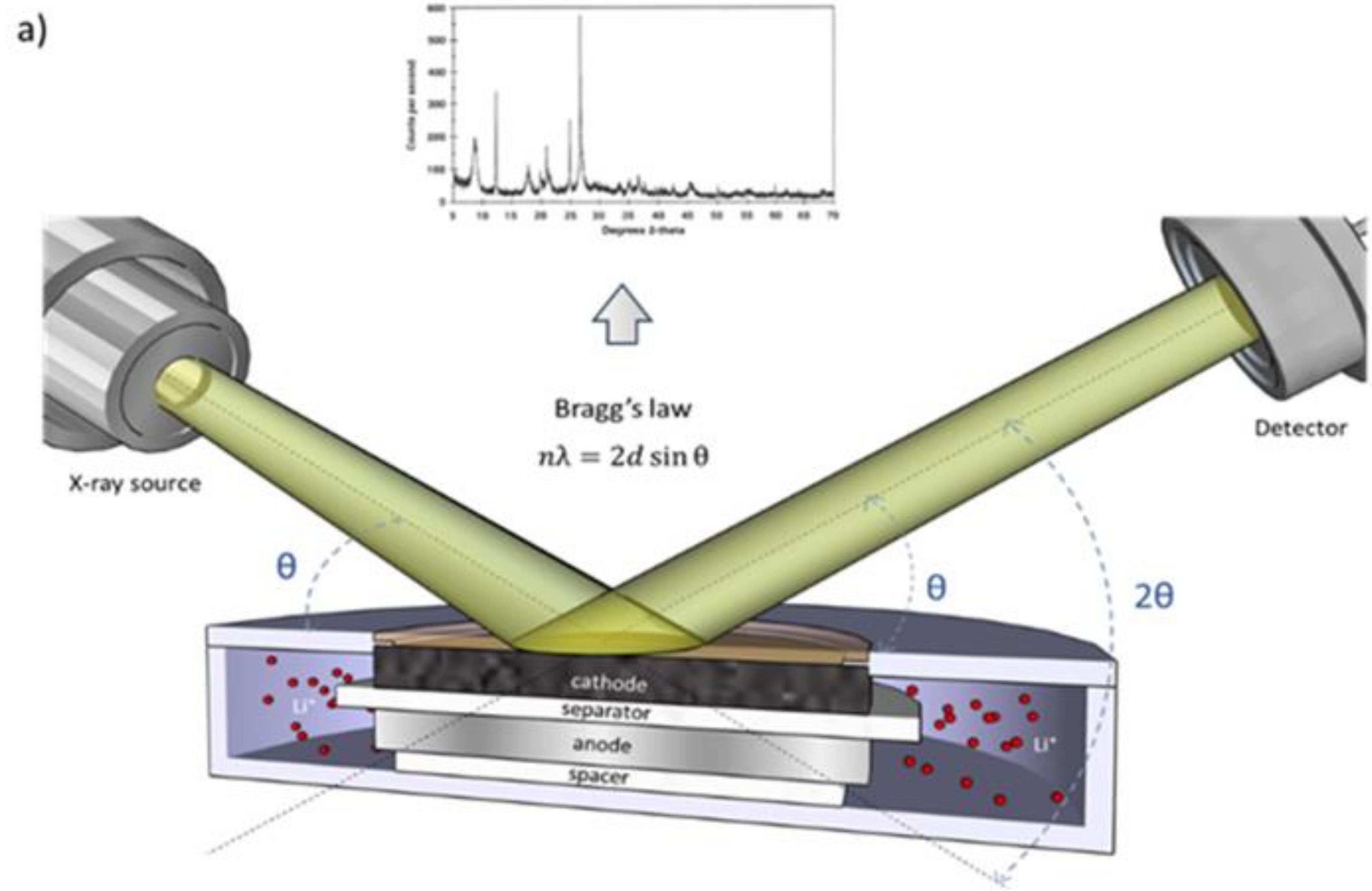
S.S. Fedotov et al. Chemistry of Materials, 28, 411–415 (2016).

# Possible effects before measurements

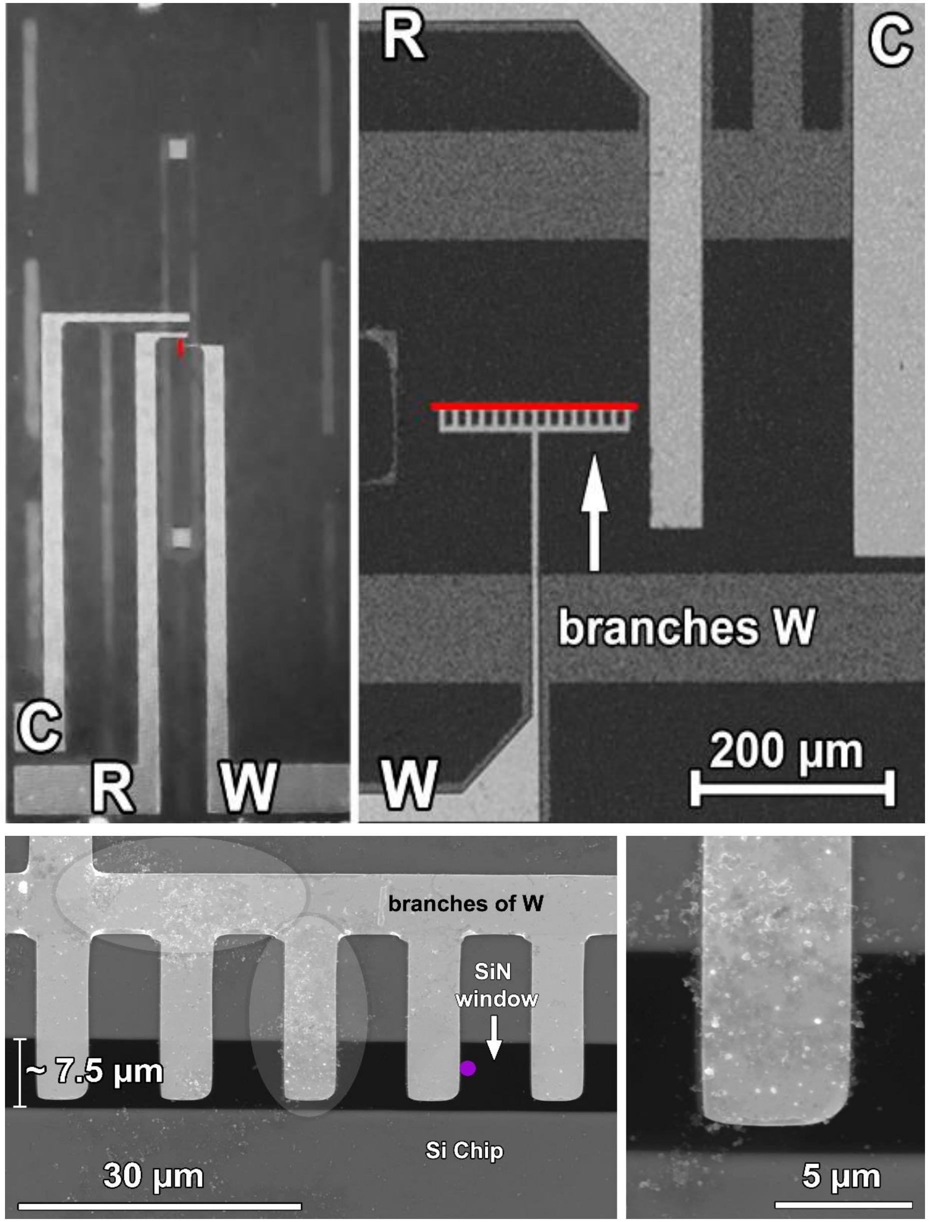
**In situ**

- ~~relaxation time~~
- ~~strong reducing effect of $e^-$ beam in vacuum~~
- ~~small number of cycling stages~~
- ~~each measurement on a different crystal~~

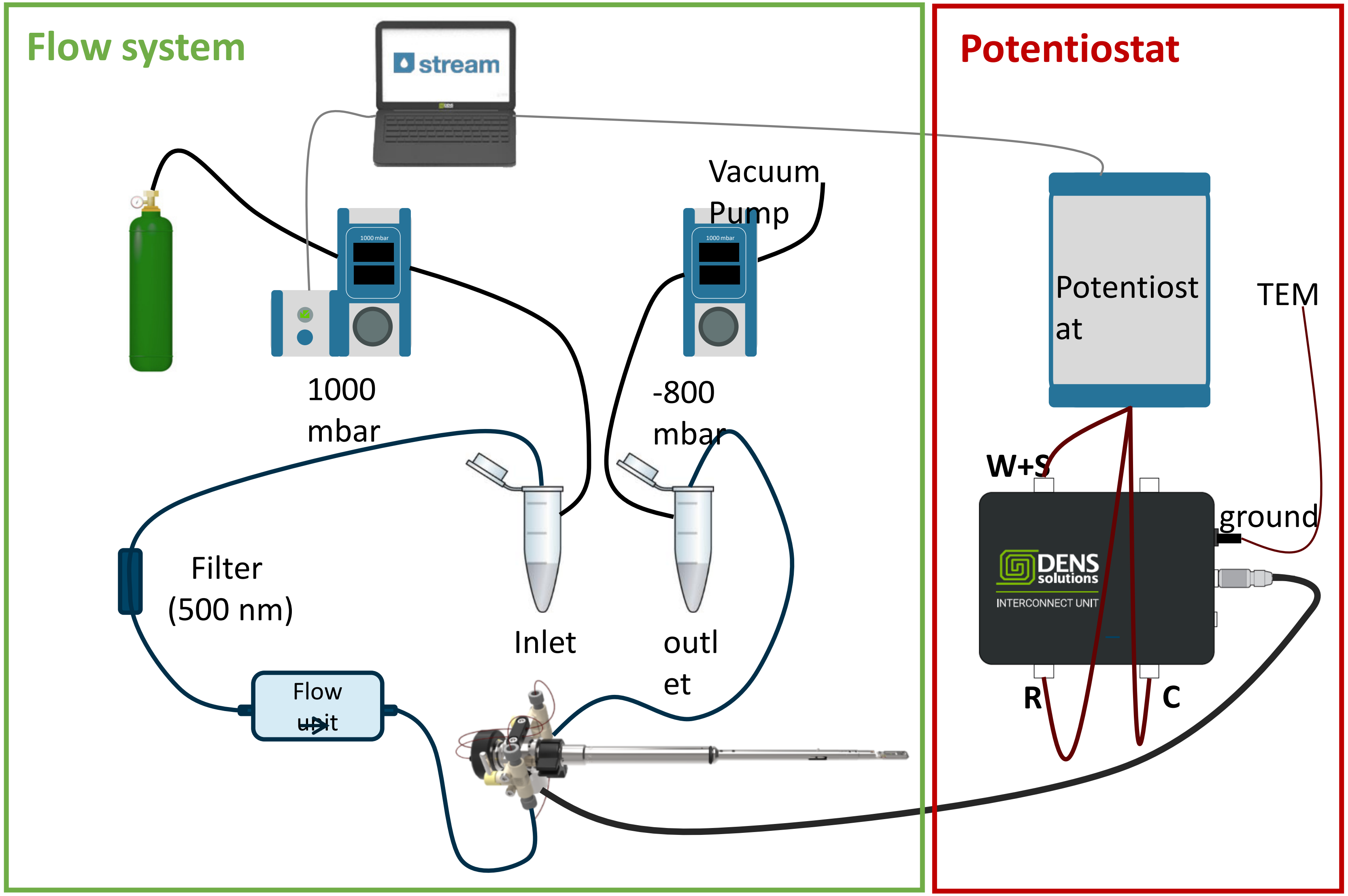
# In situ XRD- in situ ND



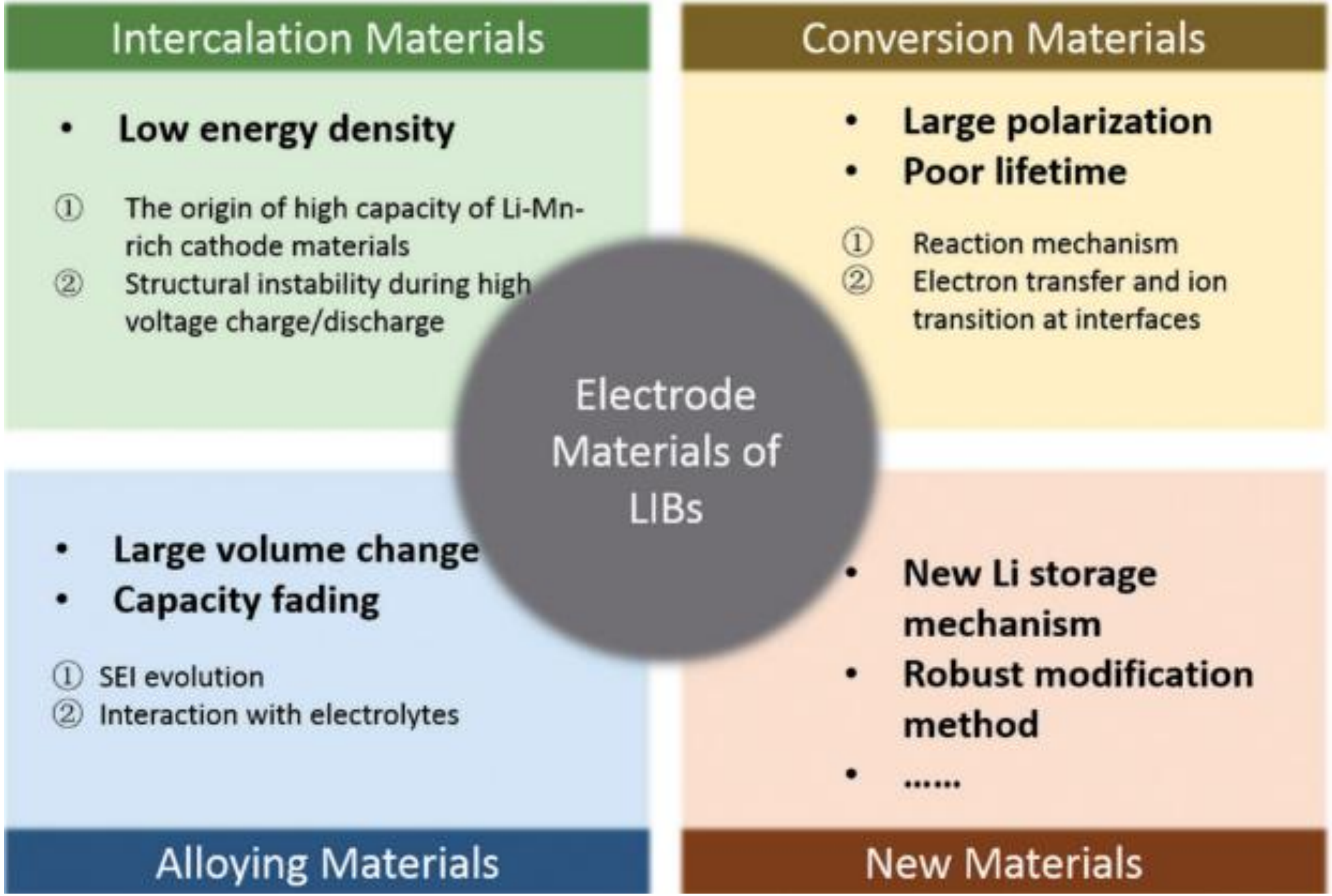
# In situ TEM


C
R
W
R
C
branches W
W
200 µm
branches of W
SiN
window
~ 7.5 µm
Si Chip
30 µm
5 µm

# Setup in situ electrochemistry in TEM

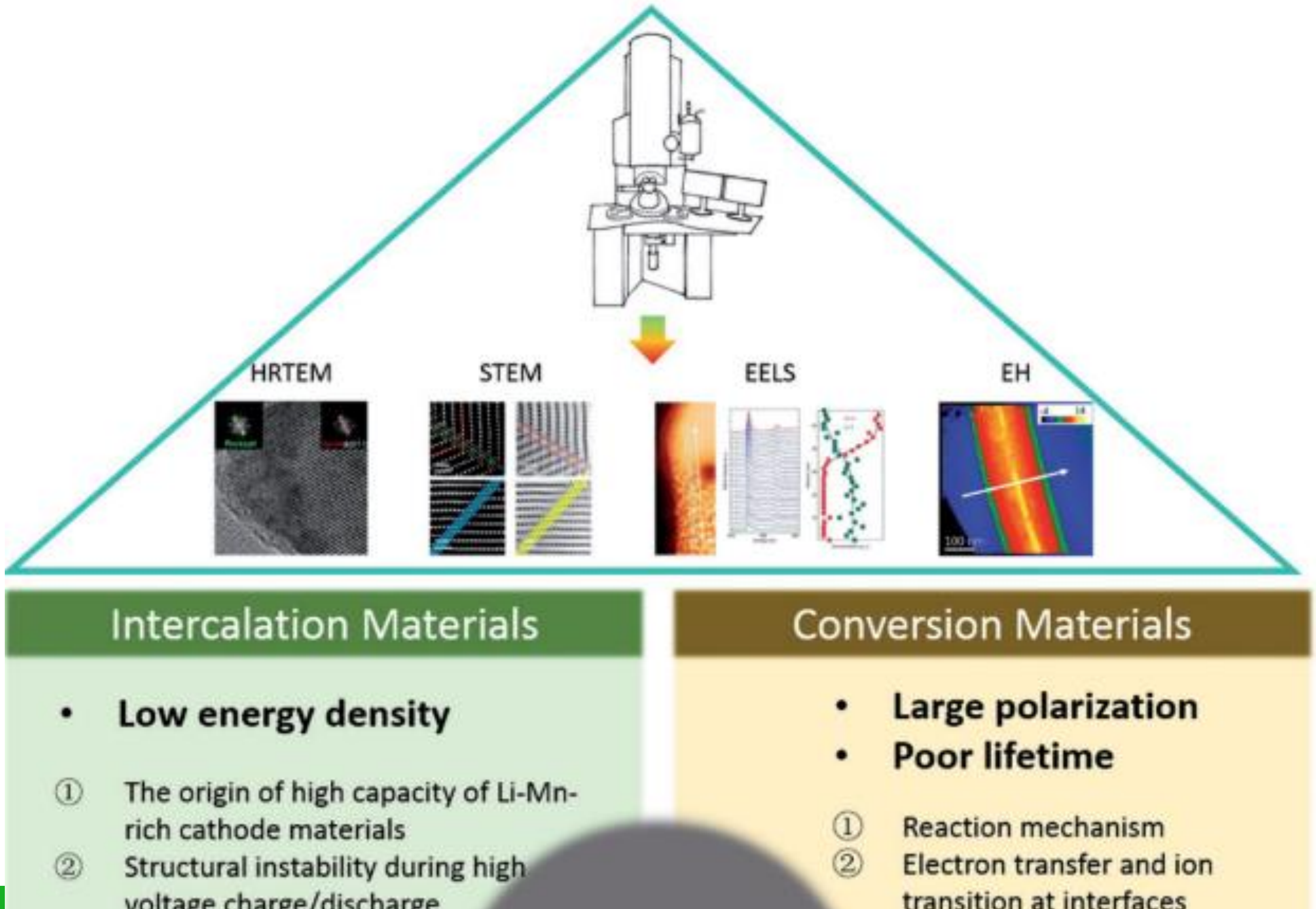


# In situ TEM in literature

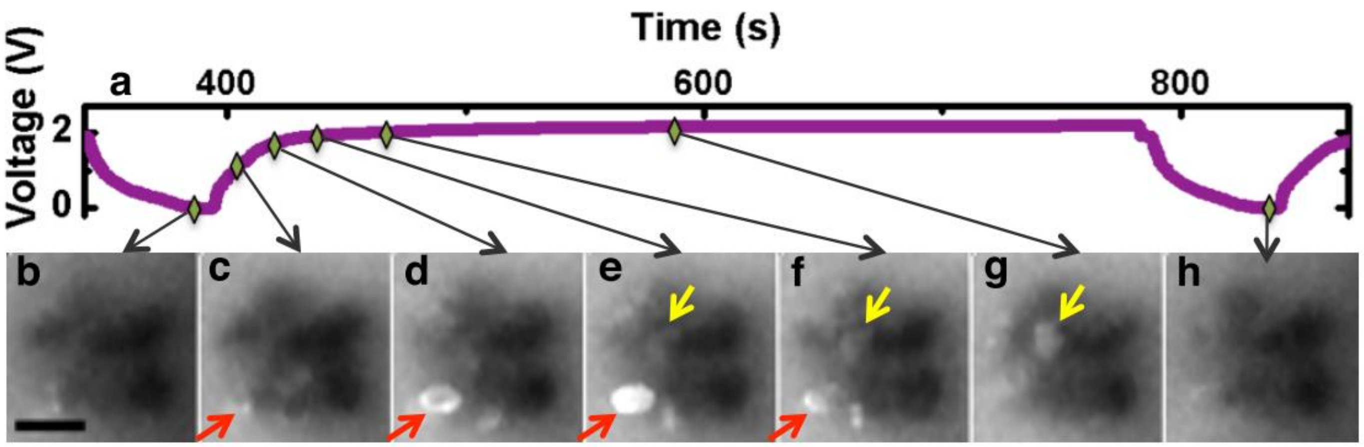



Shang, T., Wen, Y., Xiao, D., Gu, L., Hu, Y. S. & Li, H. (2017). *Adv. Energy Mater.* **1700709**, 1–16.

# In situ TEM in literature



# In situ TEM imaging in an EC cell

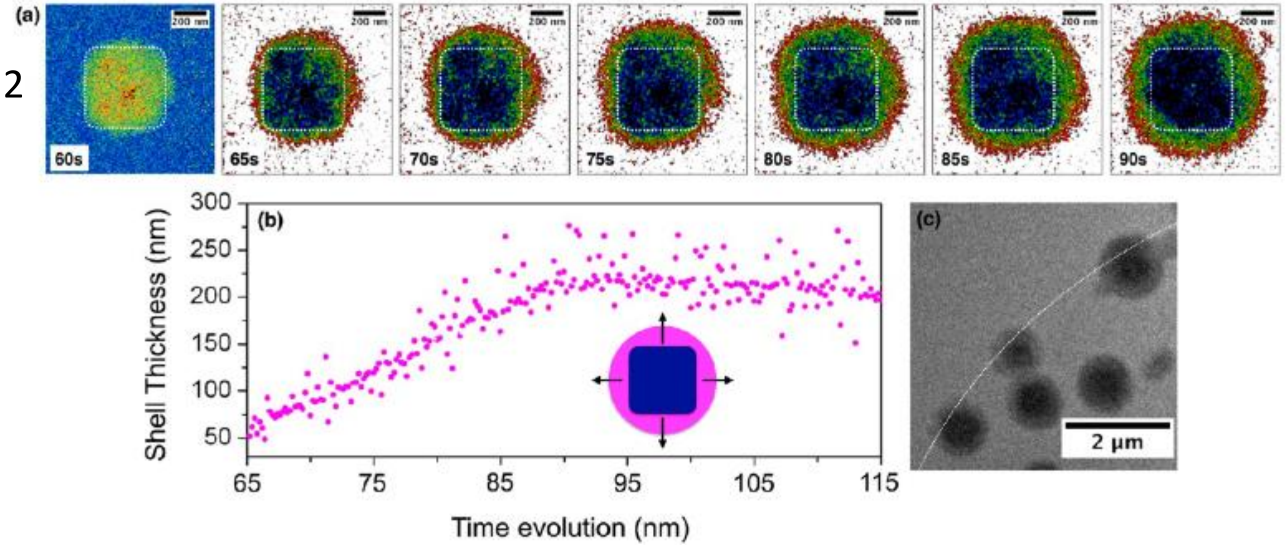



The evolution of a cluster of LiFePO4 /FePO4 during one charge/discharge cycle

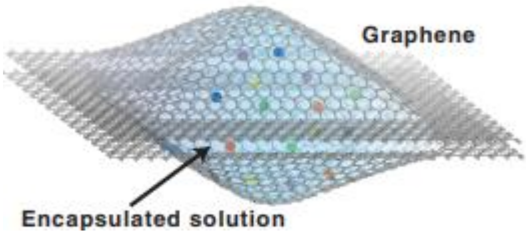
M. Holtz et al. (2014) *Nano Lett.* **14**

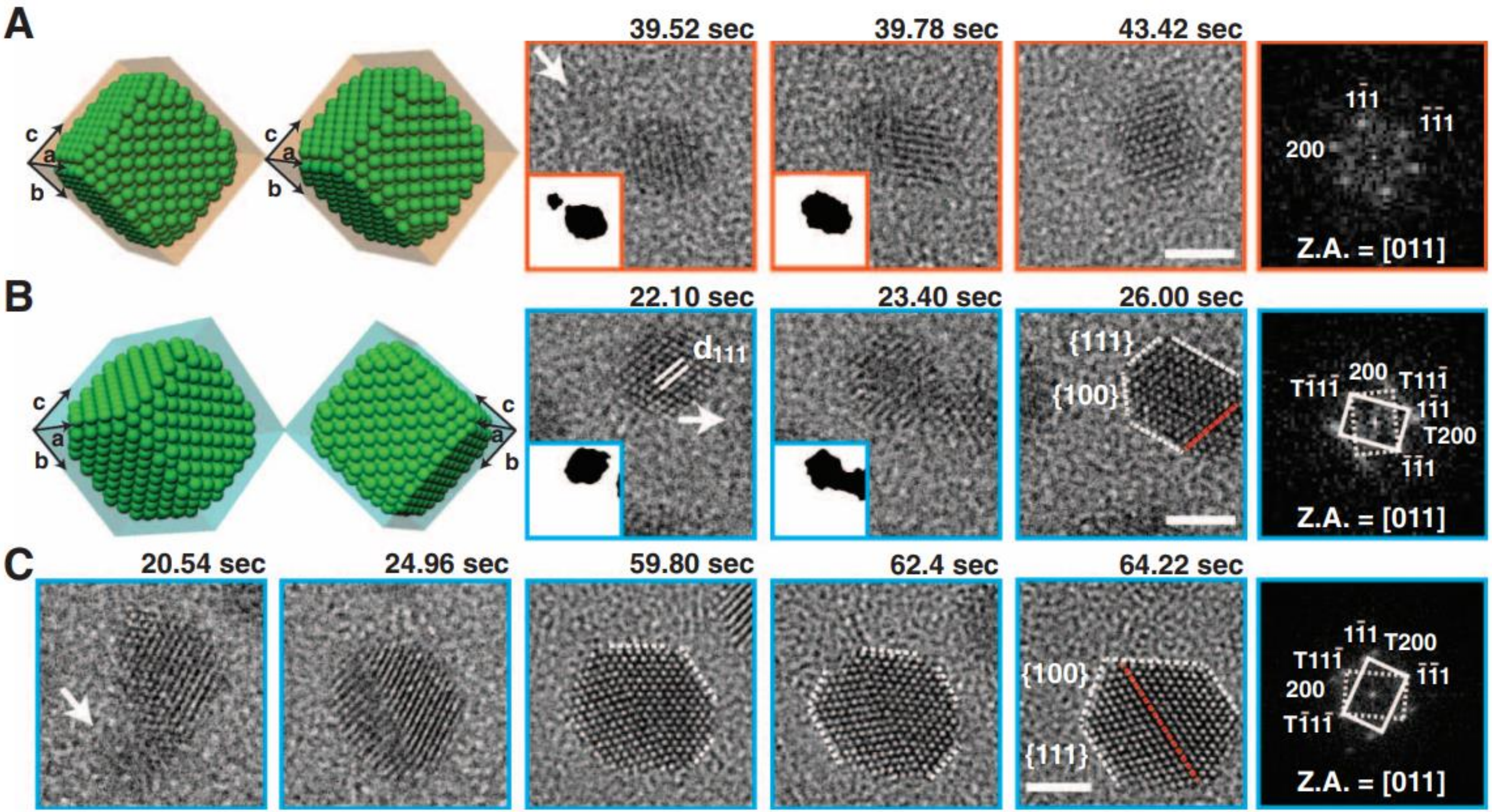
The growth of nanocubes in Na-$O_2$ batteries.

L. Lutz et al. (2018) *Nano Lett.* **18**



# In situ TEM imaging in a graphene cell




No electrochemistry possible!

Min Yuk et al. Science, 336 (2012)61

# State-of-the art of electron diffraction in electrochemical TEM cells

NANO LETTERS

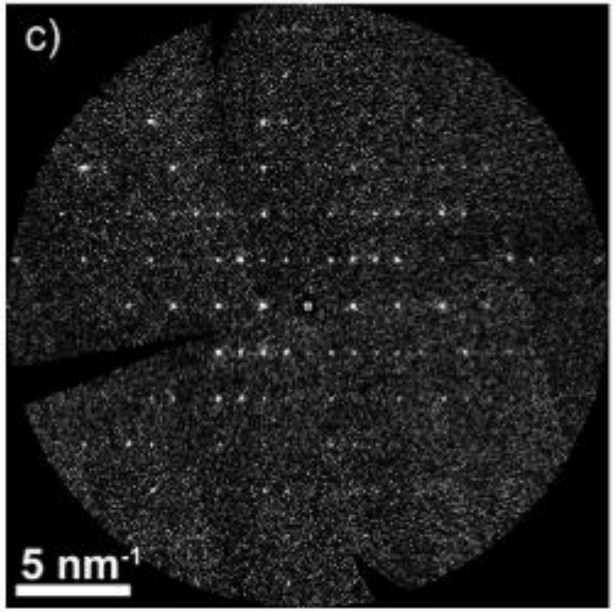
Letter

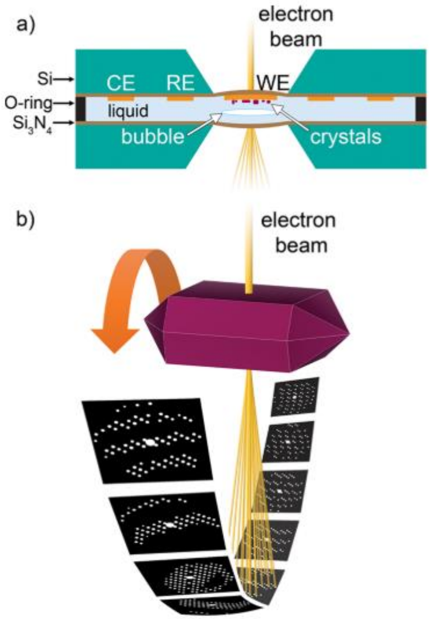
Cite This: *Nano Lett.* 2018, 18, 6286–6291

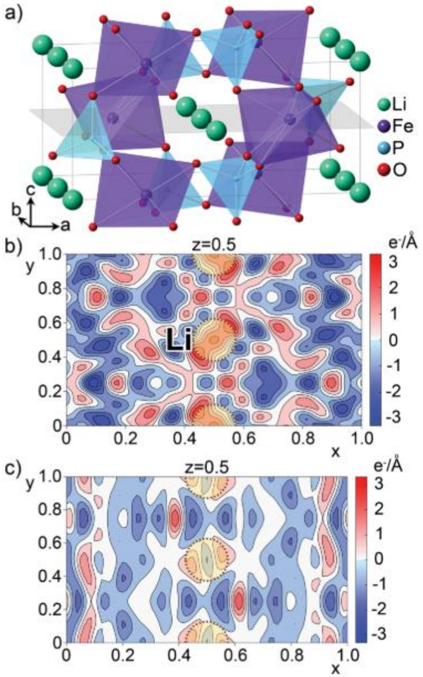
pubs.acs.org/NanoLett

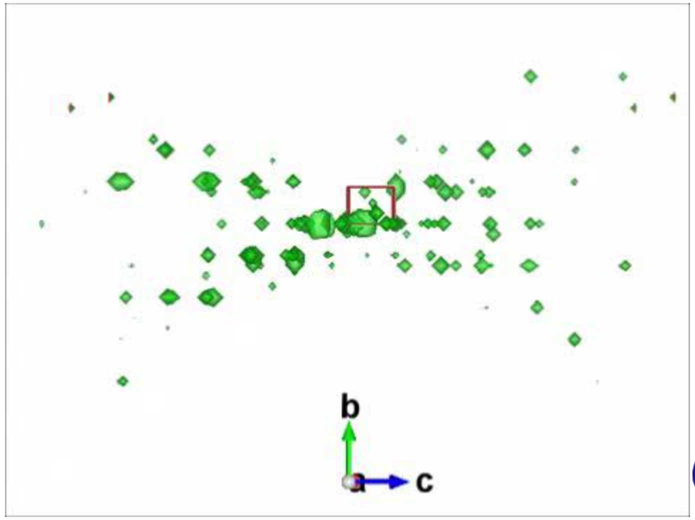
**In Situ Electron Diffraction Tomography Using a Liquid-Electrochemical Transmission Electron Microscopy Cell for Crystal Structure Determination of Cathode Materials for Li-Ion batteries**

Olesia M. Karakulina,[†] Arnaud Demortière,[*,‡,§] Walid Dachraoui,[§] Artem M. Abakumov,[||] and Joke Hadermann[*,†]



# Lessons learned

Need to avoid intense beam → Need thinner cell

→ DensSolutions Stream 200 nm instead of 500 nm

**Confinement issues?**

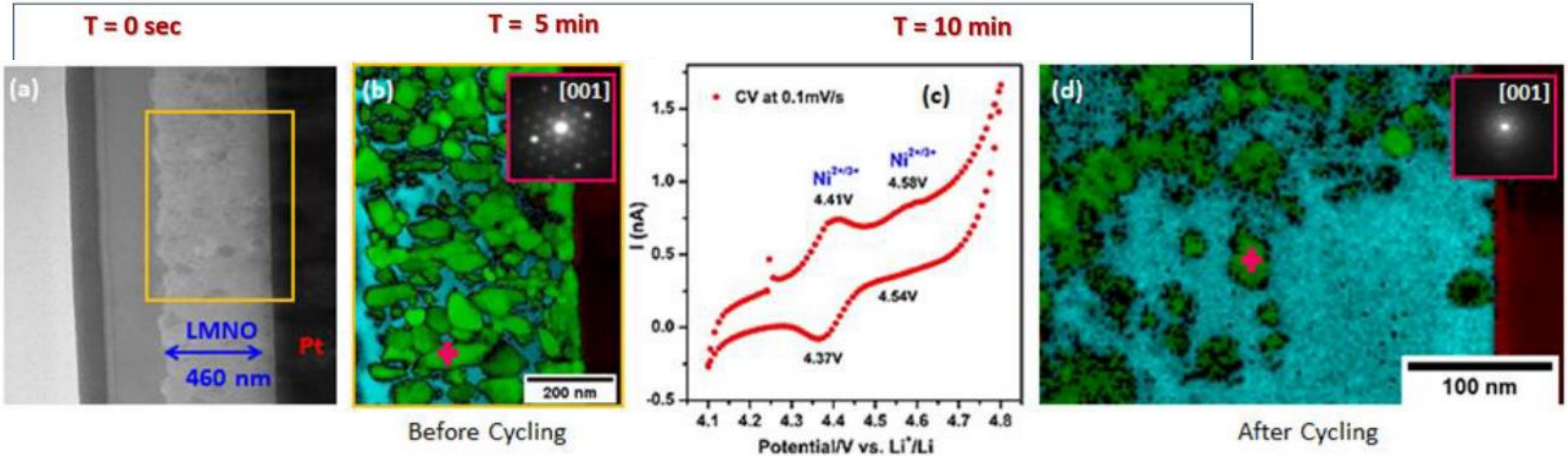
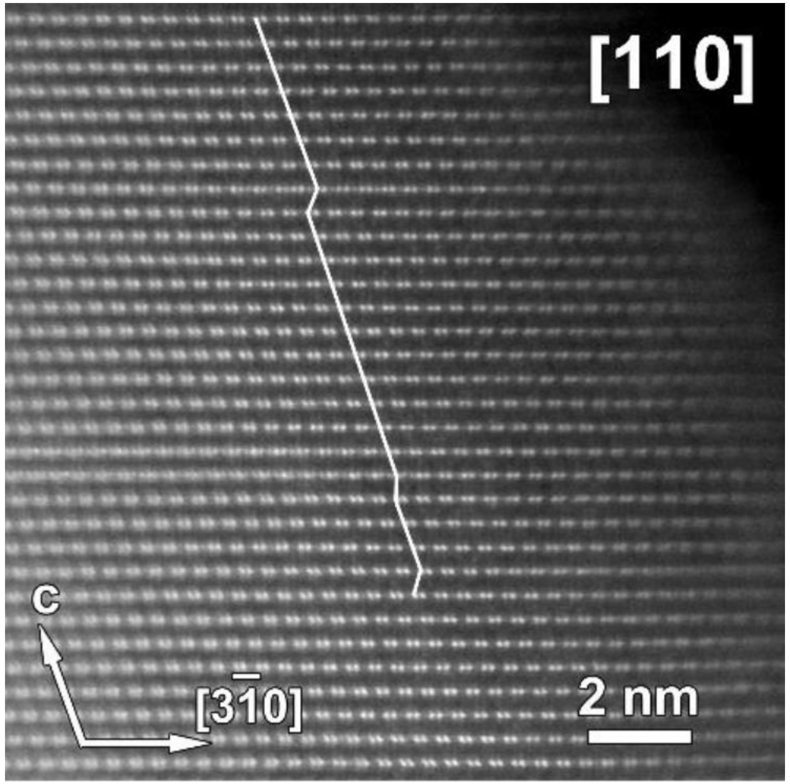


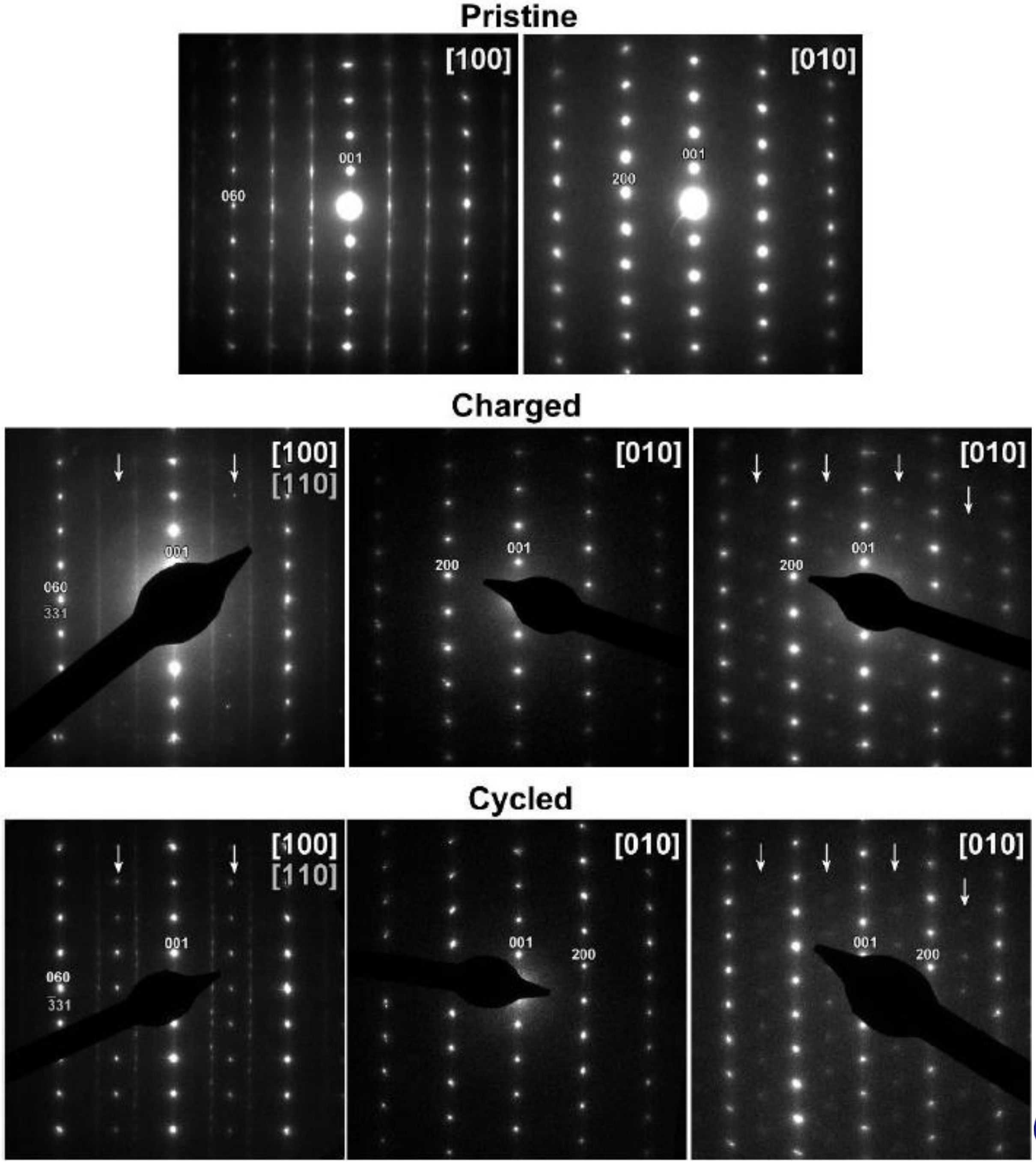

**Figure 2.** (a) Bright-field transmission electron microscopy of the LMNO FIB lamella sample before cycling; (b) phase map before cycling where dark red represents the platinum, in green the LMNO phase, and in blue the amorphous phase; insert bright red shows the electron diffraction pattern of spinel LMNO in [001] orientation; (c) Cyclic voltammogram measured in a holder with a voltage sweep rate of 0.1 mV/s in the voltage window of 4.1 V- 4.8 V vs. lithium using 1M lithium perchlorate in EC:DMC electrolyte; (d) phase map after cycling where dark red represents the platinum, in green the LMNO phase and in blue the amorphous phase; insert bright red shows the electron diffraction pattern of spinel LMNO in [001] orientation.

**Figure 2.** ASTAR orientation map of 220 nm x 220 nm (scan time 20 sec) by Medipix III detector, 20 fps, 12 bit, and step size: 11 nm. White arrows on gold nanoparticles correspond to individual ED patterns, Spacer 200 nm, 30 nm $Si_3N_4$ thickness.

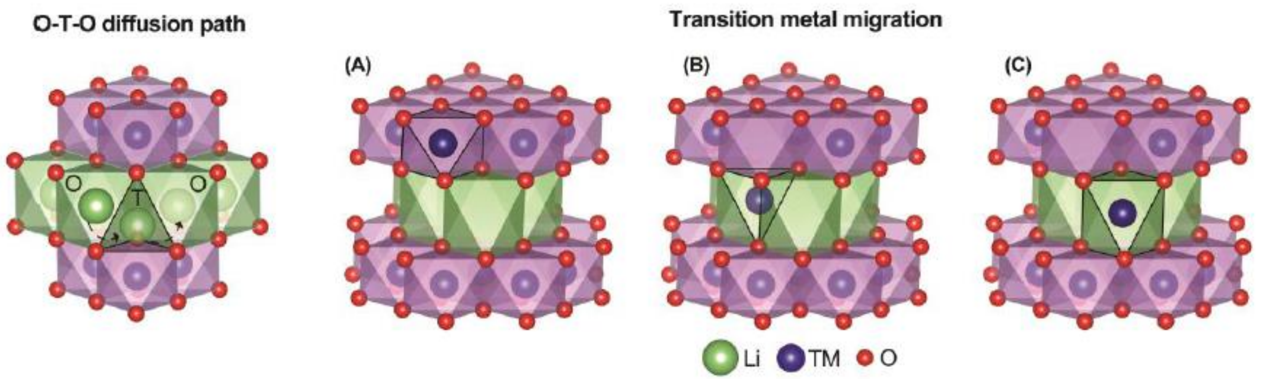
Online meeting

# LR-NMC

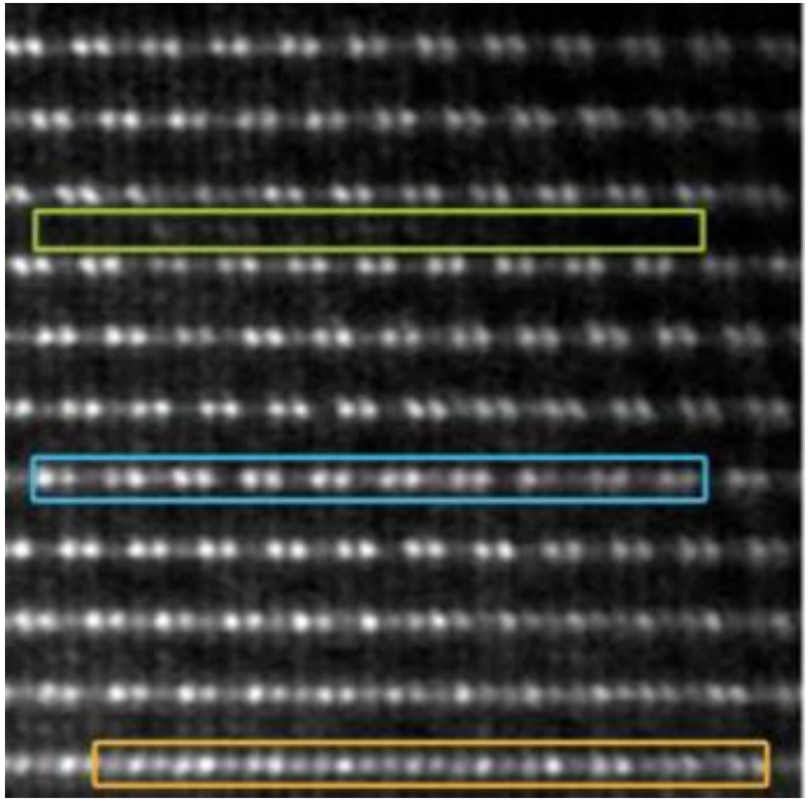

[110]
c
[3̄10]
2 nm


Pristine
[100]
[010]
001
060
200
Charged
[100]
[110]
[010]
331
Cycled

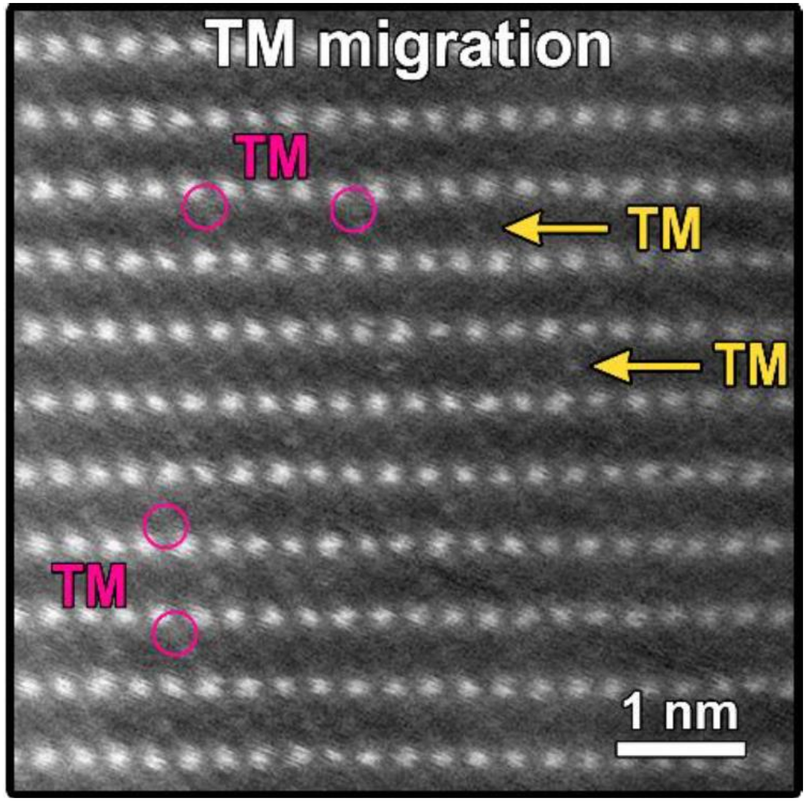
# LR-NMC




Kleiner et al. Chem. Mater. **30**, 3656 (2018)



Pristine




Charged

# ESR 3

- optimize the setup for in situ 3D ED in an electrochemical cell
- tackle contamination issues
- tackle decomposition of the electrolyte
- validate the electrochemistry in the thinner cell
- demonstrate on commercially available lithium battery elecrode compounds
- analysis: multiphased, diffuse, defects, twinning

# In situ solid - gas reactions

denssolutions.com

# Example of a successful experiment: $SrFeO_{2.5+x}$

Brownmillerite Pbcm

↓

Orthorhombic Cmmm

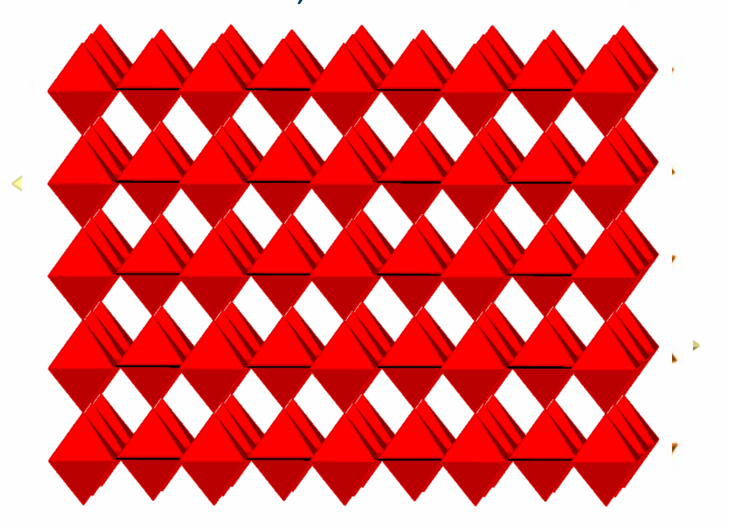
↓

Tetragonal I4/mmm

↓

Perovskite-type $Pm\bar{3}m$

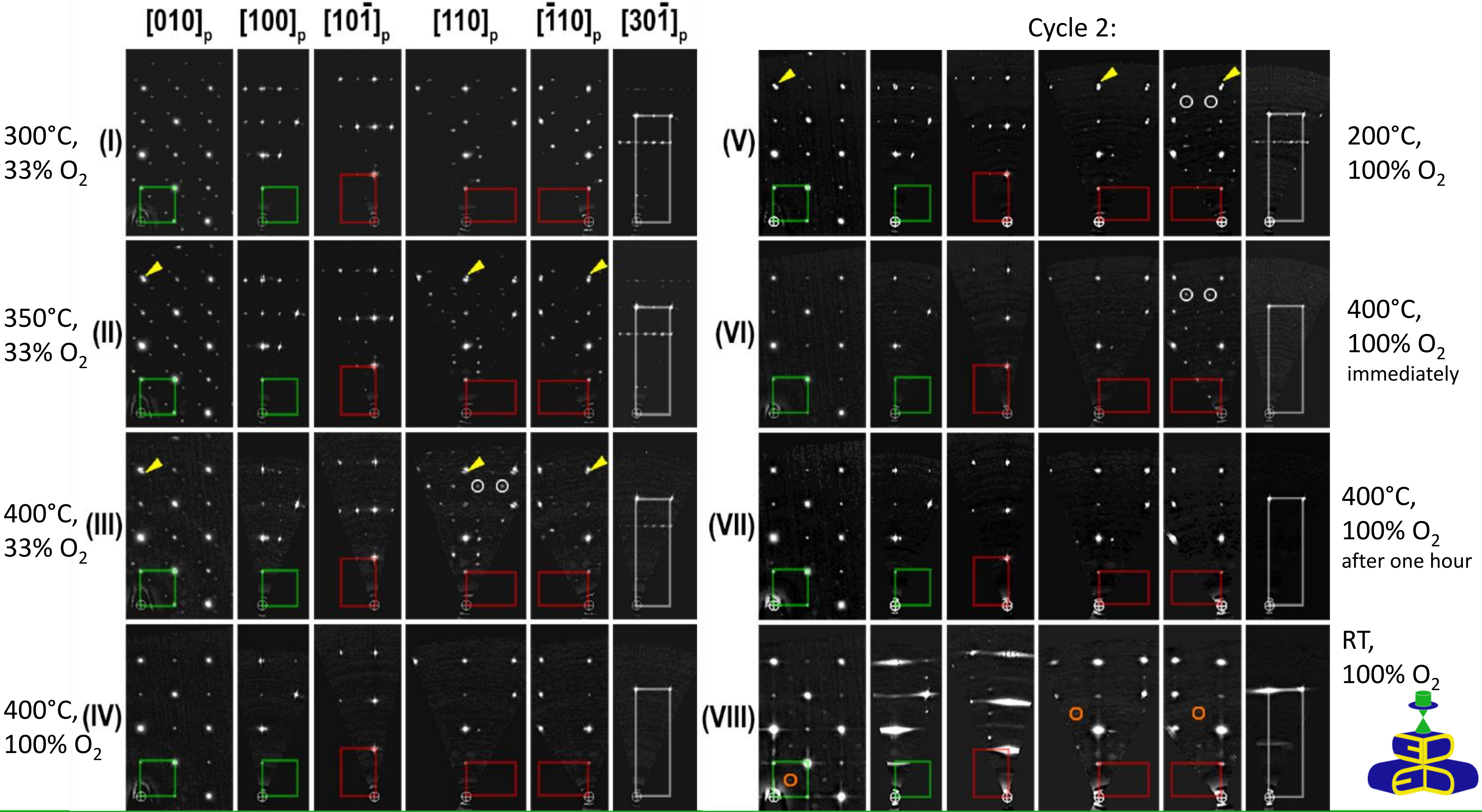
Oxidizing gas($O_2$, $H_2O$ damp, air,...)



Crystal structures from

Hodges et al. JSSC 2000, 151, 190–209.

Maity et al. J. Phys. D. Appl. Phys. 2015, 48, 504004.



$[010]_p$
$[100]_p$
$[10\bar{1}]_p$
$[110]_p$
$[\bar{1}10]_p$
$[30\bar{1}]_p$
Cycle 2:
300°C, $33\%\ O_2$
(I)
350°C, $33\%\ O_2$
(II)
400°C, $33\%\ O_2$
(III)
400°C, $100\%\ O_2$
(IV)
(V)
200°C, $100\%\ O_2$
(VI)
400°C, $100\%\ O_2$ immediately
(VII)
400°C, $100\%\ O_2$ after one hour
(VIII)
RT, $100\%\ O_2$

# ESR 3

- optimize the reaction uniformity among crystals for in situ 3D ED in a gas environment
- increase reproducibility related to temperature and gas pressures
- make merging possible
- optimize the practical experiment to allow detection of the best acquisition moment to have pure phase patterns

@ (1) reference sample, (2) $SrCoO_{2.5}$ thin films

# Expected results

(1) A working methodology for future acquisition of in situ crystallographic data.

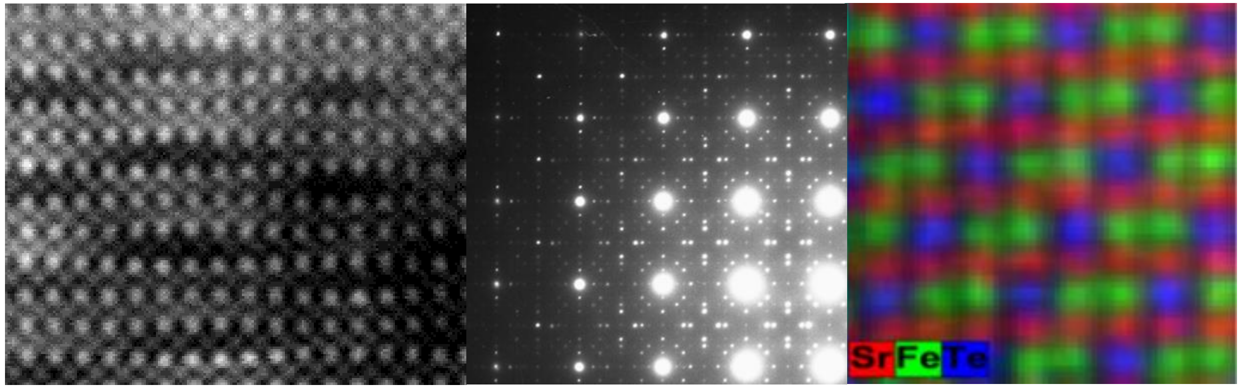
(2) Characterized structure evolution of relevant complex inorganic compounds during in situ reactions

# University of Antwerp


## EMAT
## Electron Microscopy for Materials Research


# Electron Microscopy lab

- Atomic resolution imaging and spectroscopy (HRTEM, HAADF/ABF-STEM, iDPC, EELS, EDX)
- Electron tomography and electron diffraction tomography (3DED)
- 6 TEMs, including 3 state-of-the-art aberration corrected Titan instruments
- specialized holders for various in situ experiments
- dedicated sample preparation facilities


# Electron Crystallography group

- Focus on crystal structure determination
- 3DED
- Diffuse scattering, defects, SRO
- In situ structure evolution in gas-solid reactions
- Atomic resolution imaging and spectroscopy