Time-resolved atomic-scale chemical imaging for study of dynamic phase transformation in Li-rich layered cathode materials

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Outlines

- **Development of a fast atomic-scale chemical imaging technique based on STEM-EDS that can be used for:**

  1. **Time-resolved EDS mapping**
  2. **Study of the electron beam sensitive materials**
  3. **Study of dynamic phase transformations**
  4. **In-situ TEM experiments**

  - ✓ **Fast – on order of few seconds or on a time-scale comparable to HAADF imaging**
  - ✓ **Current atomic-scale EDS mapping typically requires few hundred seconds**

- **Study of dynamic phase transformation in Lithium-rich, manganese-rich (LMR) layered oxides - $Li[Li_xMn_yTM_{1-x-y}]O_2$ (TM = transition metal)**

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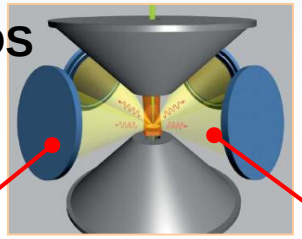
AC-STEM capabilities for atomic-scale chemical characterization

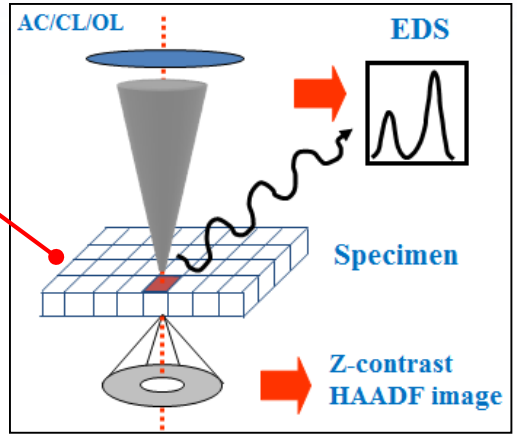
FEI Titan™ G2
80-200 STEM

Super-EDS



- 4 SDD geometry around the sample

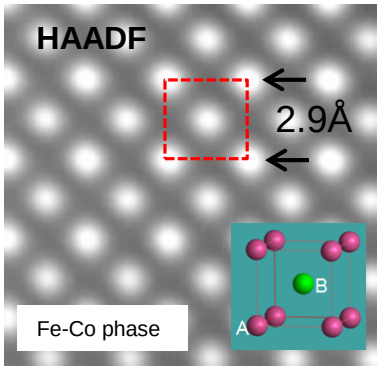
Aberration correction and four in-lens EDS X-ray detector technologies.



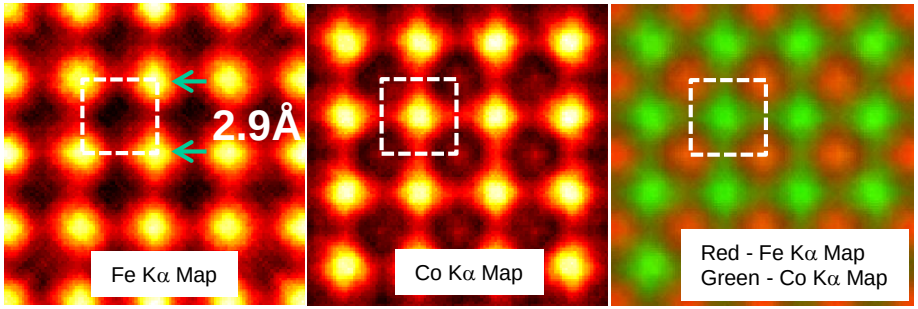
Small, intense electron probe + Super efficient EDS detector

➔ **Sub-atomic-scale imaging (0.8Å at 200 kV)**

& <u>Atomic-scale chemical mapping by EDS</u>



Collection time of ~5 s



Collection time of > few 100 s

P. Lu *et al*, *Sci. Rep*. 2014, 4, 3945-3950.

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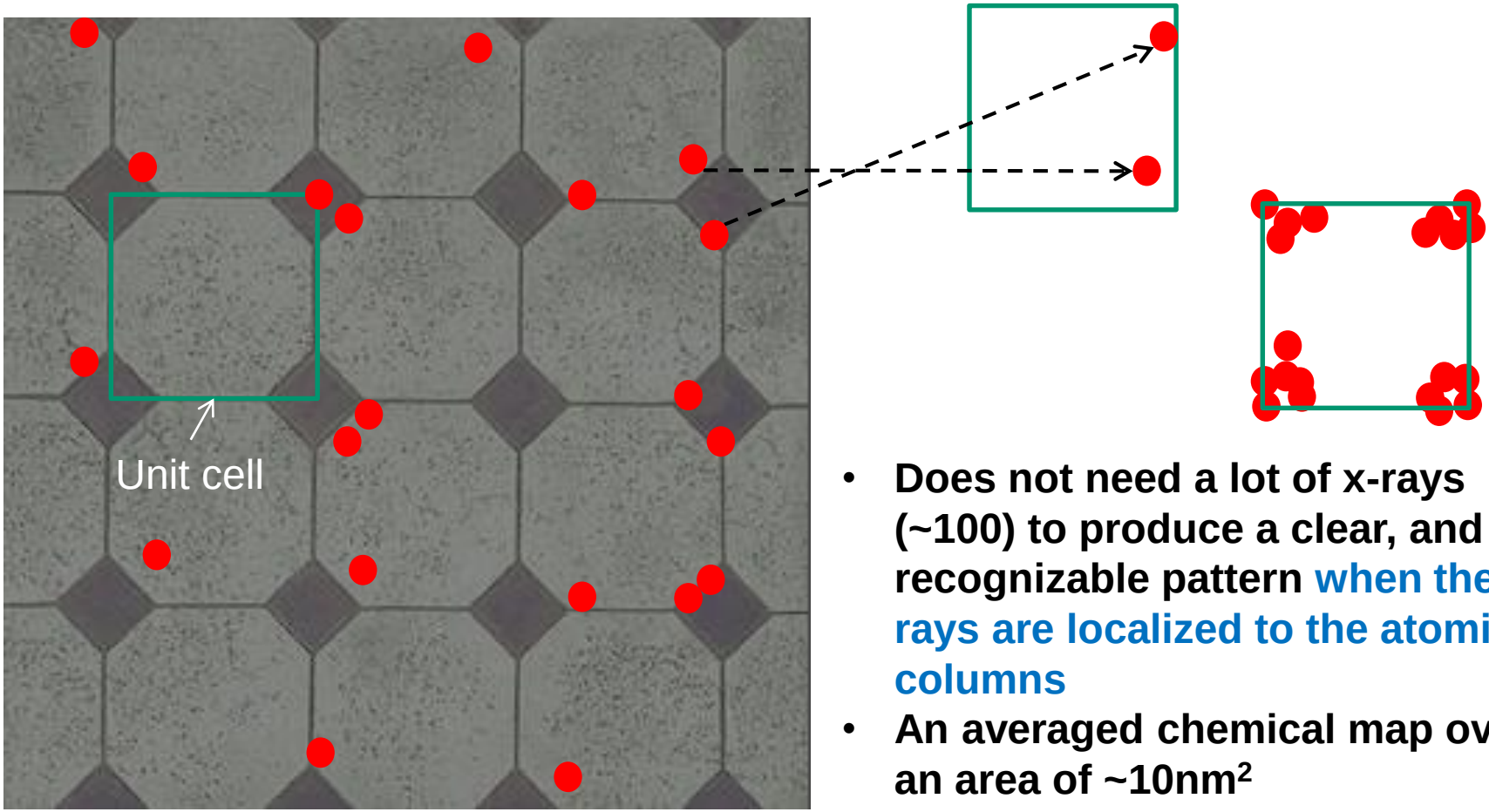
Fast Atomic-scale Chemical Imaging of Crystalline Materials

- ● - Single x-ray count
  20 – x-ray counts
  ~ 100 ms collection time

- **Lattice-vector translation method (lattice averaging)**



- **Does not need a lot of x-rays (~100) to produce a clear, and recognizable pattern when the x-rays are localized to the atomic columns**
- **An averaged chemical map over an area of ~10nm^2**
- **Collection time can be less than 1 s**

P. Lu *et al*. Nano Lett. 2016, 16, 2728

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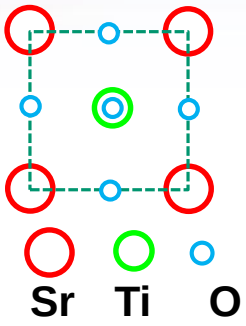
Experimental data from $SrTiO_3$ crystal

A collection time of ~2 s

a



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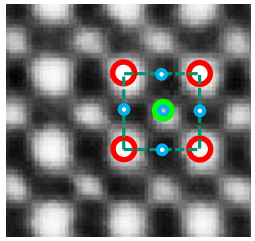
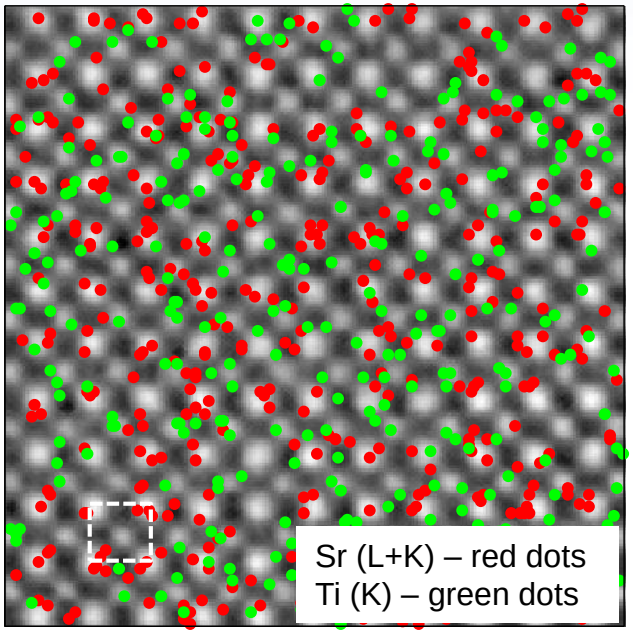
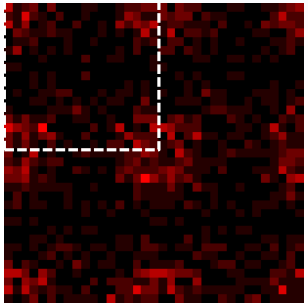
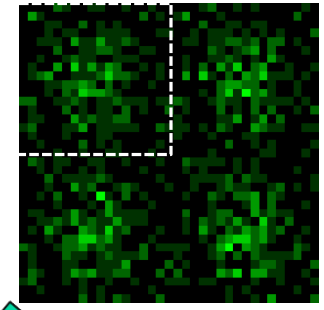


c



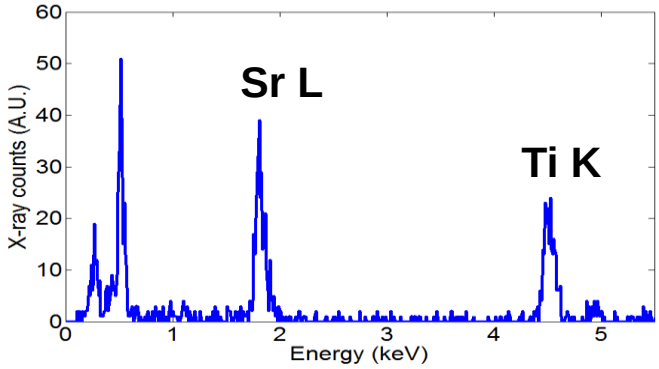


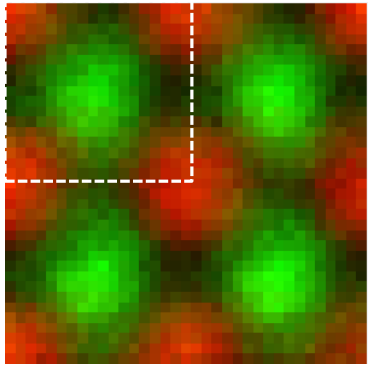
Sr (L+K)



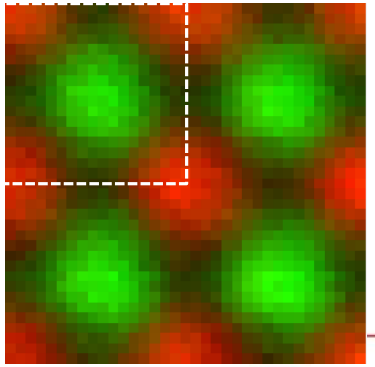
Ti (K)

The summed spectrum





2 s



4 s

The EDS peaks of high P/B ratio enable the technique.

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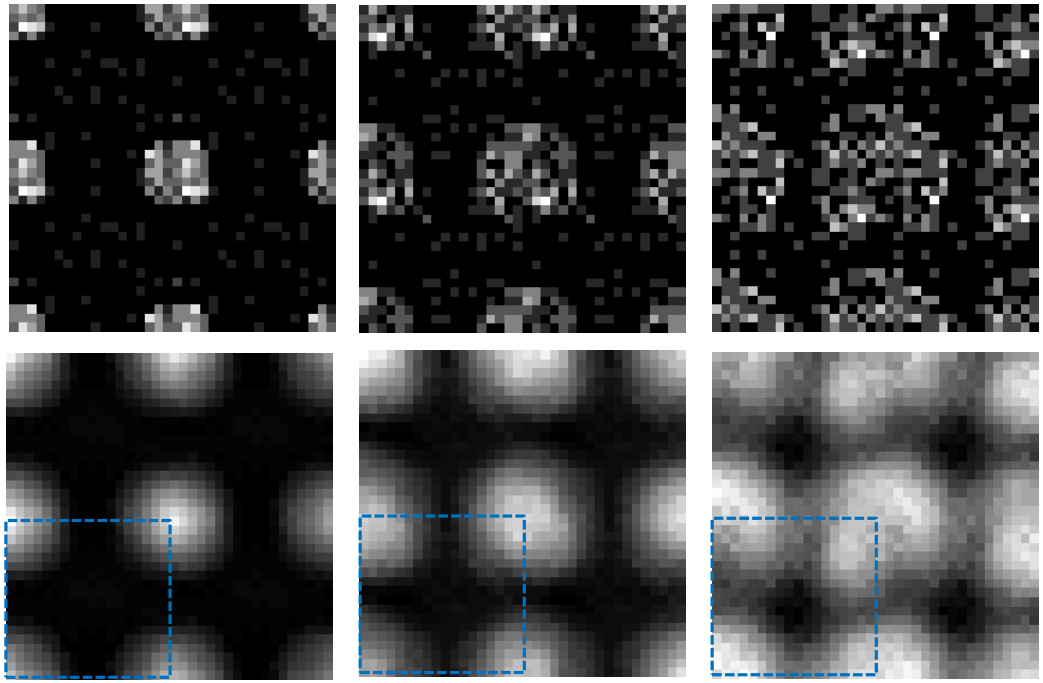
X-rays localization to the atomic column is the key!

Signal (*S*):
- localized to atomic column with a certain radius *R*;

Noise (*N*):
- randomly distributed

***S*=200; *N*=42**

***R*= 0.09nm or 4 pixels** | ***R*= 0.13nm or 6 pixels** | ***R*= 0.18nm or 8 pixels**



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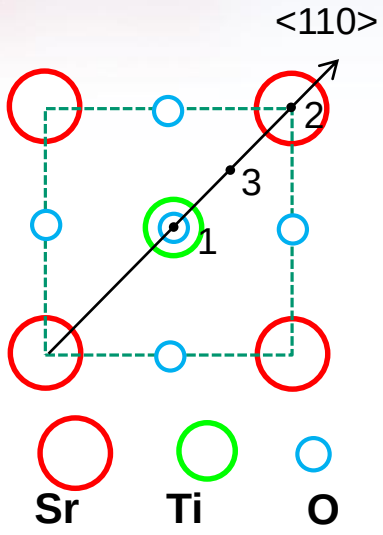
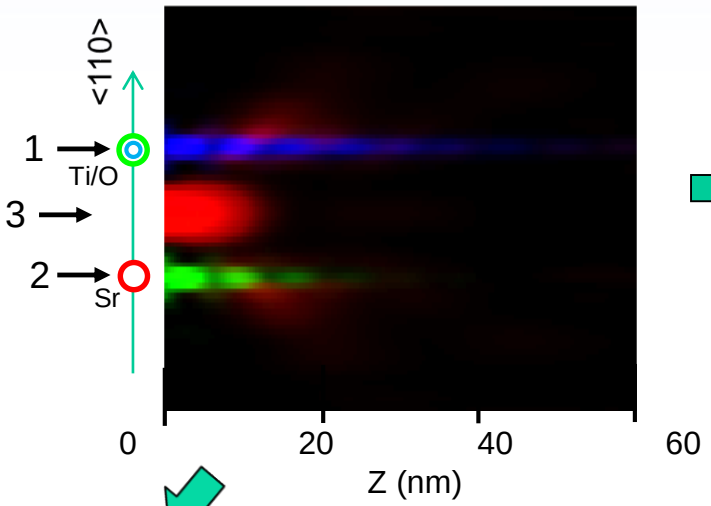
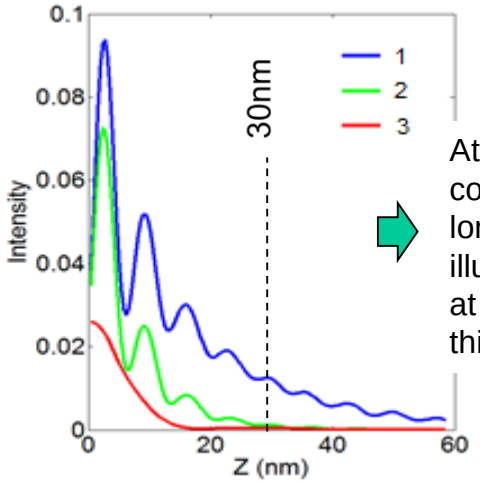
Multislice image simulation → the thin specimen is preferred



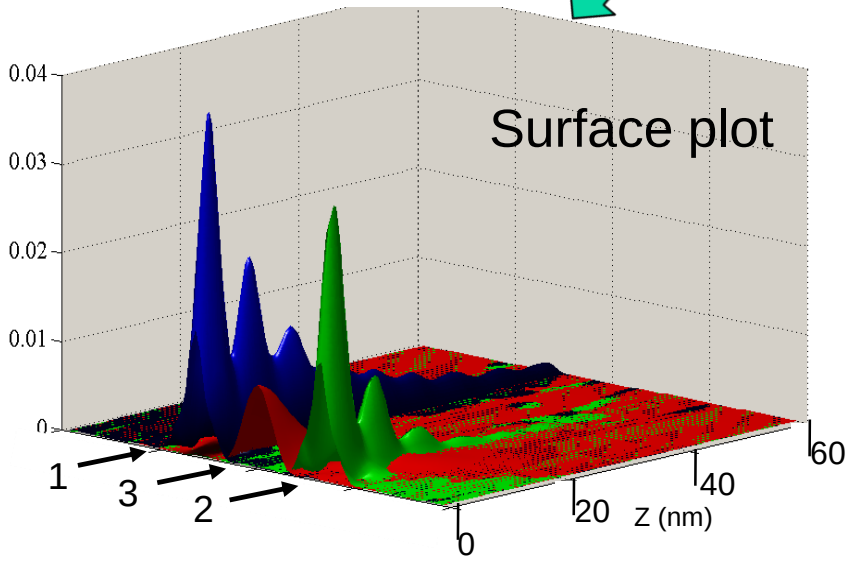
Elastic electron intensity distribution



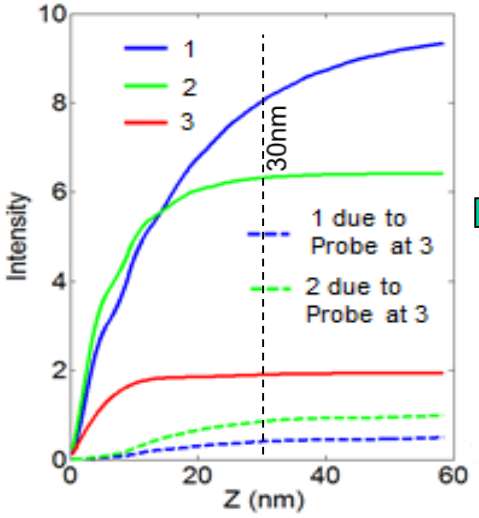
Intensity line-profile



Atomic columns no longer illuminated at higher thickness



Integrated intensity line-profile



At higher thickness, *Localized x-ray* no longer produced; Non-localized x-ray increases with the thickness.

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Conditions for achieving the fast atomic-scale EDS

- ✓ **Usual conditions:**
  - **– probe size, beam convergence, probe current, EDS detector, low index zone**

- ✓ **Specimen conditions:**
  - **– Clean specimen – free of amorphous layers on the top/bottom surface**

  - **– Thin specimen conditions – limiting the specimen to certain thickness (<30nm for STO)**

Study of the dynamic phase transformation

- **Lithium-rich, manganese-rich (LMR) layered oxides**
  - $Li[Li_xMn_yTM_{1-x-y}]O_2$ (TM = transition metal, e.g., Ni, Co or Fe)

  $Li[Li_{0.2}Ni_{0.2}Mn_{0.6}]O_2$ (LNMO) – this study

✓ **Cathode materials for lithium-ion batteries**

✓ **Specific capacities as high as 250 mAh/g**

× **The capacity loss, and voltage fade commonly seen during the battery charge-discharge cycling**

➢ **The local structure and its evolution by using aberration corrected STEM (AC-STEM)**

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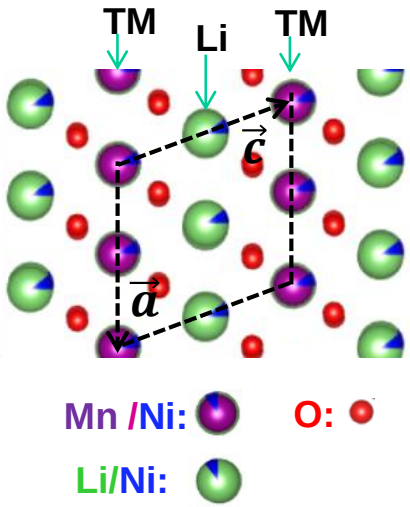
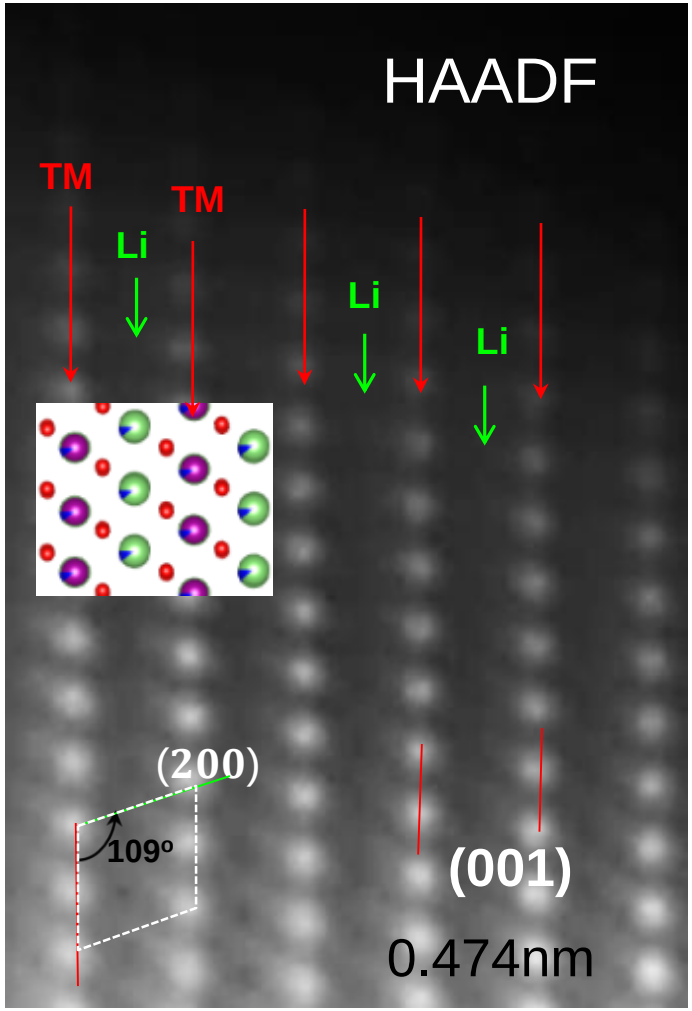
Phase transformation in layered lithium oxides

$Li[Li_{0.2}Ni_{0.2}Mn_{0.6}]O_2$ (LNMO)
–a cathode material for lithium ion battery

[010] projection



Monoclinic unit cell (*a*=0.4926 nm, *b*=0.8527 nm, *c*=0.5028nm, and b=109.22°)



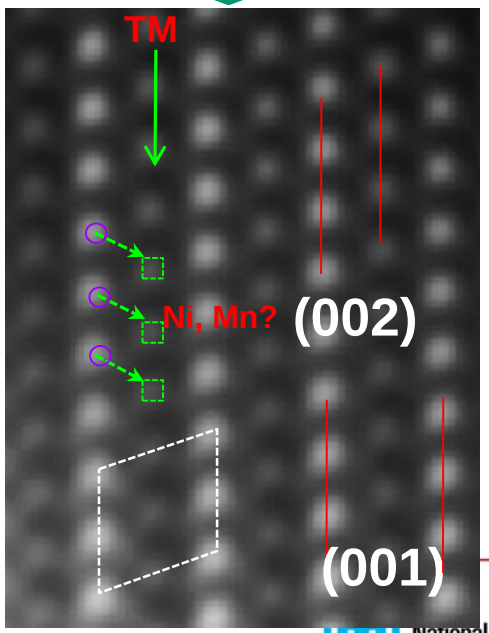
Electrochemical cycling:

- Charging cycle

– Li ions are forced out

- Discharging cycle

– Li ions are re-inserted



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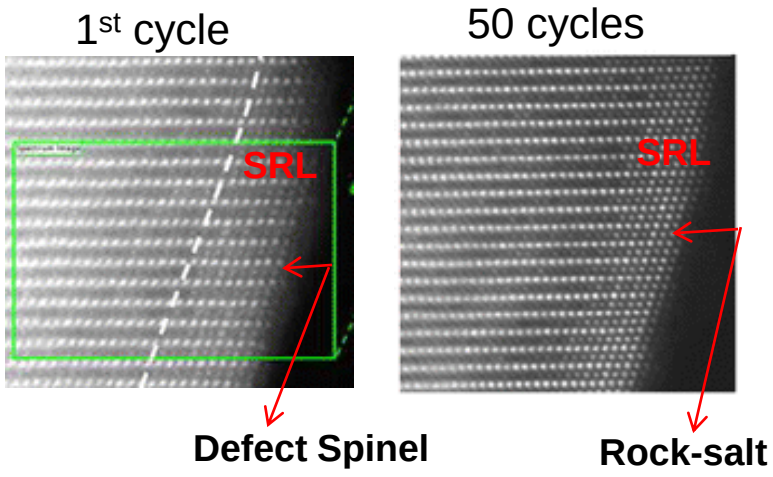
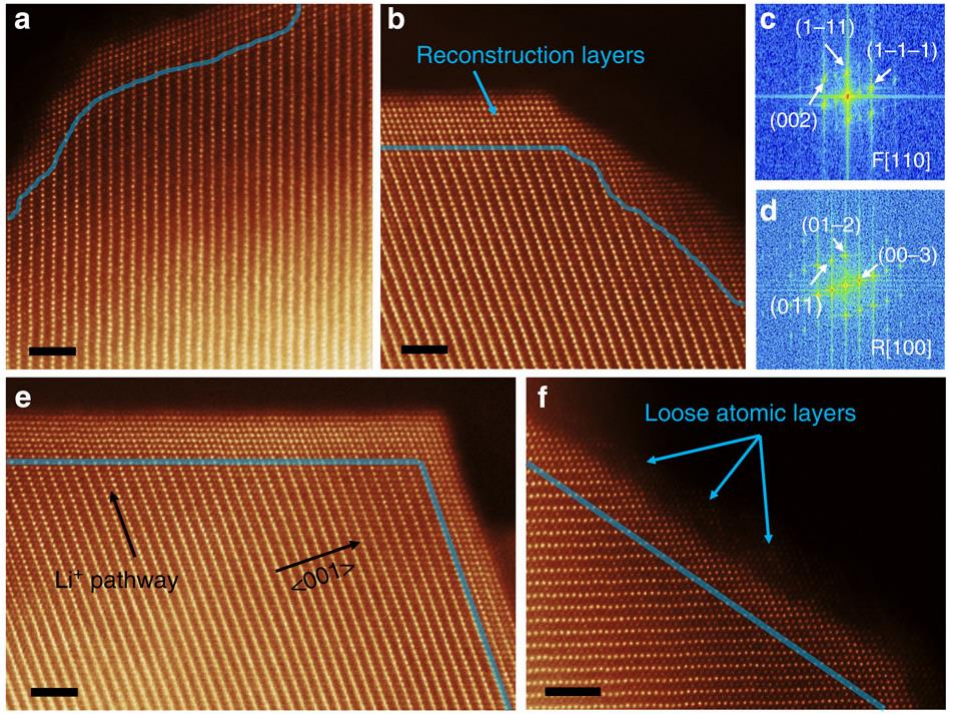
Capacity loss and voltage fade

A gradual phase transformation – from the layered structure to defect spinel and/or rock-salt structure on the surface or in the bulk



A. Boulineau, et al, *Nano Lett.* 2013, 13, 3857-3863



F. Lin, et al. *Nat. Commun.* 2014, 5, 3529-3537.

References:

A. Boulineau, et al, *Nano Lett.* **2013,** 13, 3857-3863. *Chem. Mater.* **2012**, 24, 3558-3566.
B. Xu, et al., *Energ. Environ. Sci.* **2011,** 4, 2223-2233.
M. Gu, et al, *ACS Nano* 7, **2013,** 760-767
F. Lin, et al. *Nat. Commun.* **2014,** 5, 3529-3537.
P. F. Yan et al. *Nano Lett*. **2015**, 15, 515-522.

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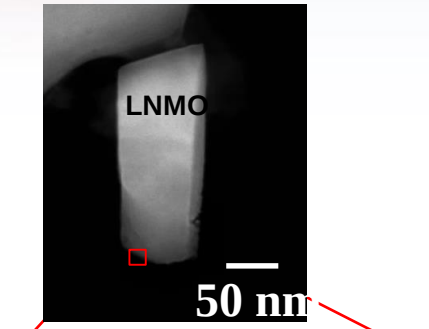
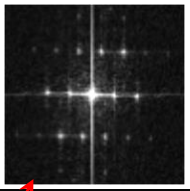
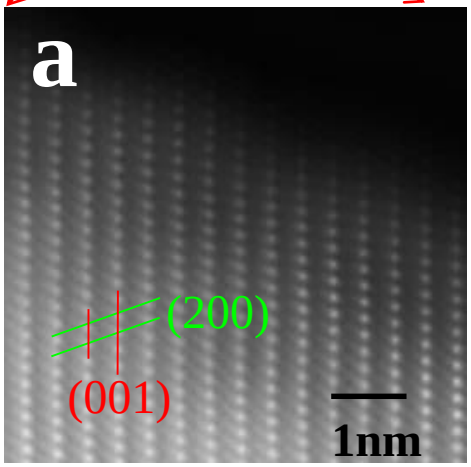
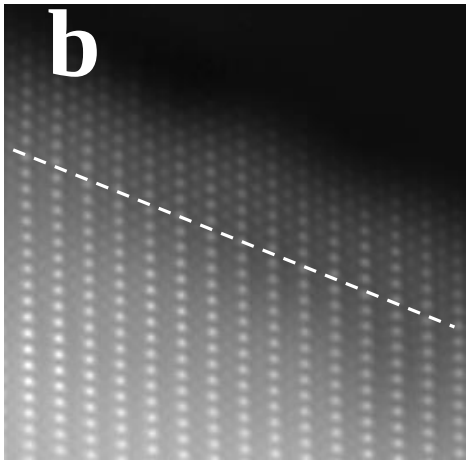
Electron beam irradiation induces *same* phase transformation

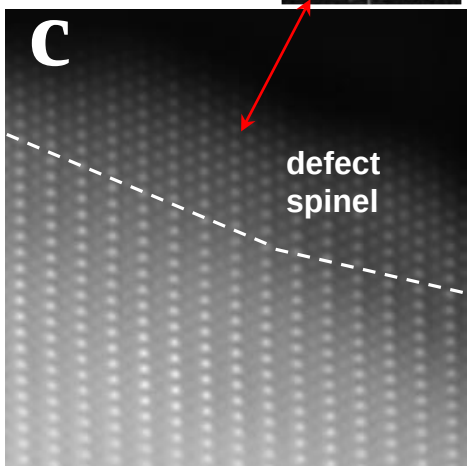


At mag 3600kx→ an equivalent beam current density of ~19 A/cm^2 or 1.12x10^4 electrons/Å^2/s









No pre-exposure 30 s pre-exposure 90 s pre-exposure

"*Mimic*" the phase transformation in the battery environment by using high-energy election beam

P. Lu *et al.* ***Chem. Mater***. 2015, 27,1375-1380

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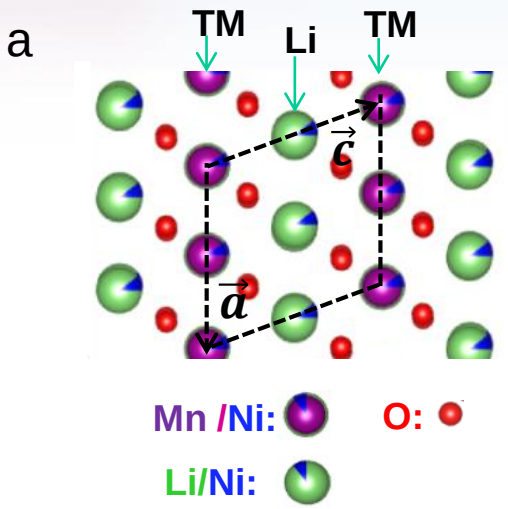
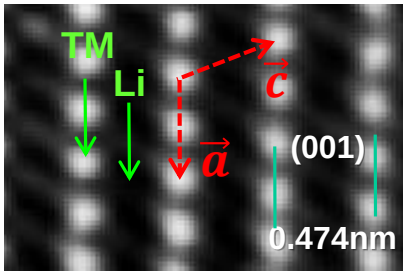
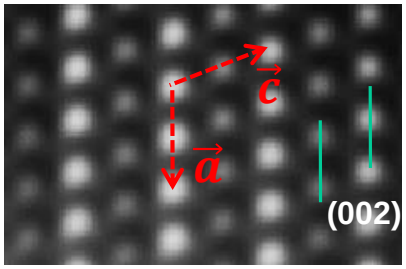
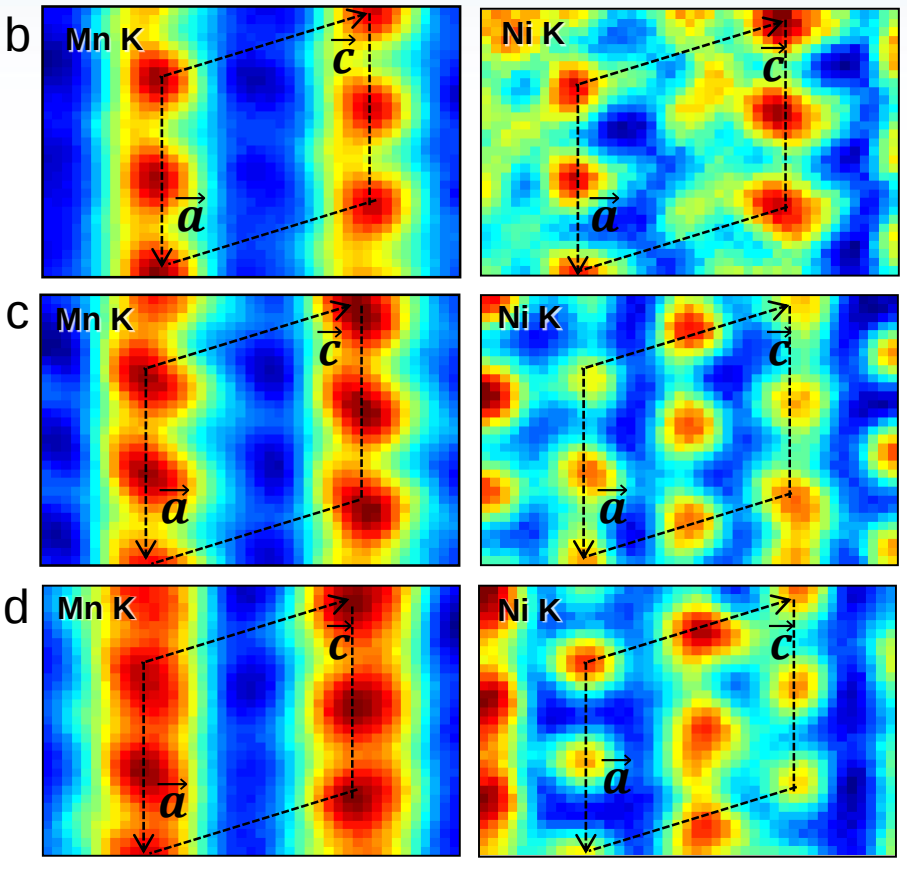
Time-resolved atomic-scale chemical imaging









- Preferred jumping of Ni atoms (relative to Mn) from the TM layers to the Li layers
- Mn maintaining its position in the TM layer

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Summary

- **We have developed a fast atomic-scale chemical imaging based on STEM-EDS.**
  - **Lattice-vector translation method**
  - **Chemical structure averaged over area of ~10 nm^2**
  - **Acquisition time on order of 1 s, a 100X reduction**
  - **Conditions for achieving the fast EDS mapping**
    - **Thin specimen condition is preferred**
    - **For STO, thickness < 30 nm**
- **Time-resolved atomic-scale EDS mapping has been applied to the study of phase transformation in Lithium transition-metal oxide (LNMO).**

  - A new kinetic transformation mechanism is uncovered

  - Ni atoms jump preferably over Mn atoms in the transformation

  - The new mechanism corroborates the electrochemical data

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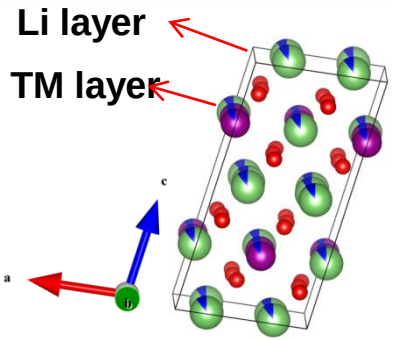
Additional Slides

Bulk Structures

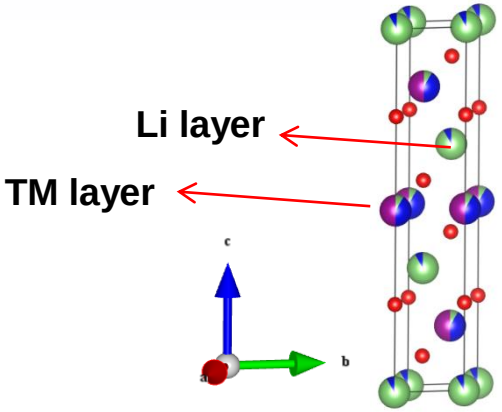
$Li[Li_{0.2}Ni_{0.2}Mn_{0.6}]O_2$ (LNMO)

Monoclinic C2/m $Li_{1.2}Ni_{0.2}Mn_{0.6}O_2$



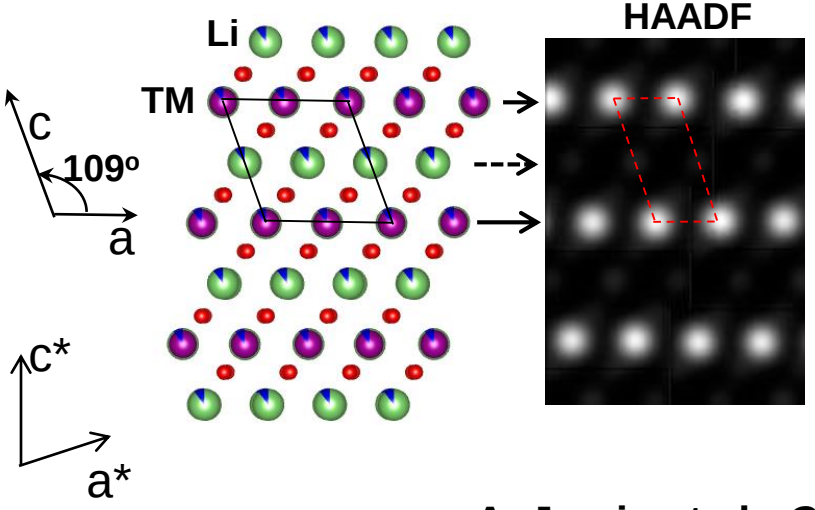
OR

Hexagonal $R\bar{3}m$ $LiNi_{0.5}Mn_{0.5}O_2$

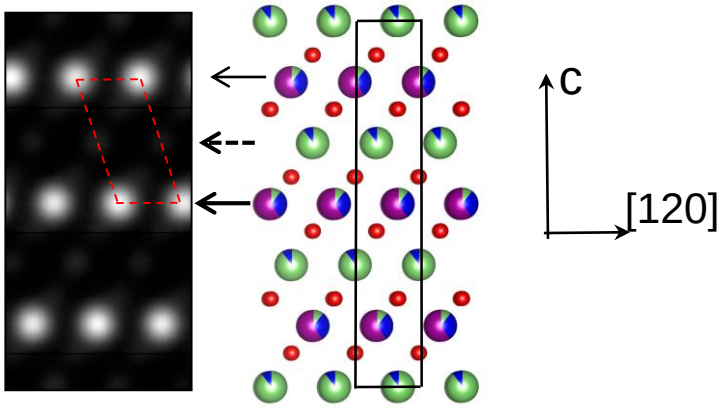


Red: O
Green: Li
Purple: Mn
Blue: Ni

[010] zone



[100] zone



A. Jarvis et al., *Chem. Mater*. 2011, 23, 3614

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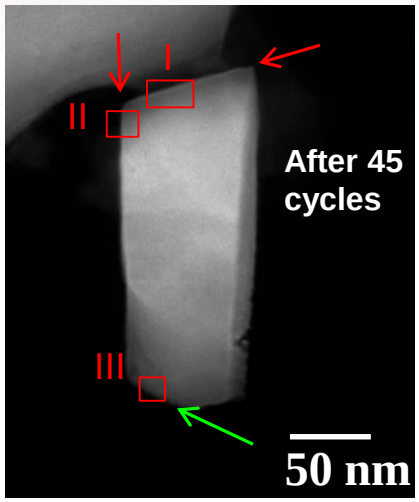
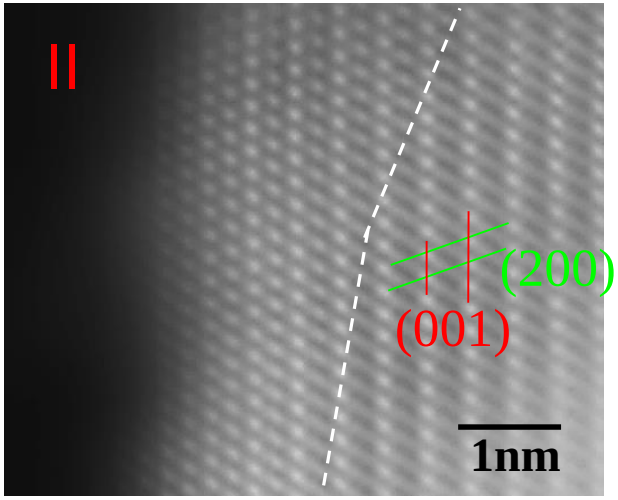
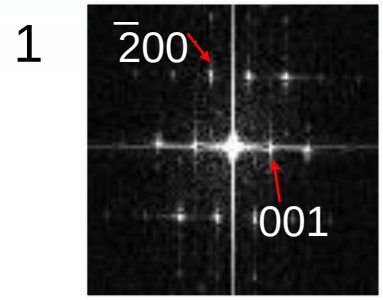
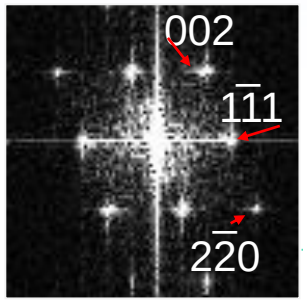
Charge-discharge cycling induced phase transformation



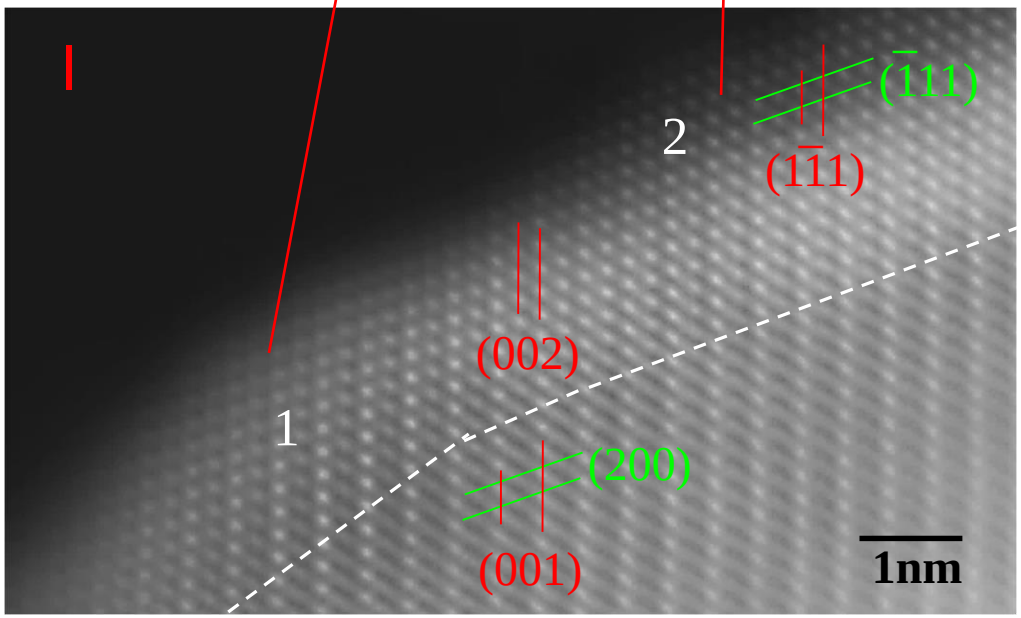






Defect spinel

Rock-salt



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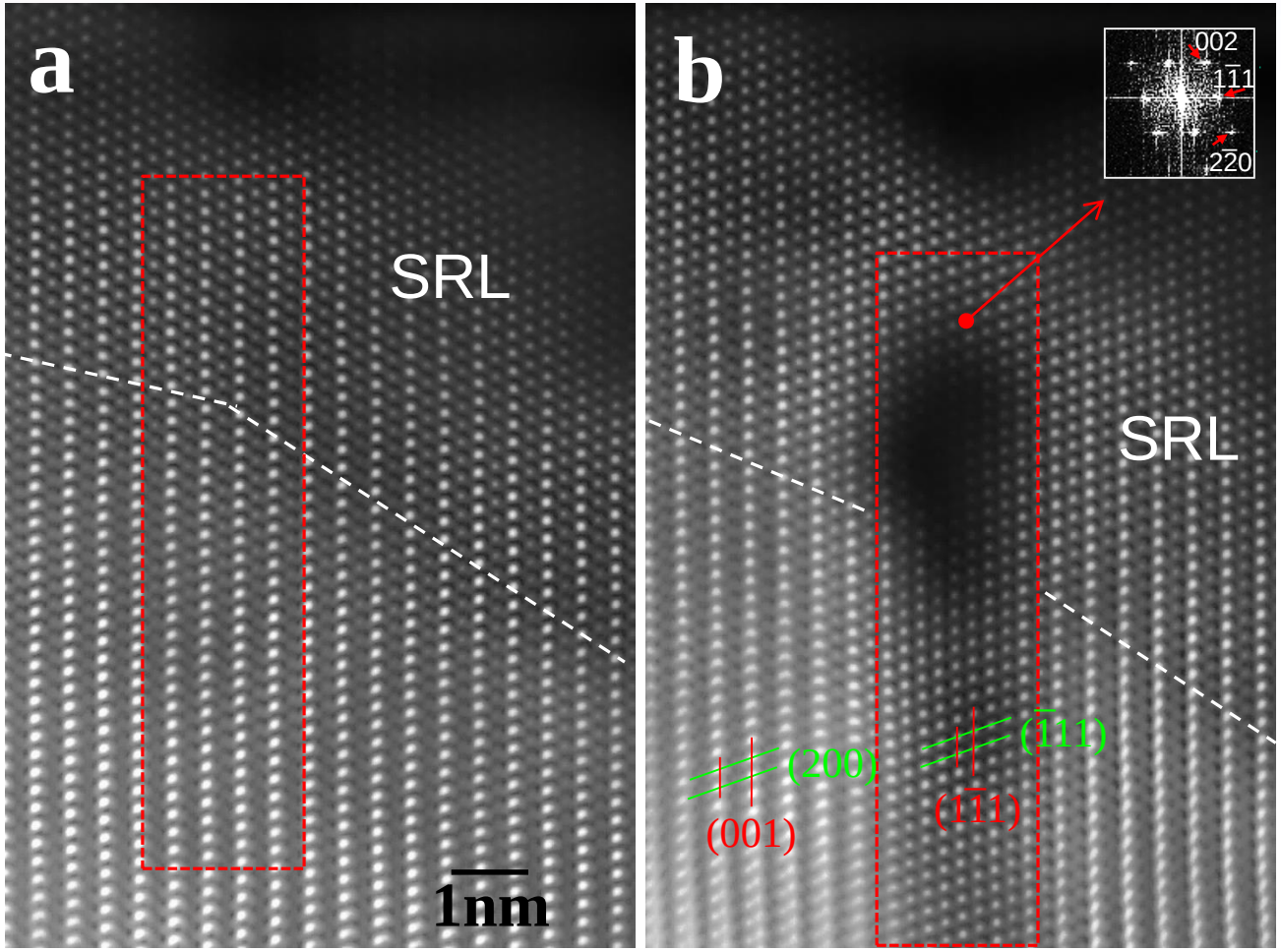
Electron beam induced phase transformation

~320A/cm^2 for 30 s



OR

$[010]_{LNMO}$ //$[110]_{rock\text{-}salt}$
$(001)_{LNMO}$//$(1\bar{1}\bar{1})_{rock\text{-}salt}$

$d(001)_{LNMO}$ = 0.474nm,
$2*d(1\bar{1}\bar{1})_{rock\text{-}salt}$ = 0.475nm.

$d(200)_{LNMO}$ = 0.233nm,
$d(\bar{1}\bar{1}1)_{rock\text{-}salt}$ =0.237nm.

A nearly perfect orientation relationship and lattice match
➔ the rock-salt phase on the surface and within the bulk

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Why do the charge-discharge cycling and electron beam irradiation lead to same phase evolution?

Charge-discharge cycling

- Charging
  – removal of Li+, formation of O vacancies, TM cations hopping into Li-sites, structural transformation;

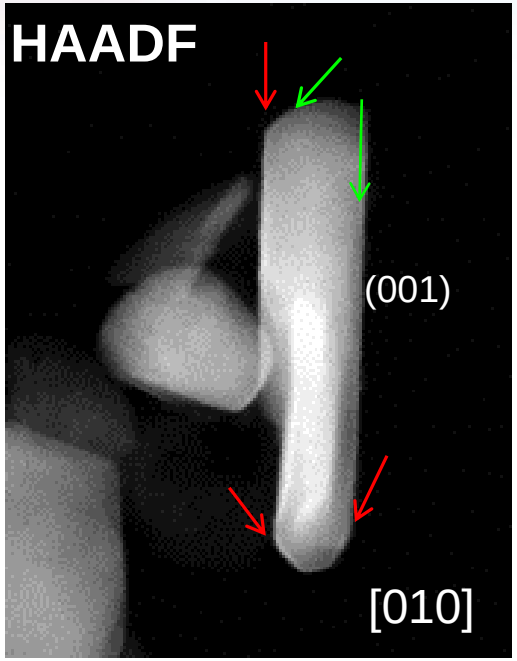
- Discharging (a recovery process)
  – Li+ insertion

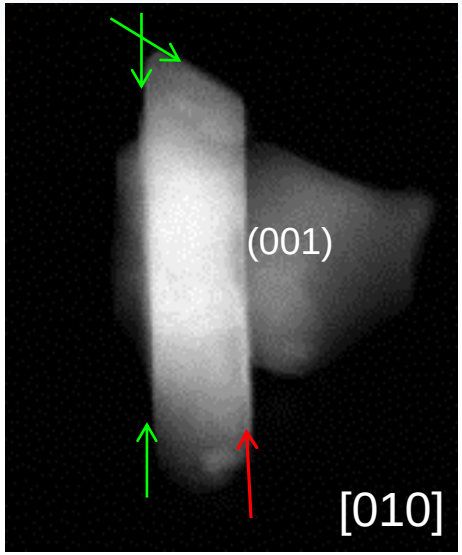
Electron beam irradiation

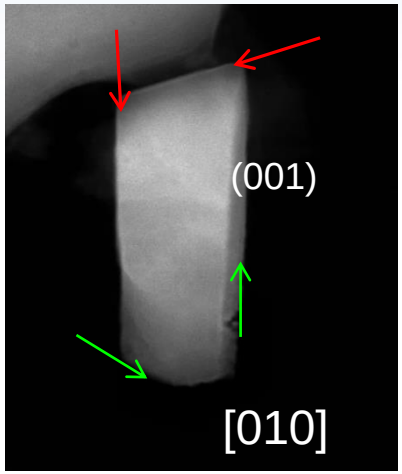
– removal of Li+ by high energy electrons (critical energy for direct displacement <30keV)
– removal of O by high energy electrons → O vacancies (direct displacement + radiolysis)
– TM cations hopping into Li-sites
– structural transformation

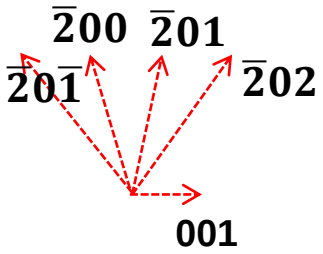
No recovery process

LNMO NPs after 45 charge-discharge cycles









100 nm

- Ni-rich layers are visible on some but not all facets.
- The Ni-rich facets are typically associated with SRLs.

✓ Not all surfaces are with the SRLs
– do not seem to be strongly dependent on the crystallographic orientations

➢ The SRLs can be developed quickly under electron beam irradiations.

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Synthesis and electrochemical measurements

(1) a co-precipitation process - nickel sulfate hexahydrate ($NiSO_4.6H_2O$), manganese sulfate monohydrate ($MnSO_4.H_2O$), sodium hydroxide (NaOH), and ammonium hydroxide ($NH_3.H_2O$) as the starting materials to prepare $Ni_{0.25}Mn_{0.75}(OH)_2$ precursor

(2) washing, filtering and drying the precursor, and mixing it with Li_2CO_3 at a stoichiometric ratio and final calcination at 900˚C for 14 hours.

(3) 80 wt.% of active material, 5 wt.% SFG-6 carbon, 5 wt.% Super-C45 carbon and 10 wt.% polyvinylidene difluoride (PVDF) binder were mixed thoroughly, forming a cathode slurry which was then coated on Al foil to make a laminate.

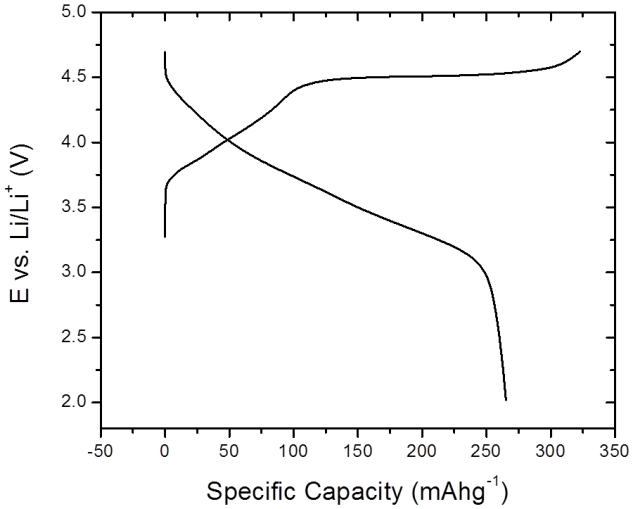
(4) After drying, electrode discs were punched out from the laminate and assembled into half cells with Li as the anode in an Argon-filled glove box. The electrolyte was 1.2 M $LiPF_6$ in ethylene carbonate and ethyl methyl carbonate (EC:EMC = 3:7 by weight).

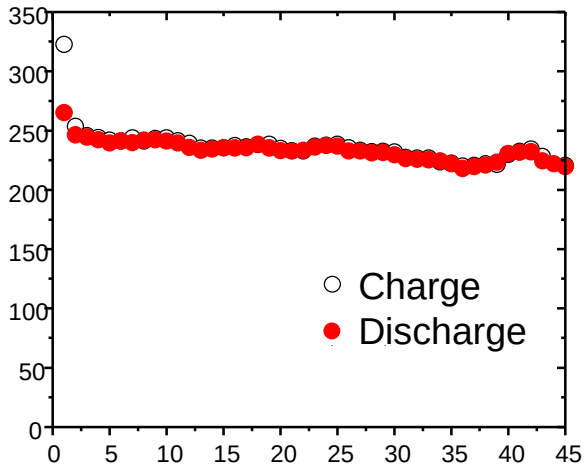
(5) The cell was activated at C/20 rate (1C = 200 mA/g) in the first cycle and cycled at C/10 rate between 2.0 and 4.7 V vs. Li/Li+ at the room temperature. All the samples are at fully discharged state where the potential stopped at 2 V vs. Li metal.

Reference:

Zhang, X.; Xu, R.; Li, L.; Yu, C.; Ren, Y.; Belharouaka, I. *J. Electrochem. Soc.* 2013, 160, A1079-A1083.

Electrochemical performance





First cycle charge/discharge profile (left figure); and charge-discharge capacities as function of cycle numbers at voltage window 2.0-4.7V vs. Li/Li^+ (right figure).

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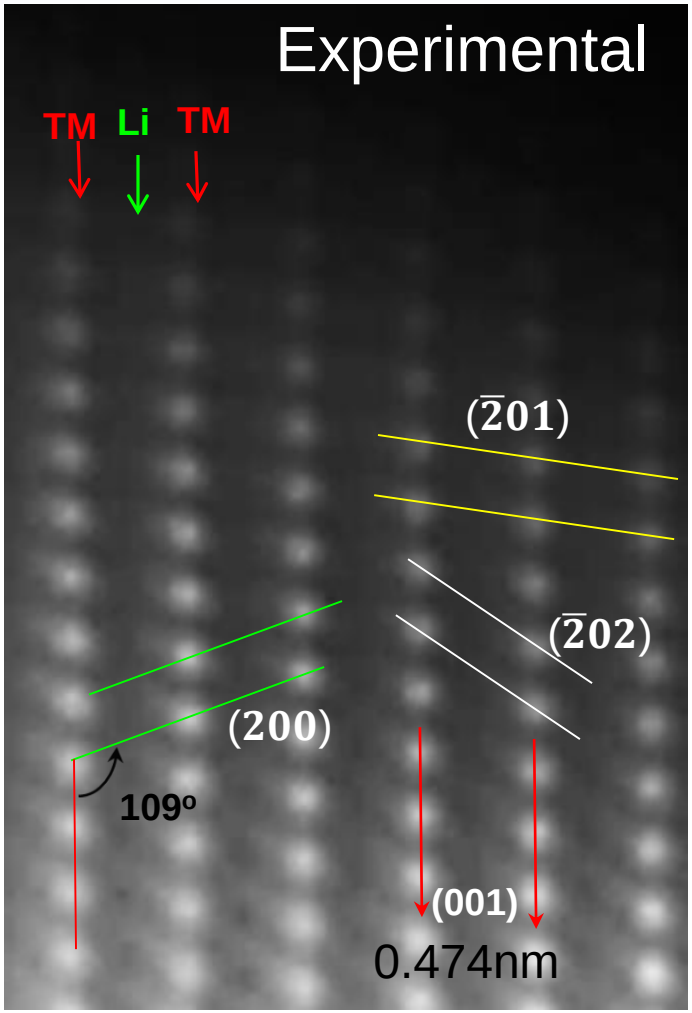
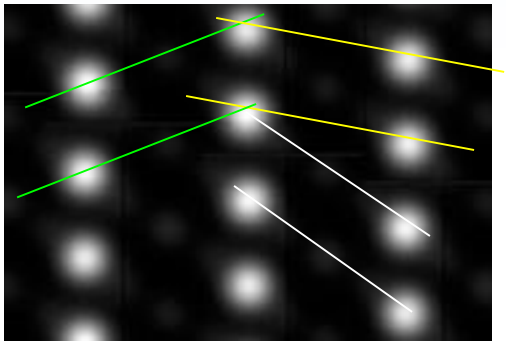
Bulk Structures

HAADF



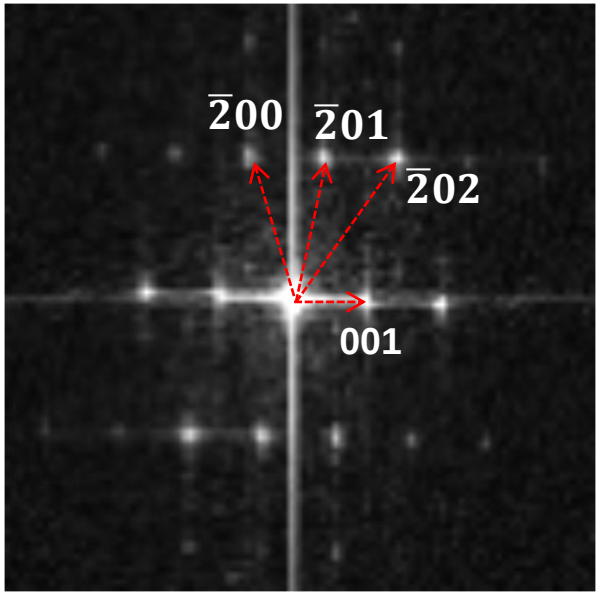
FFT

Simulated



d**001**=0.474nm

d**201**=0.243nm
d**200**=0.233nm
d**202**=0.203nm



$Li_{1.2}Ni_{0.2}Mn_{0.6}O_2$ in [010] zone
Monoclinic C2/m

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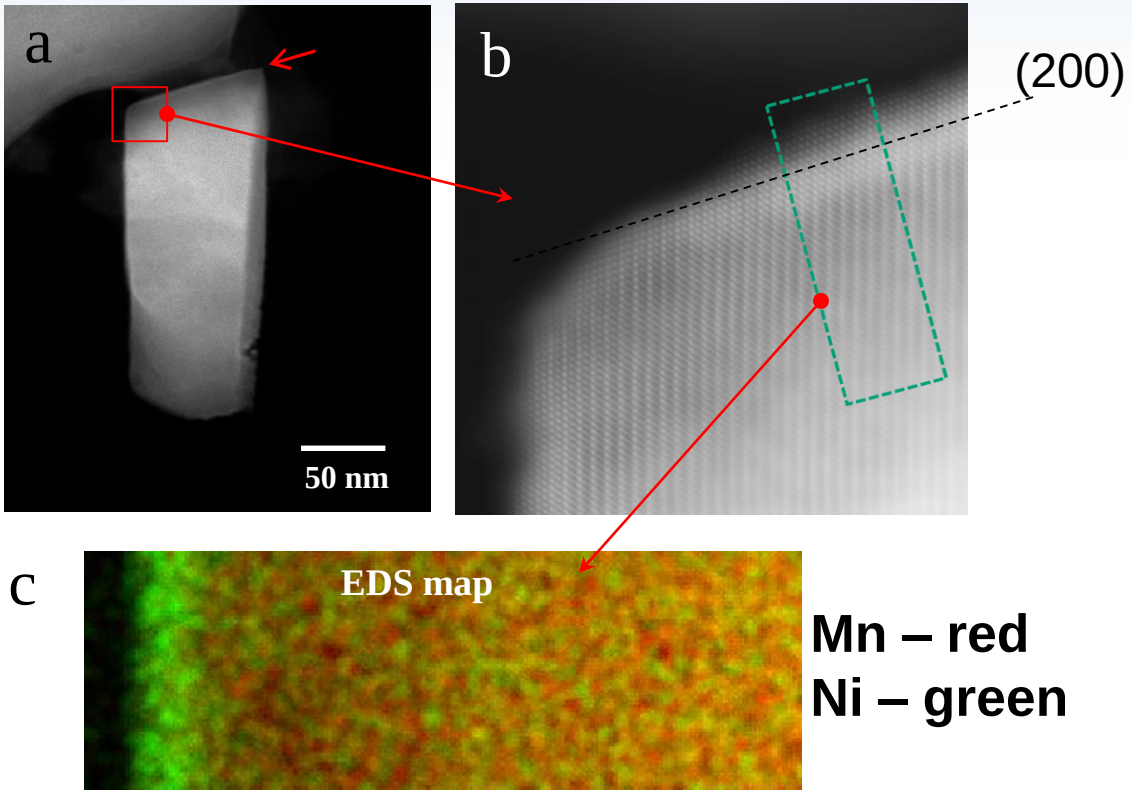
The SRLs are Ni-rich.



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