Structure analysis of Li-excess materials

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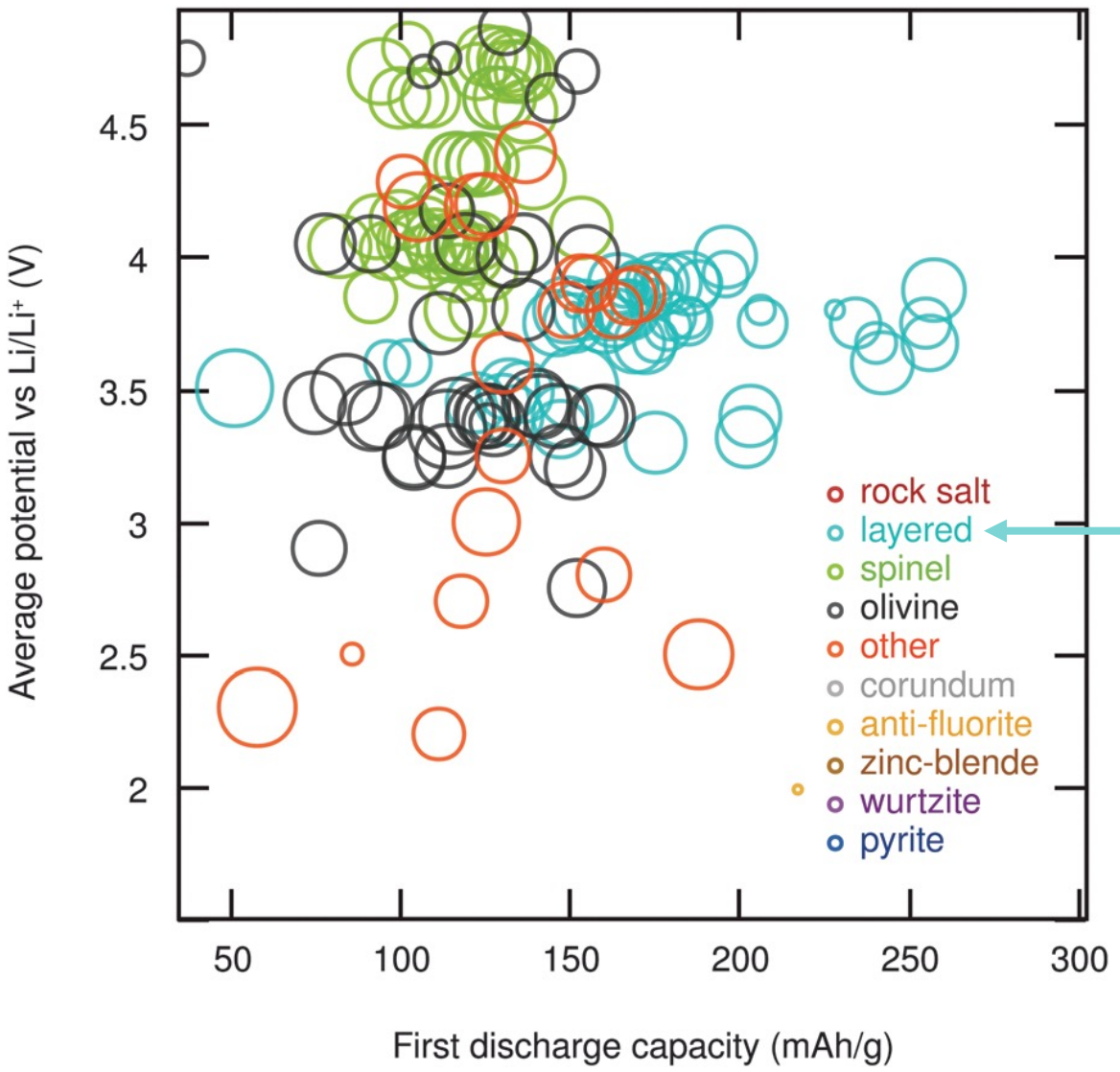
Materials 286G
June 2016

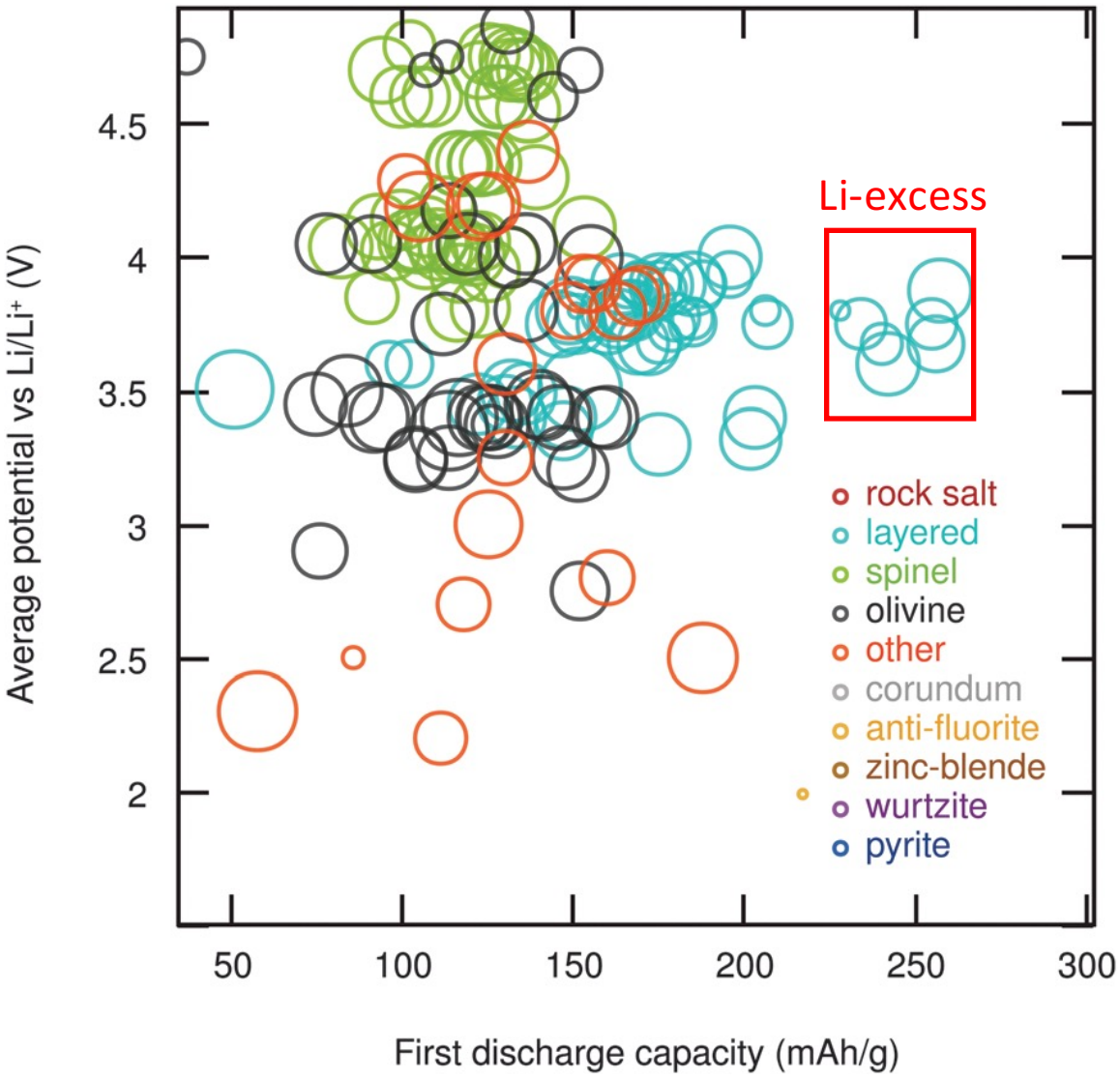
Overview of Li-excess materials

Layered oxide materials show high capacities at a good voltage range



Sparks, Ghadbeigi, Harada, & Lettiere (2015). Performance and resource considerations of Li-ion battery electrode materials. *Energy Environ. Sci.*, *8*, 1640–1650.

Li-excess materials have the highest capacities

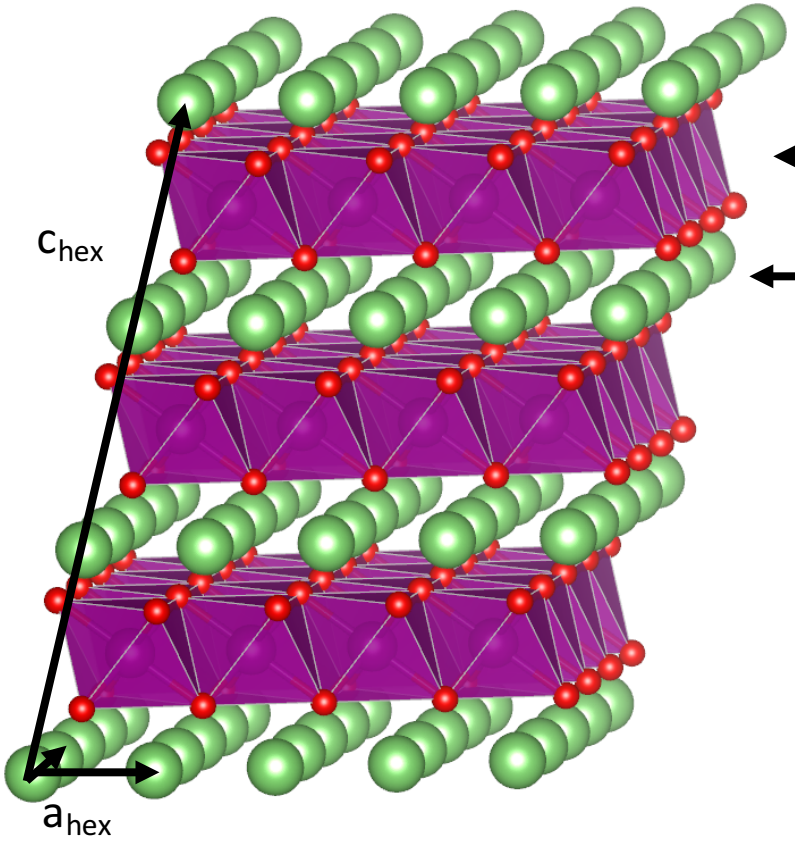


Sparks, Ghadbeigi, Harada, & Lettiere (2015). Performance and resource considerations of Li-ion battery electrode materials. *Energy Environ. Sci.*, *8*, 1640–1650.

Classical Li layered oxides consist of layers of TM with Li^+ in between

Classical layered oxide

$R\bar{3}m$ in most cases



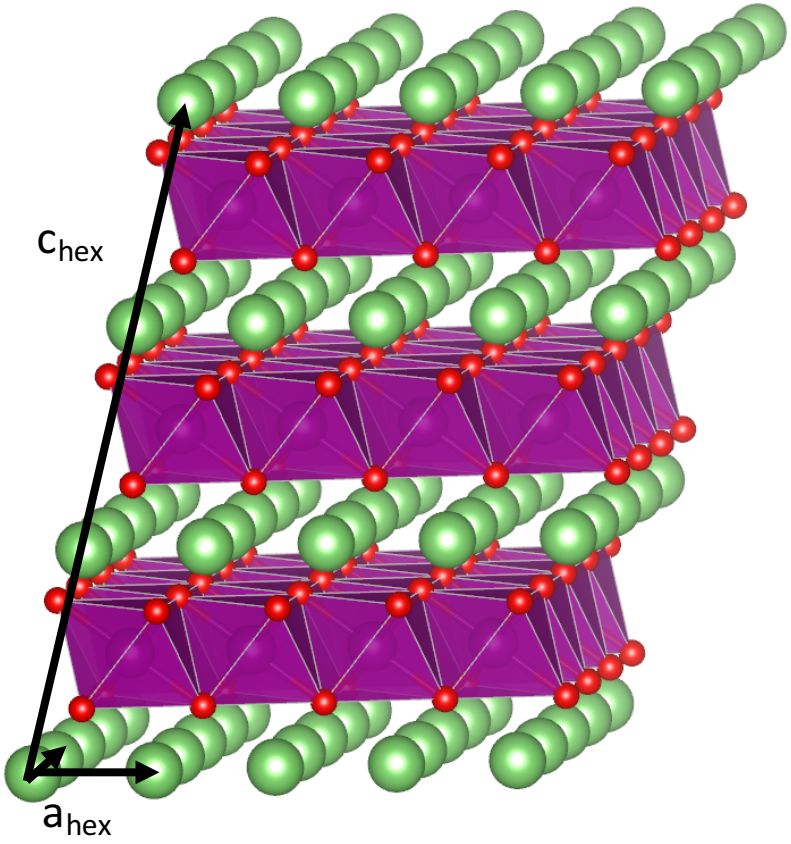
Transition metal layer (TM layer)

Lithium layer (Li layer)

Li_2MnO_3 has extra Li^+ in TM layers

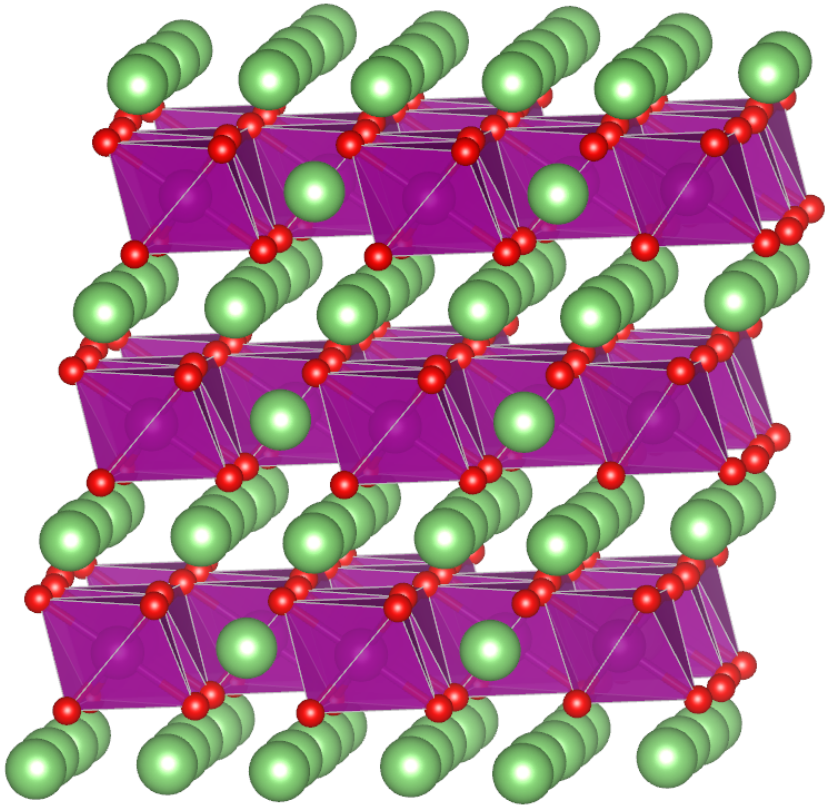
Classical layered oxide

$R\bar{3}m$ in most cases



Li_2MnO_3

$C2/m$ due to J-T distortions



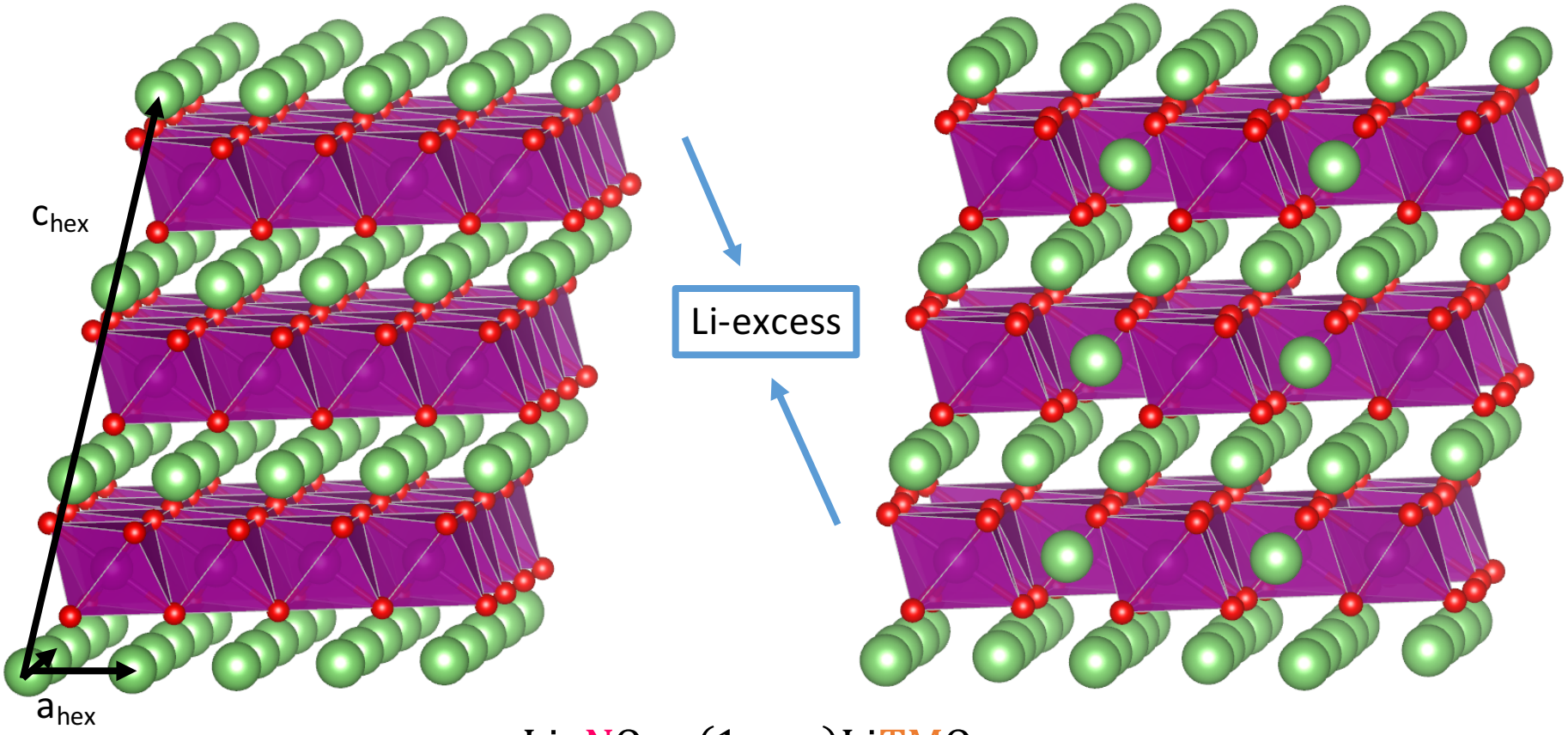
Li-excess materials are a mixture of both

Classical layered oxide

$R\bar{3}m$ in most cases

Li_2MnO_3

$C2/m$ due to J-T distortions



$$x\ \mathrm{Li_2NO_3} \cdot (1-x)\mathrm{LiTMO_2}$$

N = **Mn**, Ti, Zr

TM = **Mn, Ni, Co**, Fe, Cr, Al, etc.

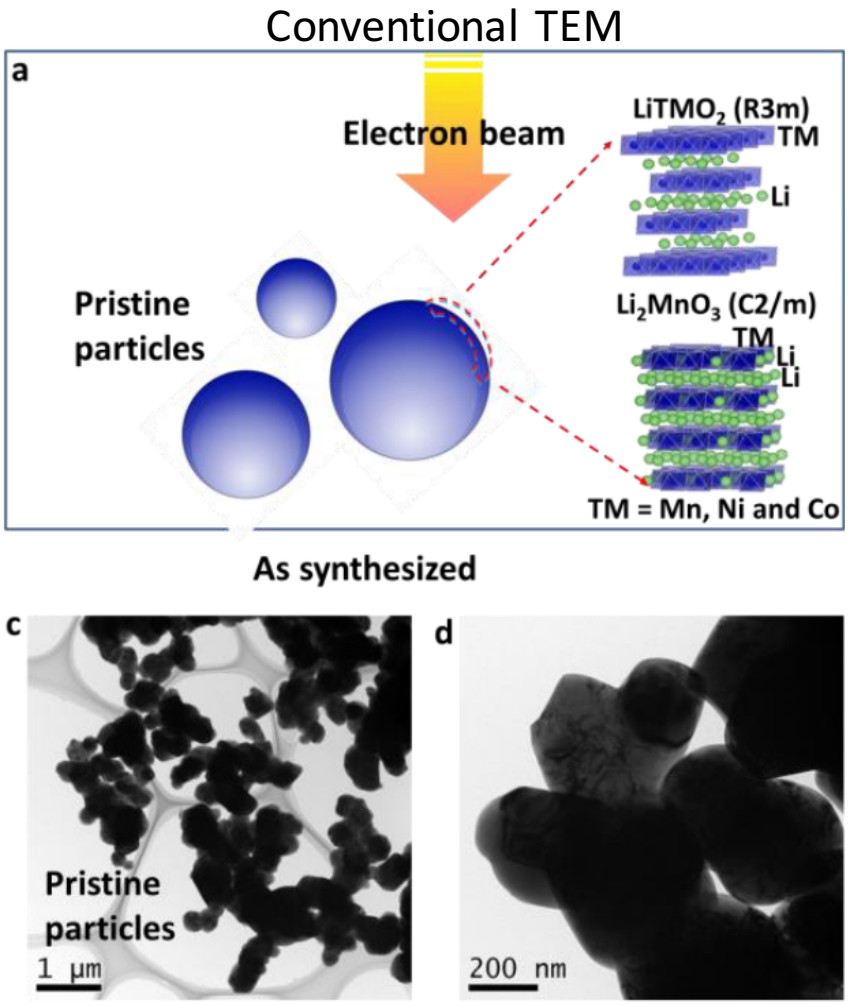
How these materials are structured remains under discussion

A study of bulk structure in Li-excess materials and its affects on Li^+ migration

Yu, So, Kuwabara, Tochigi, Shibata, Kudo, Zhou, Ikuhara. “Crystalline Grain Interior Configuration Affects Lithium Migration Kinetics in Li-Rich Layered Oxide.” *Nano Lett.* 2016, 16, 2907—2915.

Usually, only the surface of the particle can be investigated

$Li_{1.2}Mn_{0.567}Ni_{0.166}Co_{0.067}O_2$



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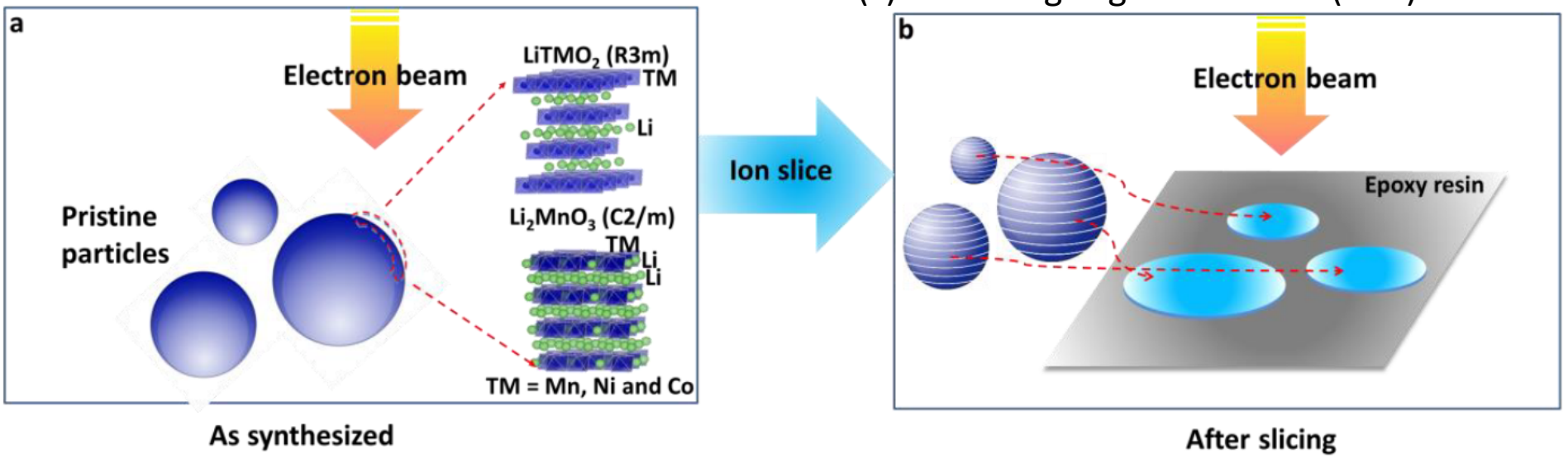
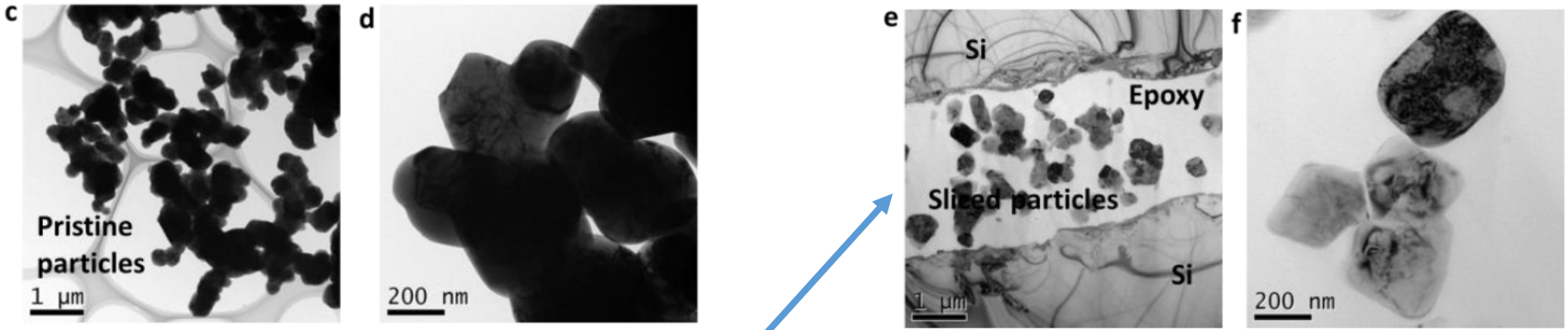
Slicing the particle allows for investigation of bulk structure

$Li_{1.2}Mn_{0.567}Ni_{0.166}Co_{0.067}O_2$

Conventional TEM

(S)TEM using argon ion slicer (ArIS) method



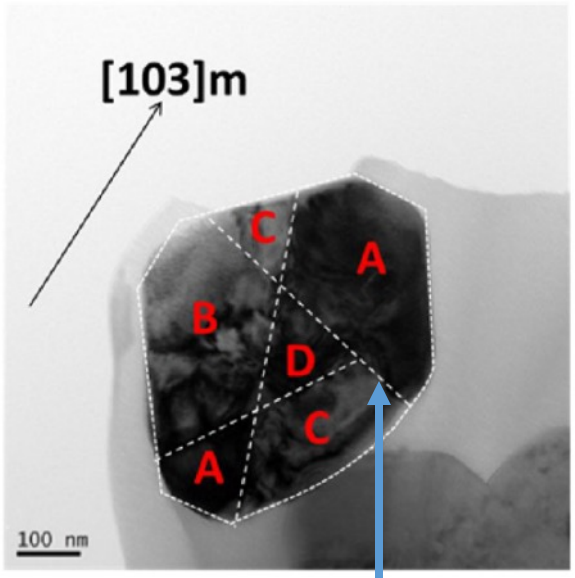


cross-sectional thin transmission electron microscopy specimens (CSTTs)

Yu, So, Kuwabara, Tochigi, Shibata, Kudo, Zhou, Ikuhara. "Crystalline Grain Interior Configuration Affects Lithium Migration Kinetics in Li-Rich Layered Oxide." *Nano Lett.* 2016, 16, 2907—2915.

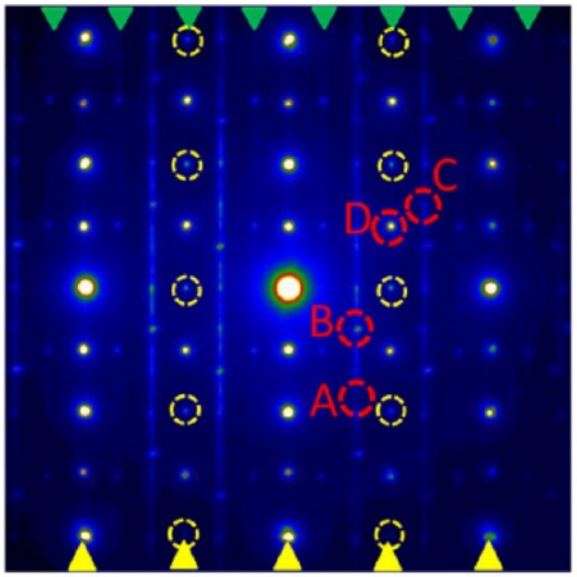
Investigation of a slice reveals multiple domains within grain

BF-TEM image of grain

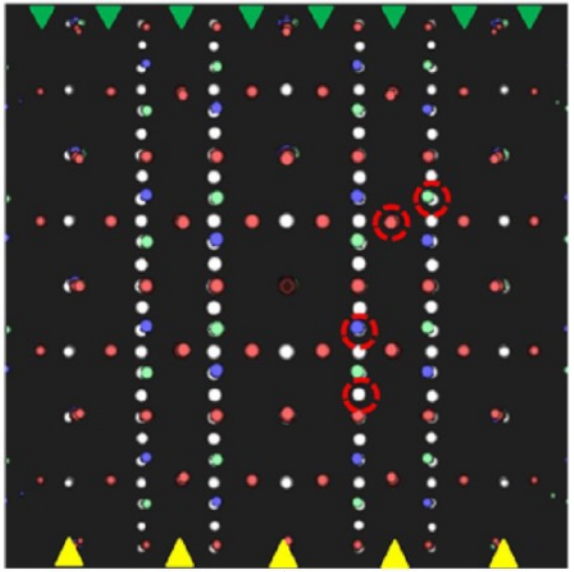


domain boundary (DB)

ED image



simulated ED image



$LiTMO_2$ and Li_2MnO_3 like structures projected along different crystallographic directions

Yu, So, Kuwabara, Tochigi, Shibata, Kudo, Zhou, Ikuhara. "Crystalline Grain Interior Configuration Affects Lithium Migration Kinetics in Li-Rich Layered Oxide." *Nano Lett.* 2016, 16, 2907—2915.

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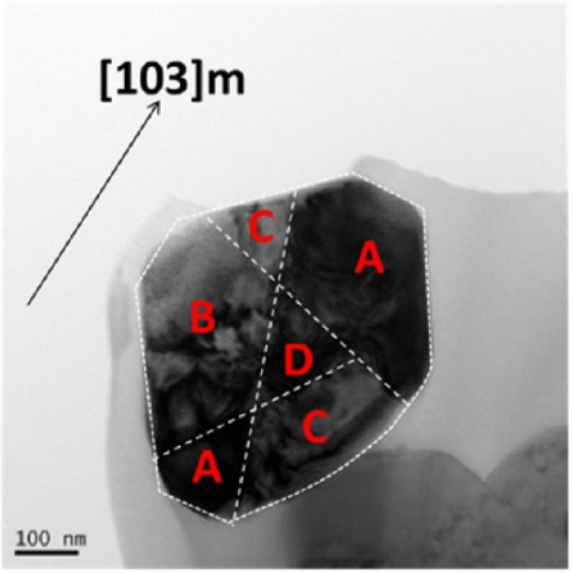
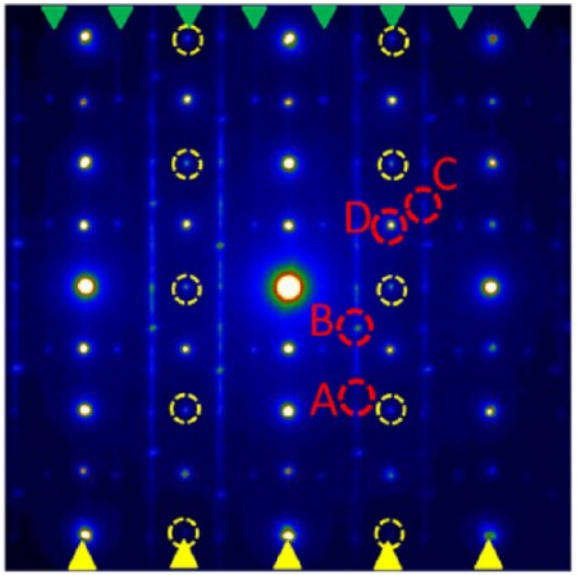
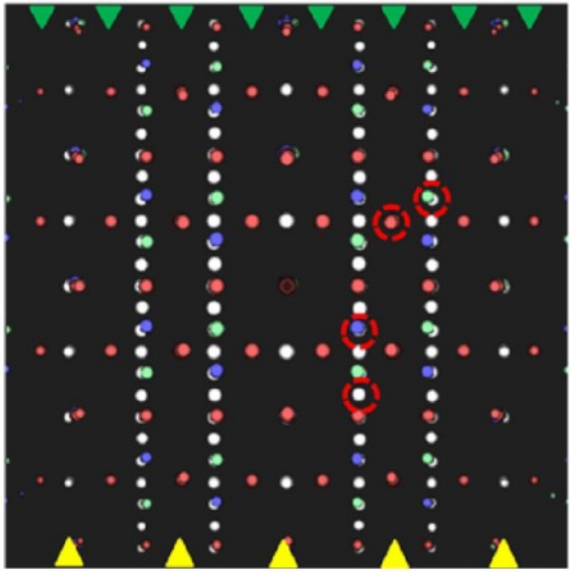


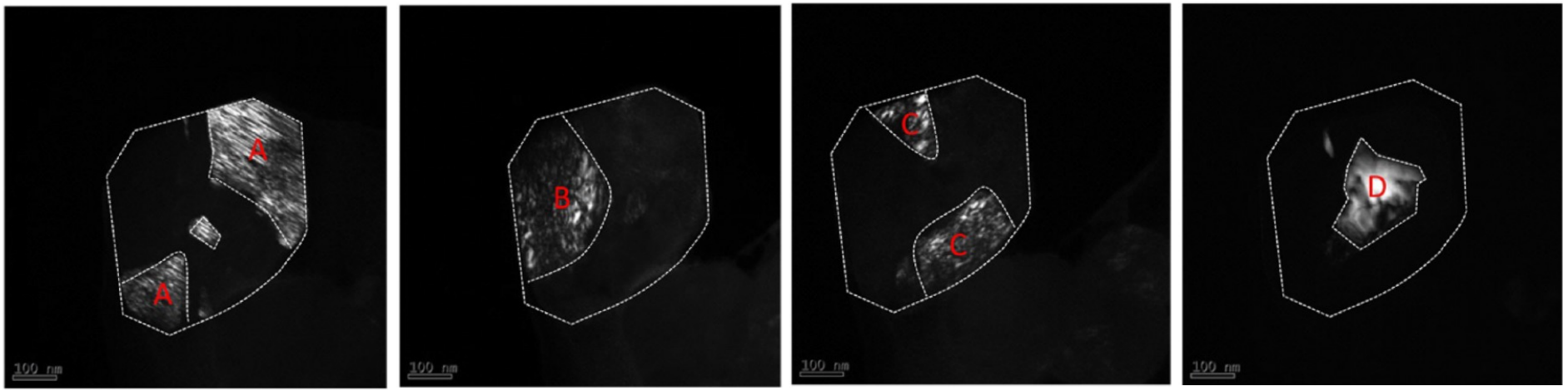
ED image



simulated ED image



DF-TEM images



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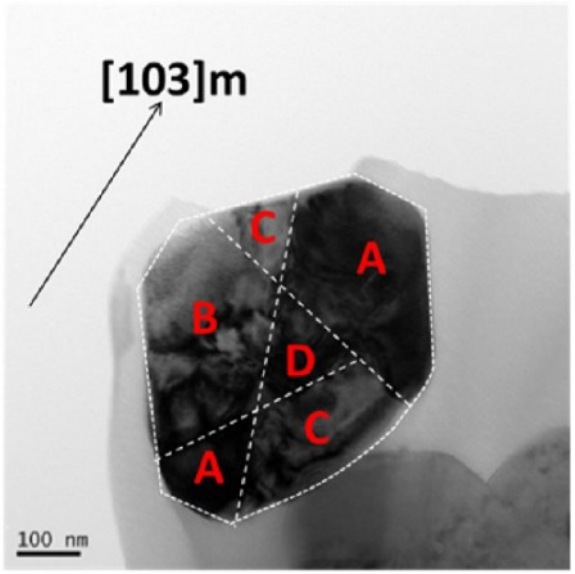
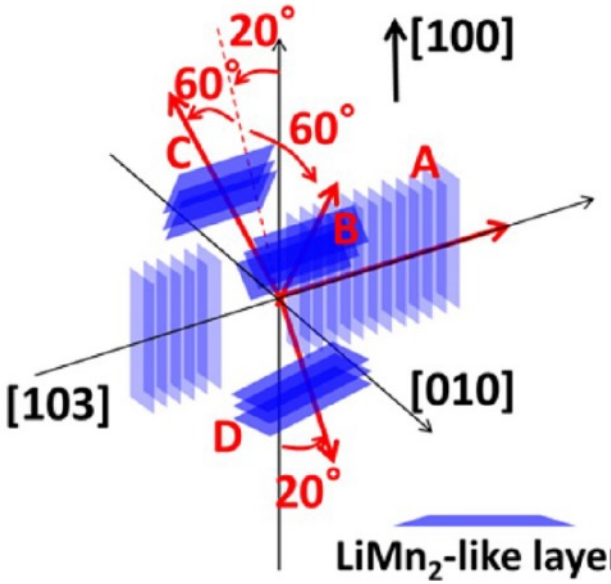
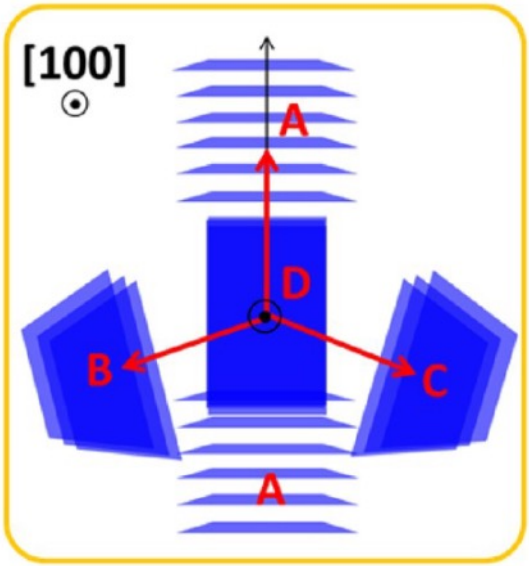
Domains are at an angle to each other

BF-TEM image of grain







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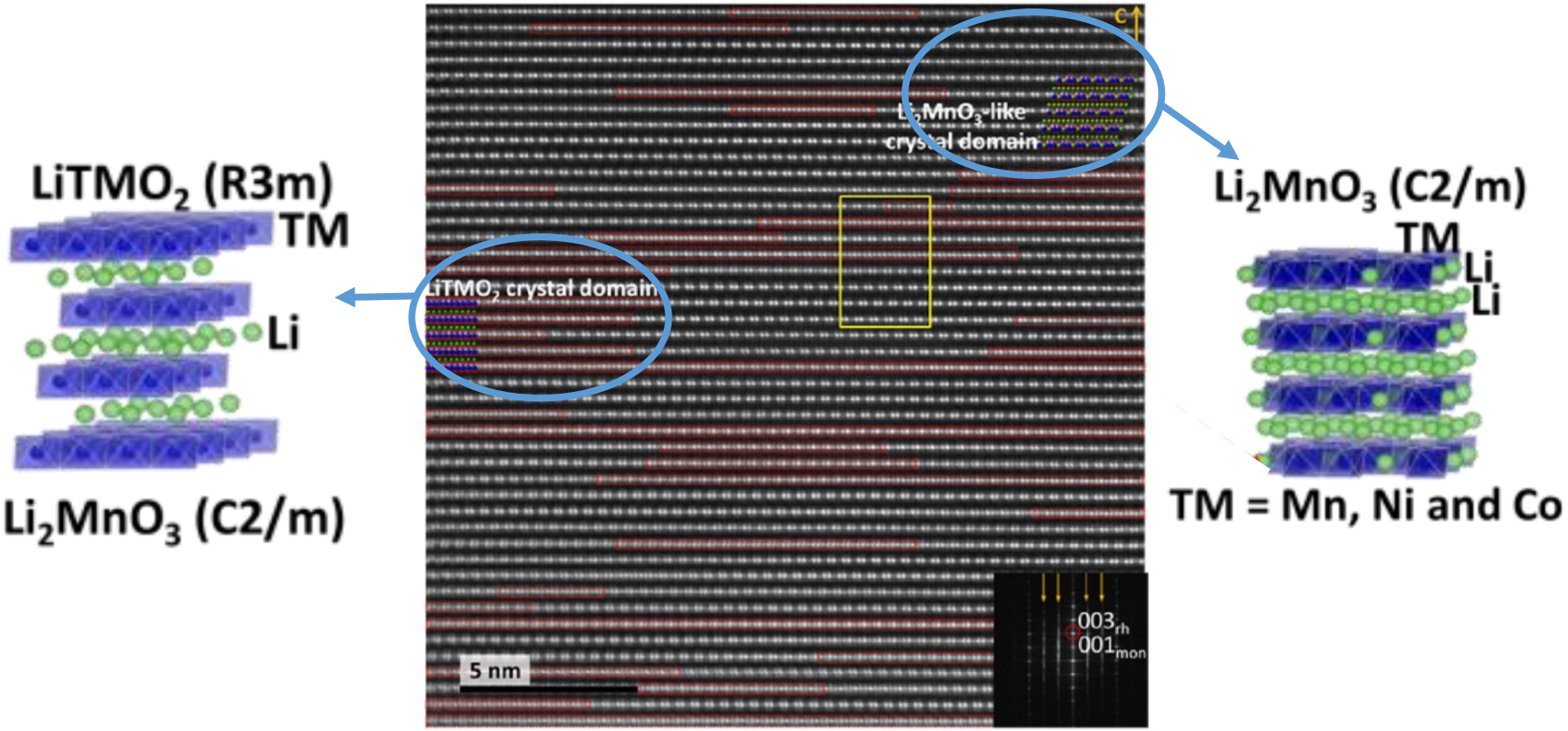
Each domain consists of regions of $LiTMO_2$ and Li_2MnO_3

Referred to as “twin domains”



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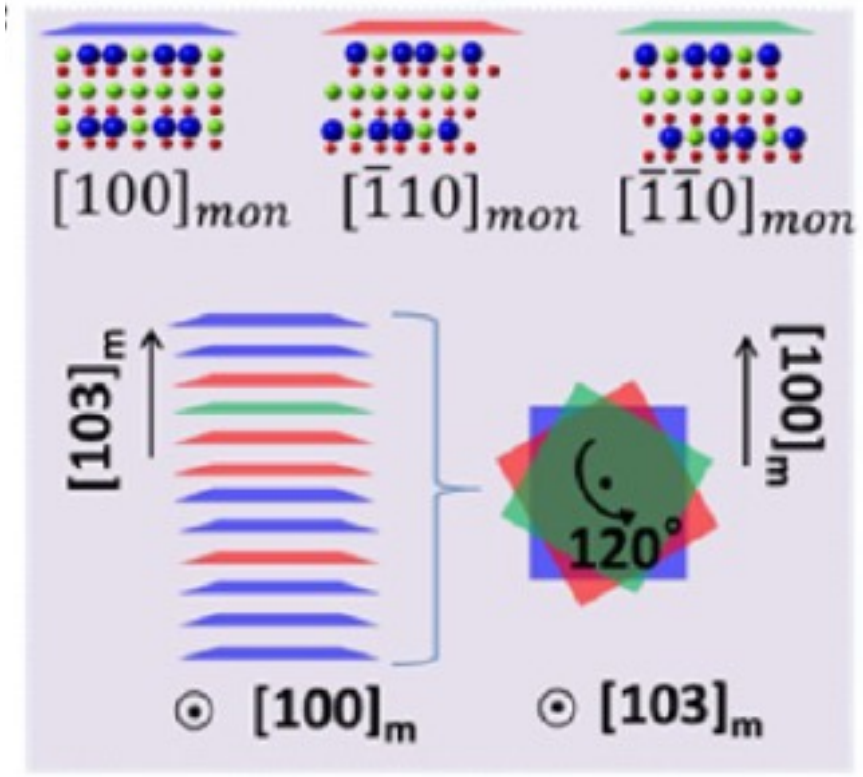
Stacking faults seen in Li_2MnO_3—like phase



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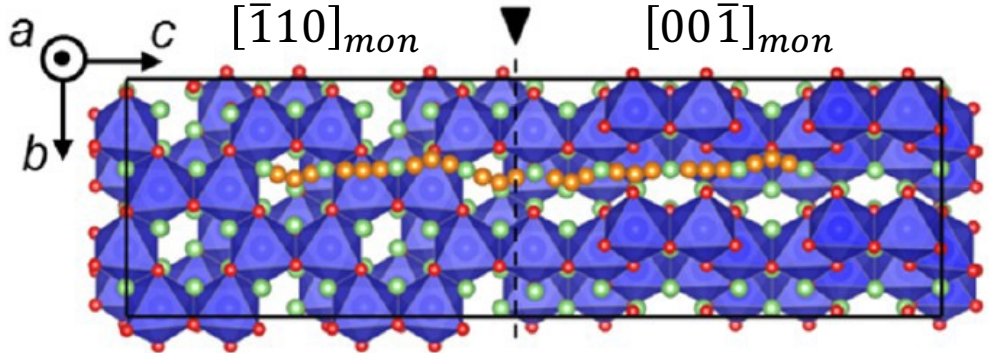
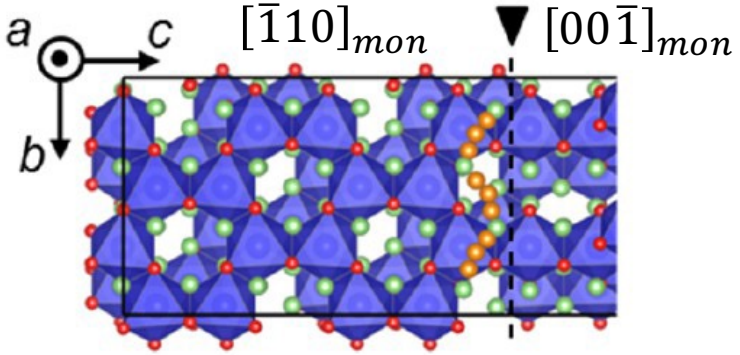
Use DFT to calculate migration formation energies

migration across DB



migration along DB



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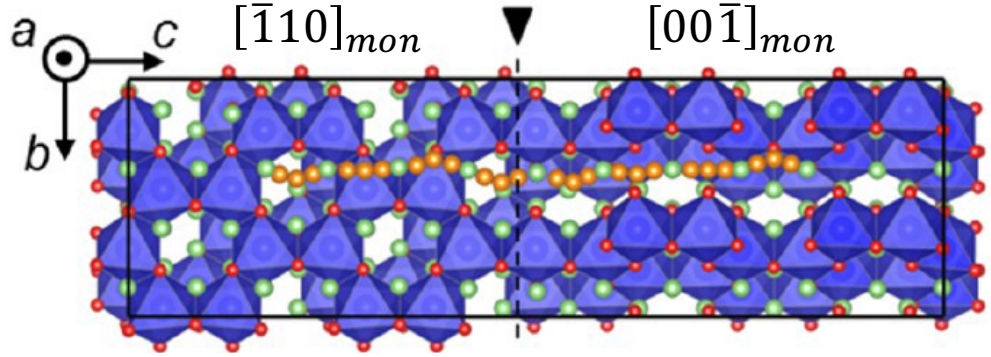
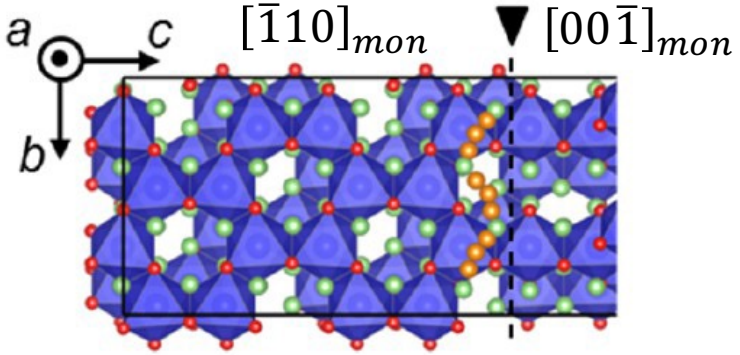
DB may reduce Li^+ mobility

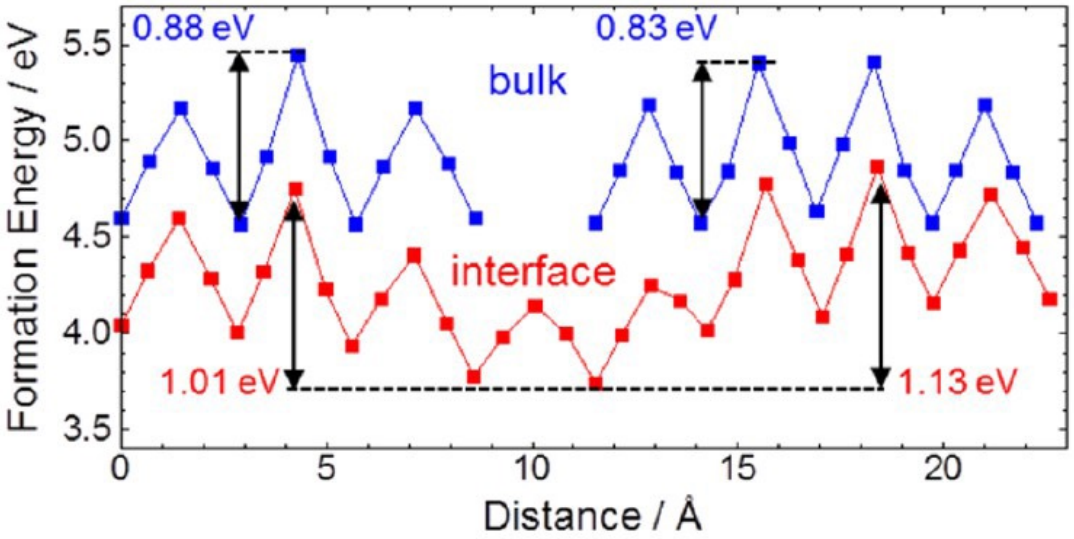
Li_2MnO_3-like

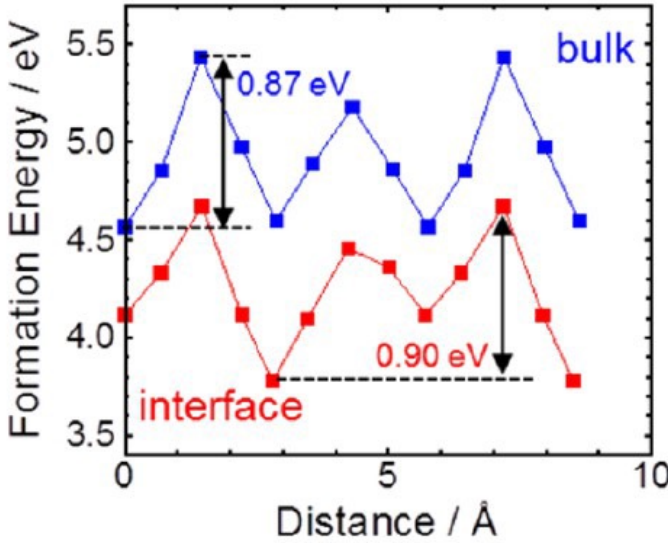
migration across DB



migration along DB







bulk = with no DB present interface = with DB present

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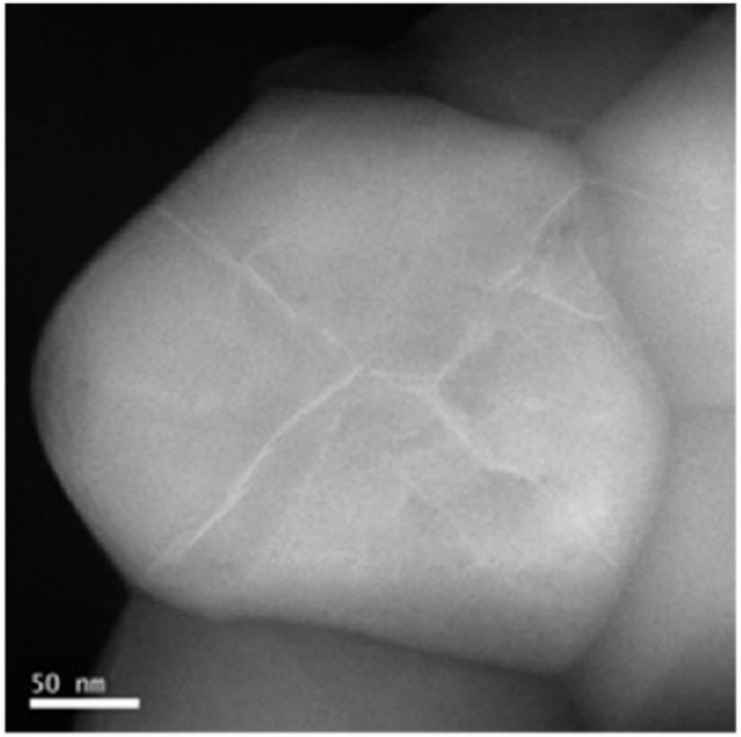
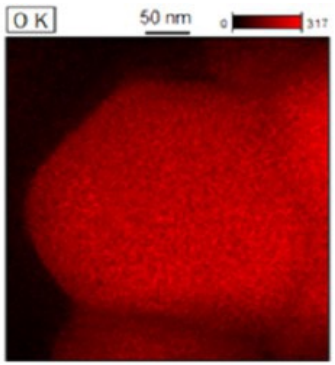
There is evidence Ni segregation at surface and DB

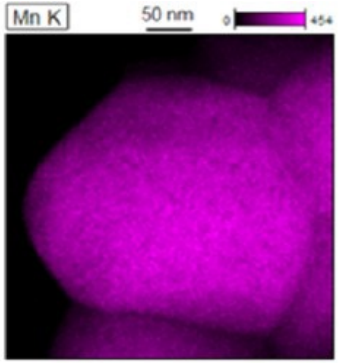
HAADF-STEM images



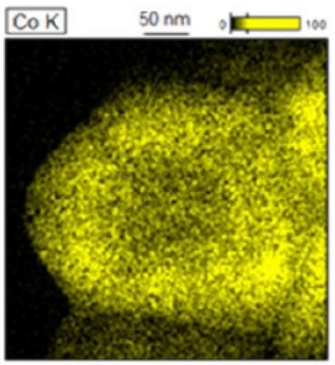
oxygen



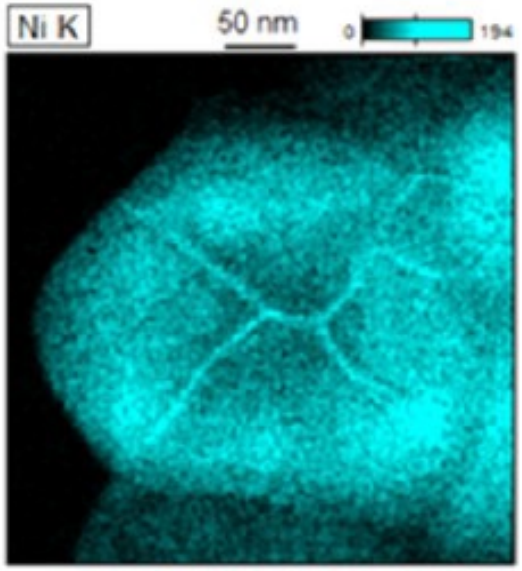
manganese



cobalt



nickel



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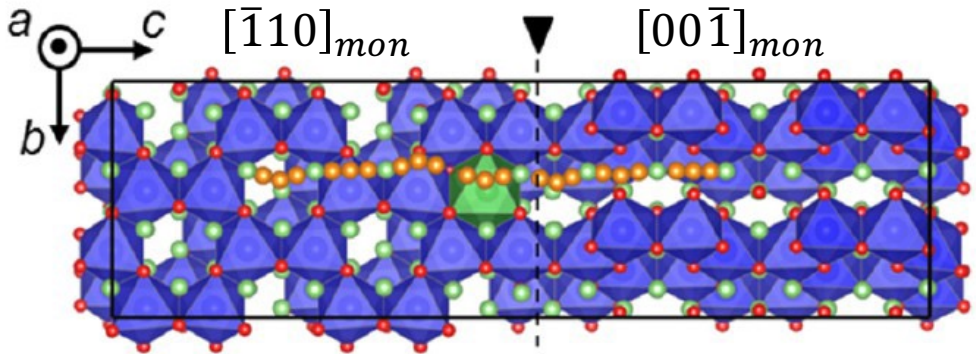
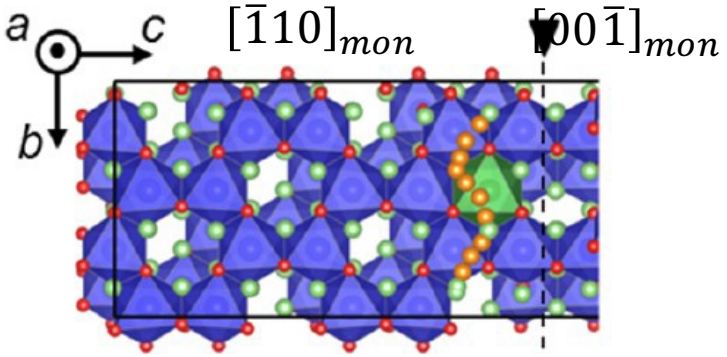
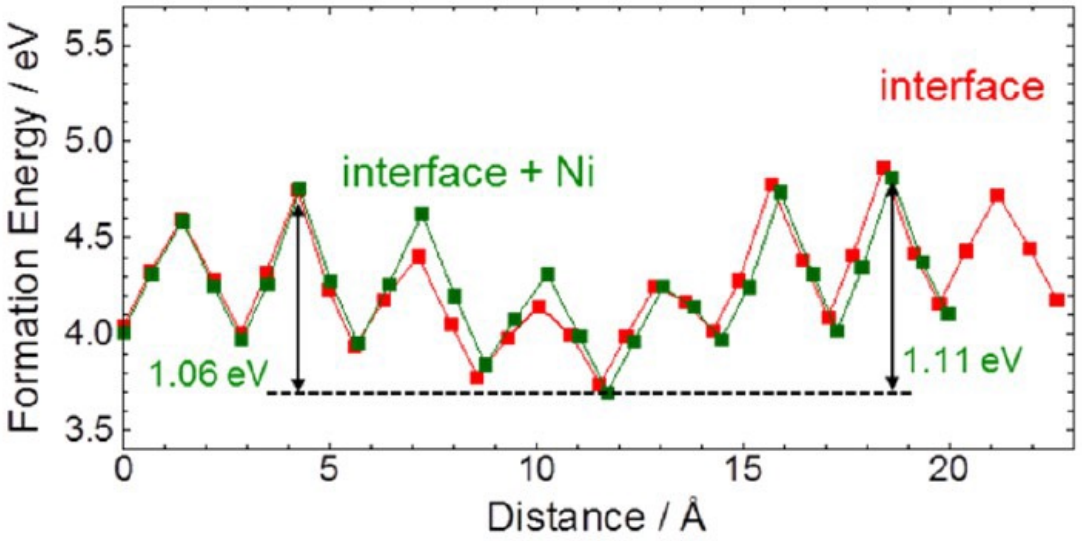
Ni segregation may further impede Li^+ mobility along DB

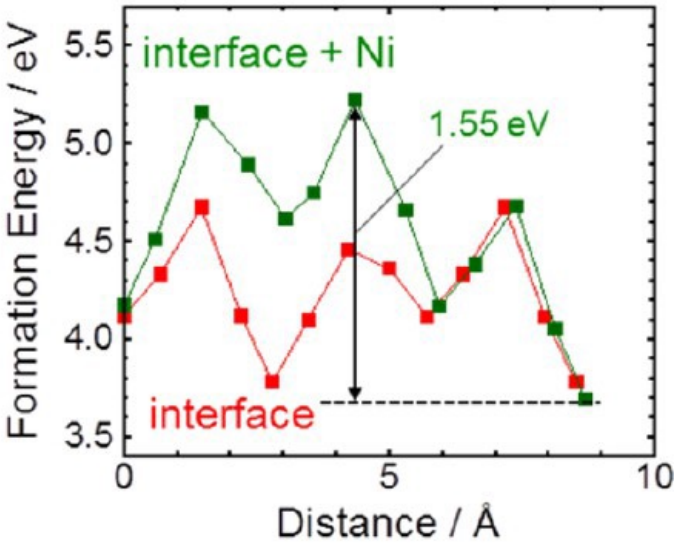
Li_2MnO_3-like migration across DB



migration along DB







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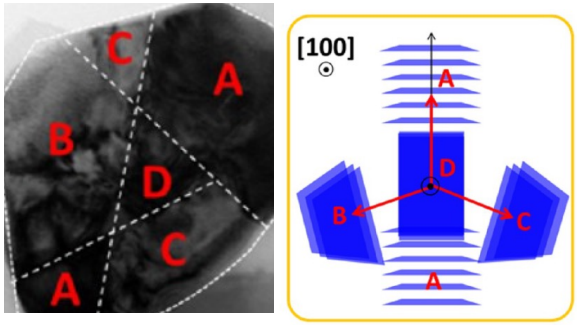
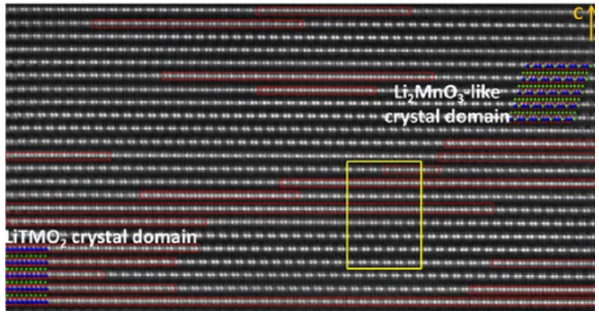
Summary:

The structure of Li-excess materials has multiple levels of ordering

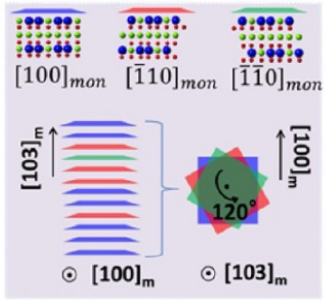
multidomains



"twin domain"

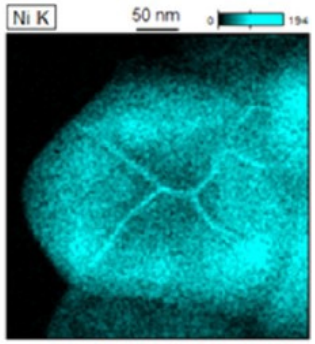


stacking faults

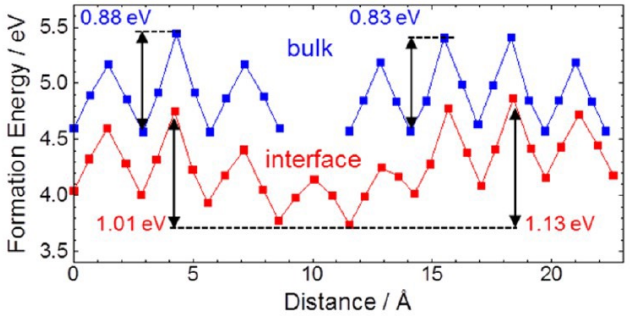


Structure could cause atom segregation and influence material properties like Li^+ diffusion

Ni segregation



Li^+ diffusion across DB



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Supplemental slides

Li^+ moves into and out of the layers during discharge and charge