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Crystallography and Crystal Chemistry
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Crystal chemical aspects of layered oxides as cathodes for lithium-ion batteries

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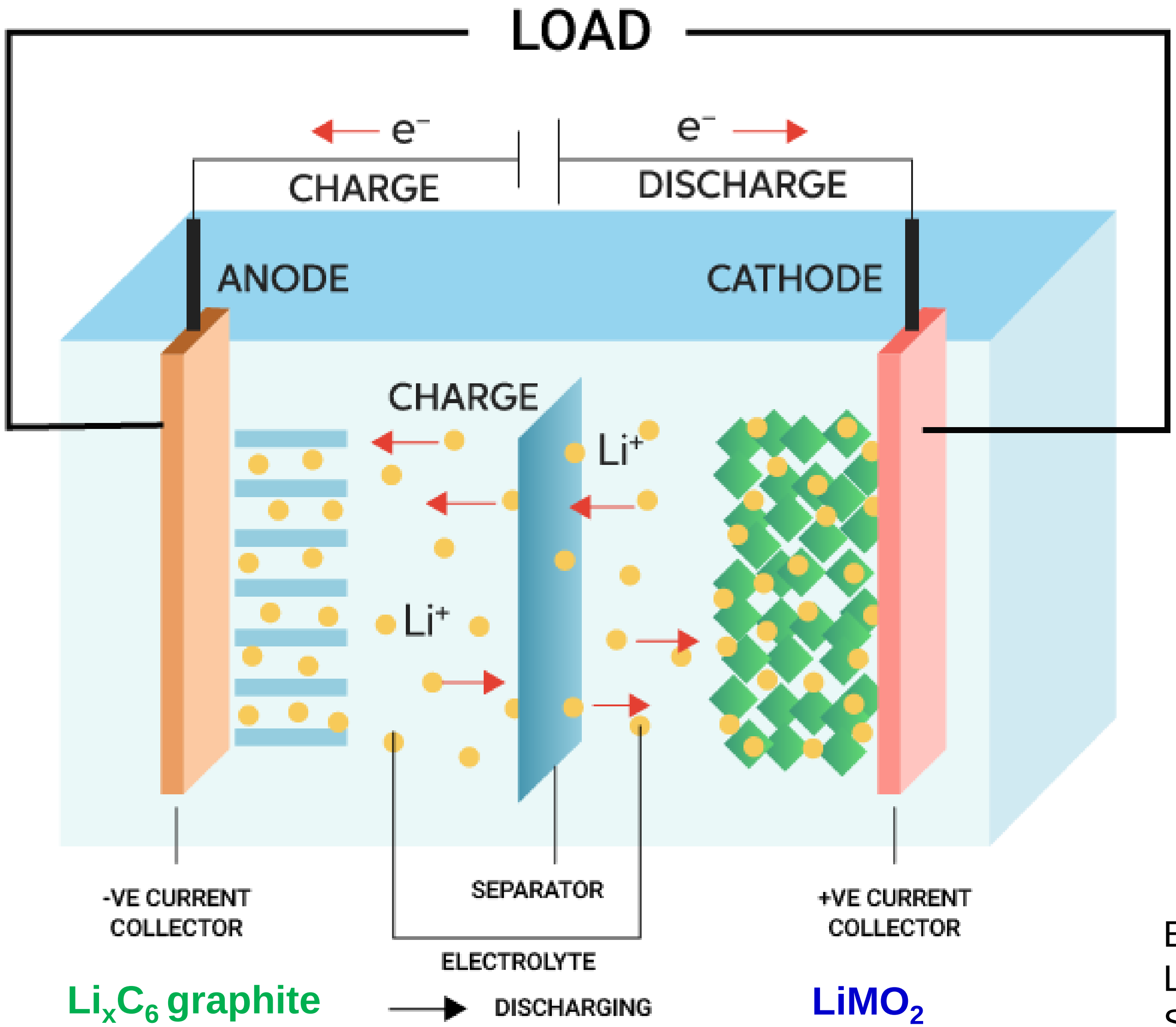
Skoltech, Moscow, Russian Federation

November 11th, 2023

Li-ion batteries



Li_xC_6 graphite

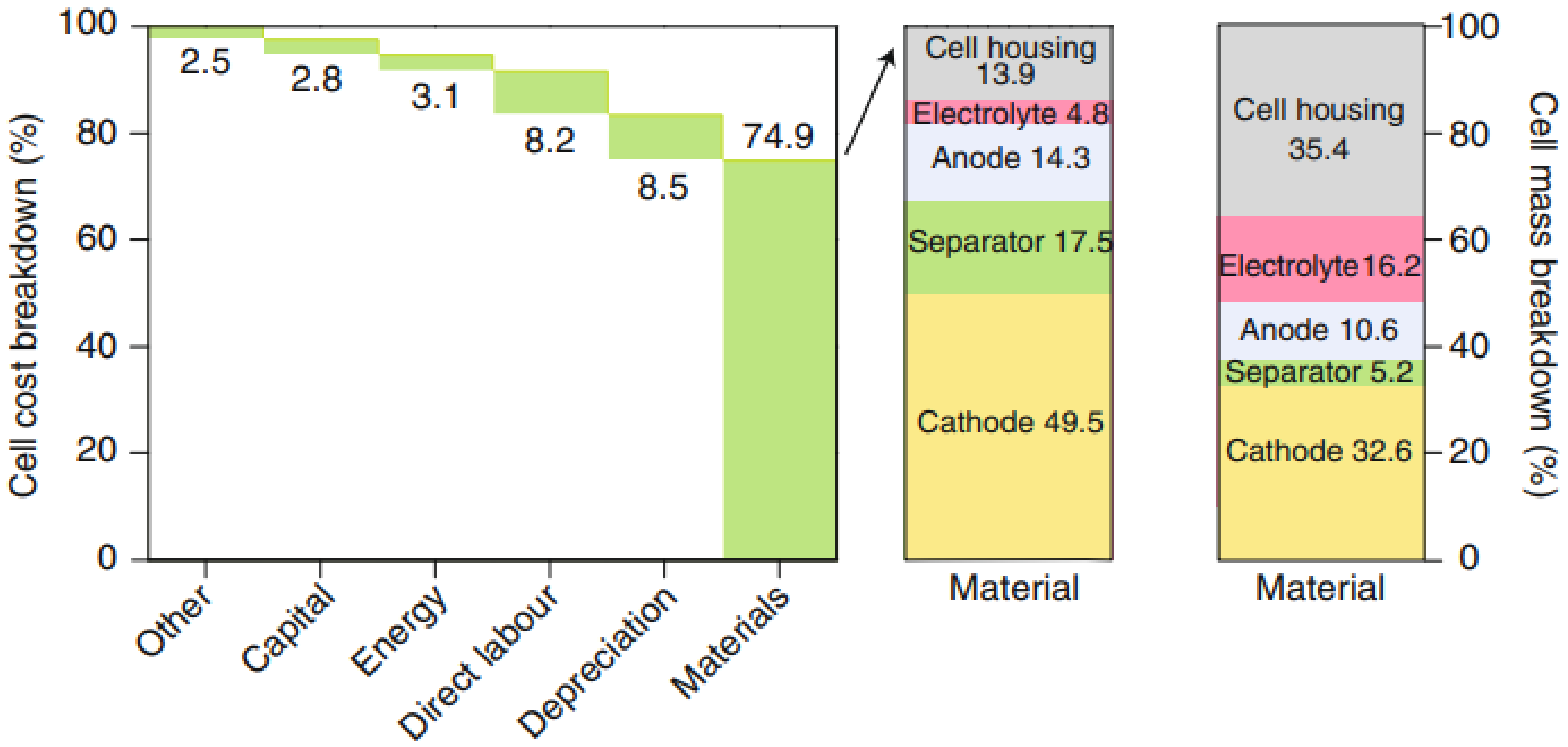
Li$^+$-conducting electrolyte

$LiMO_2$

$$C_6 + LiCoO_2 \underset{discharge}{\overset{charge}{\rightleftharpoons}} Li_xC_6 + Li_{1-x}CoO_2$$

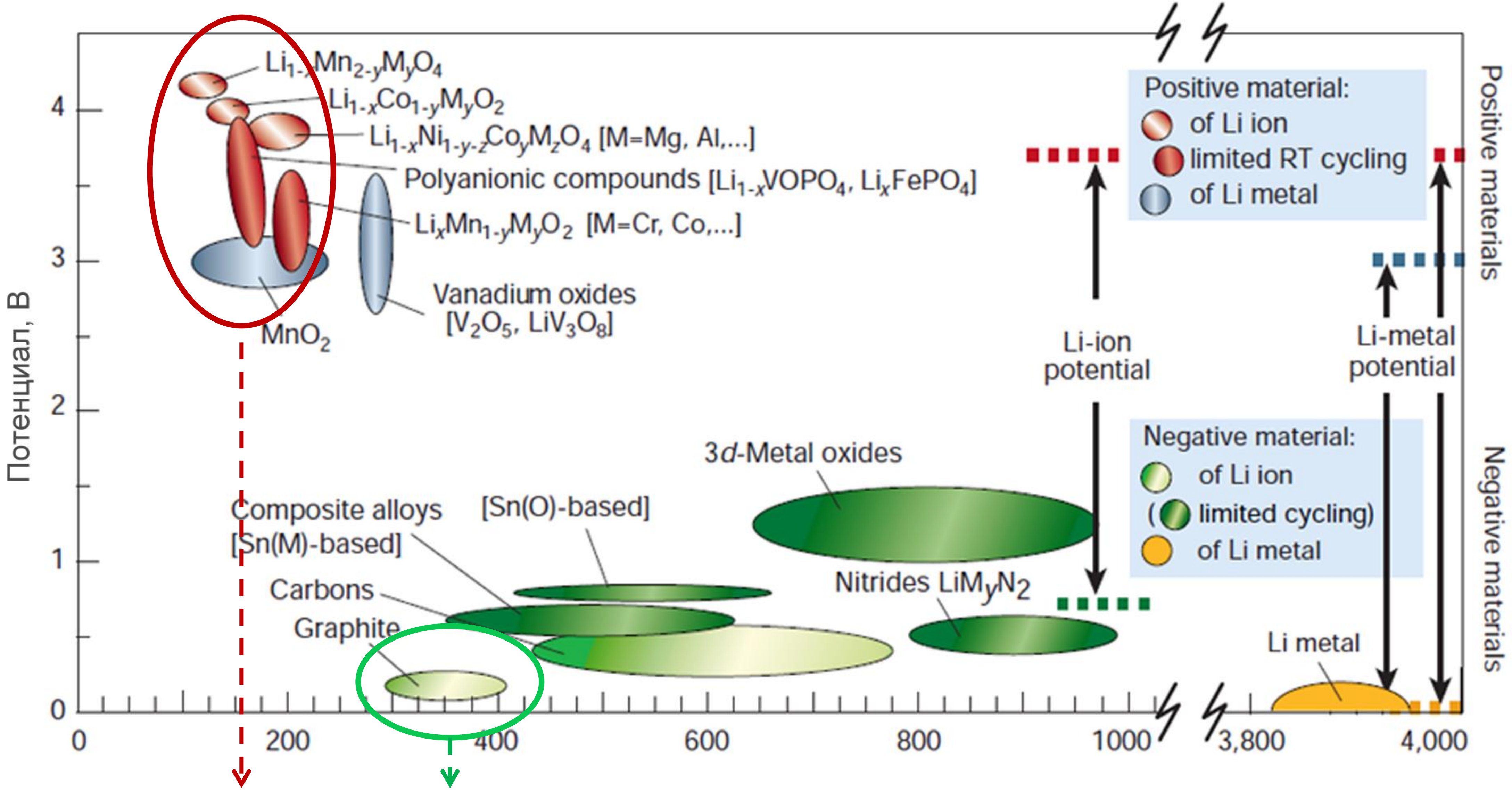
Electrolyte:
Li-salt -$LiPF_6$, $LiBF_4$($LiClO_4$, $LiAsF_6$), $LiCF_3SO_3$
Solvent–ethylene carbonate$(CH_2O)_2C$, dimethyl carbonate$(CH_3O)_2CO$ ….

Li-ion batteries



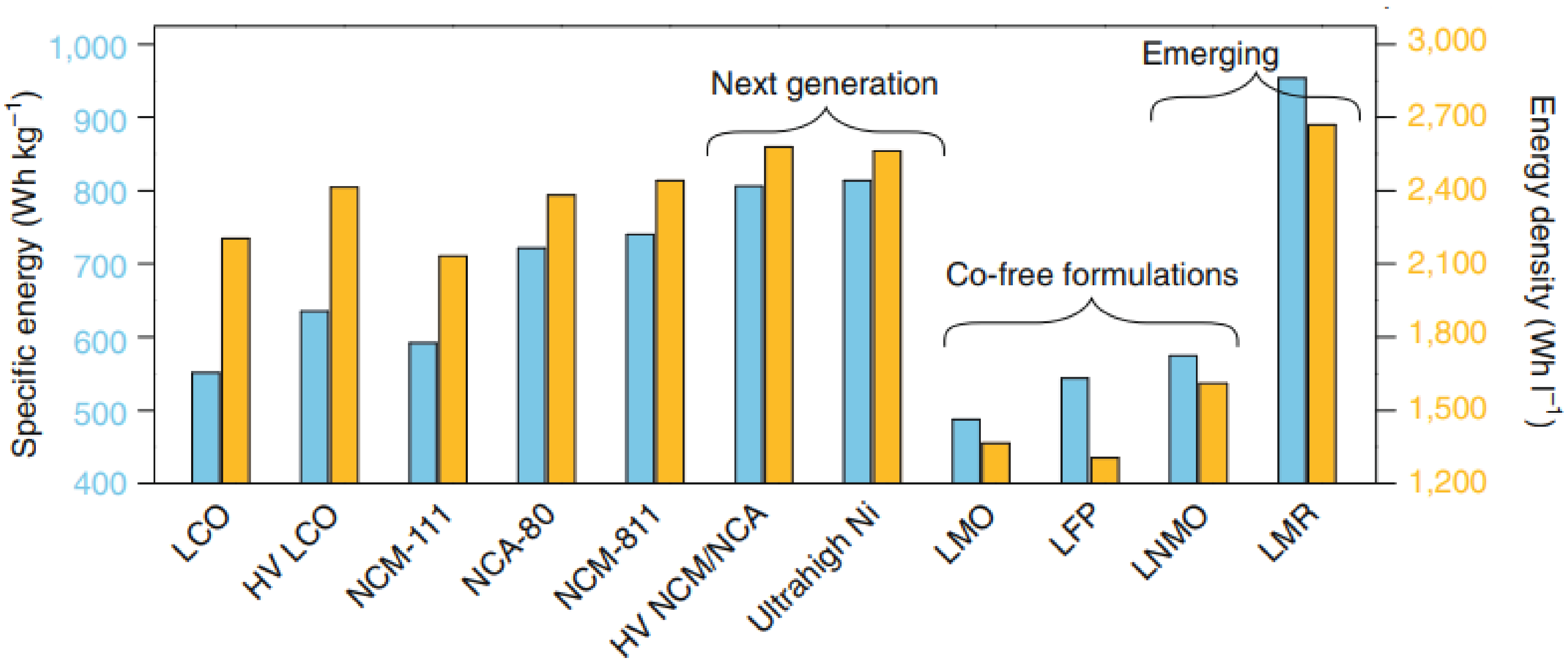
doi: 10.1038/s41560-019-0513-0

Materials for LIBs

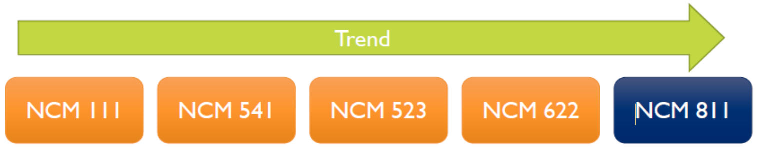


140-180 Ah/kg **>300 Ah/kg**

Cathode materials for LIBs



LCO - $LiCoO_2$
NCA - $LiNi_{0.84}Co_{0.12}Al_{0.04}O_2$
LFP - $LiFePO_4$
LMO - $LiMn_2O_4$
LNMO- $LiMn_{1.5}Ni_{0.5}O_4$
NMC - $Li(Ni_xMn_yCo_z)O_2$, $x + y + z = 1$
    NMC111 $LiNi_{1/3}Mn_{1/3}Co_{1/3}O_2$
    NMC811 $LiNi_{0.8}Mn_{0.1}Co_{0.1}O_2$
LMR – Li-rich NMC

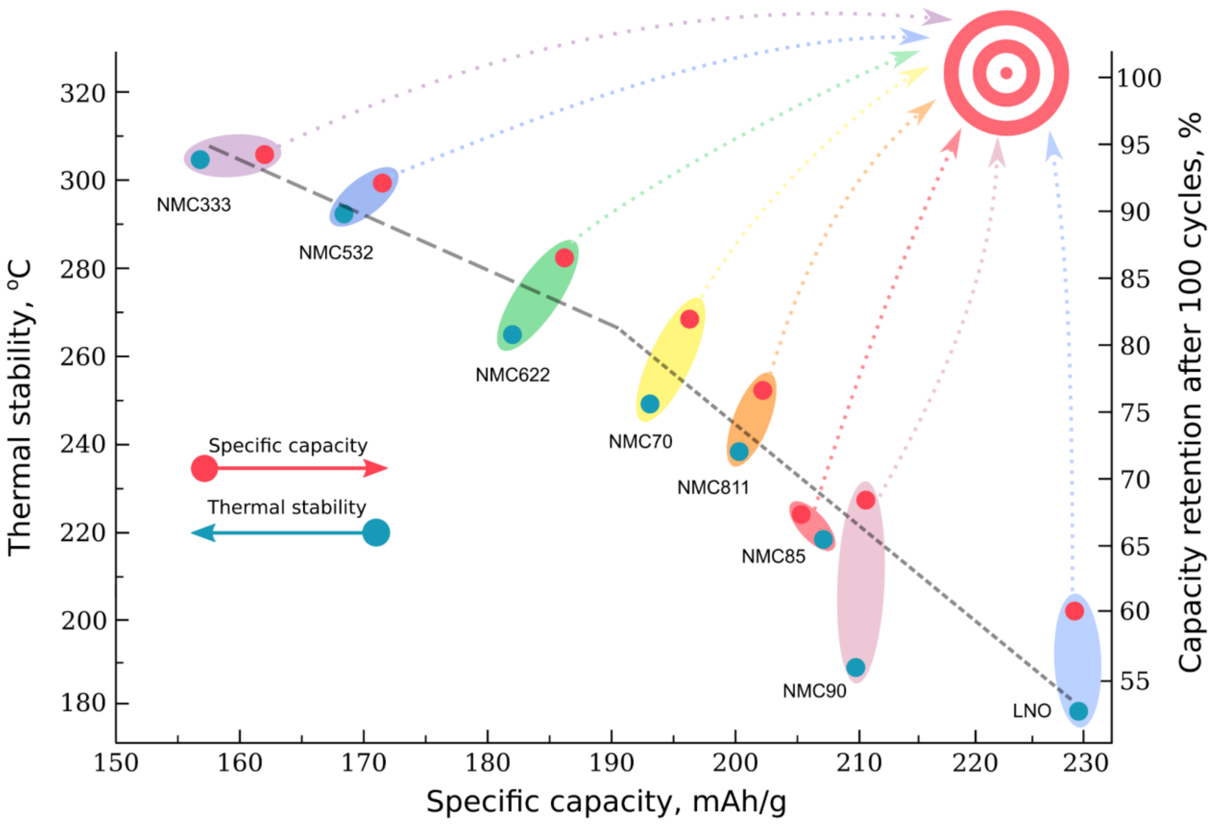


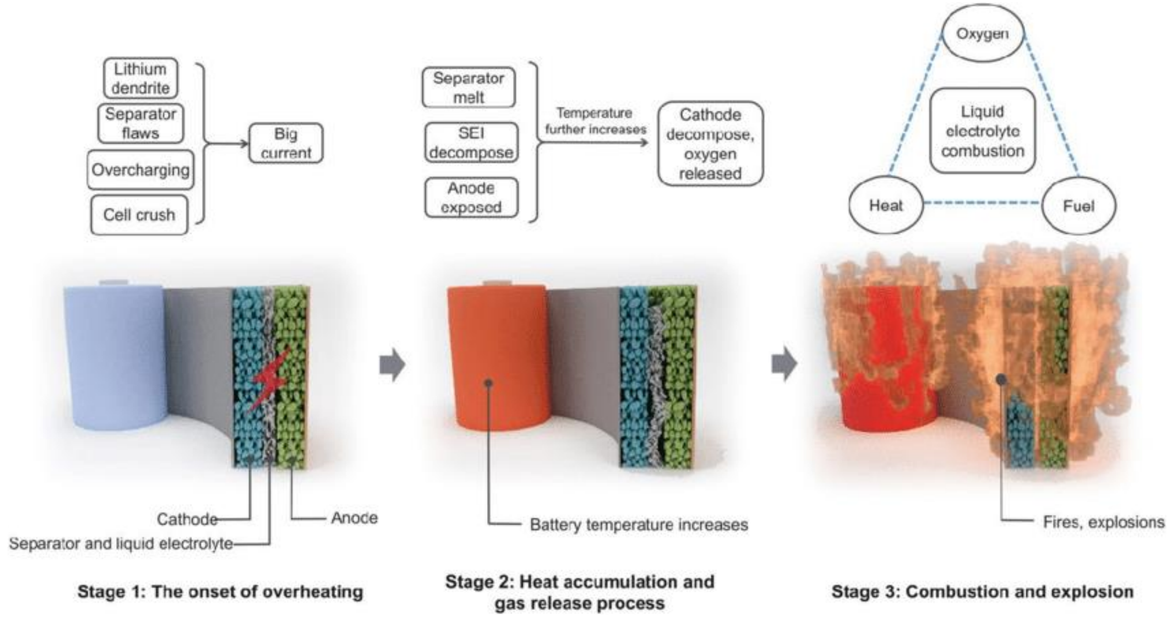
doi: 10.1038/s41560-019-0513-0

Key characteristics of cathode materials

Formula	Specific energy density, Wh/kg	Specific capacity, mAh/g	Advantages	Disadvantages
$LiMn_2O_4$ (LMO)	405	100	Low cost	Low energy density
$LiCoO_2$ (LCO)	610	150	Moderate stability	High cost
$LiFePO_4$ (LFP)	515	150	High power density High stability	Low energy density
$LiNi_{1/3}Mn_{1/3}Co_{1/3}O_2$ (NMC111)	600	160	High stability	Low energy density
$LiNi_{0.6}Mn_{0.2}Co_{0.2}O_2$ (NMC622)	685	180	Relatively high energy density	Relatively low stability
$LiNi_{0.8}Mn_{0.1}Co_{0.1}O_2$ (NMC811)	760	200	High energy density Low cost	Relatively low stability
Li-rich NMC	1000	250	High energy density Low cost	Not commercialized Slow kinetics Voltage fade

Cathode materials





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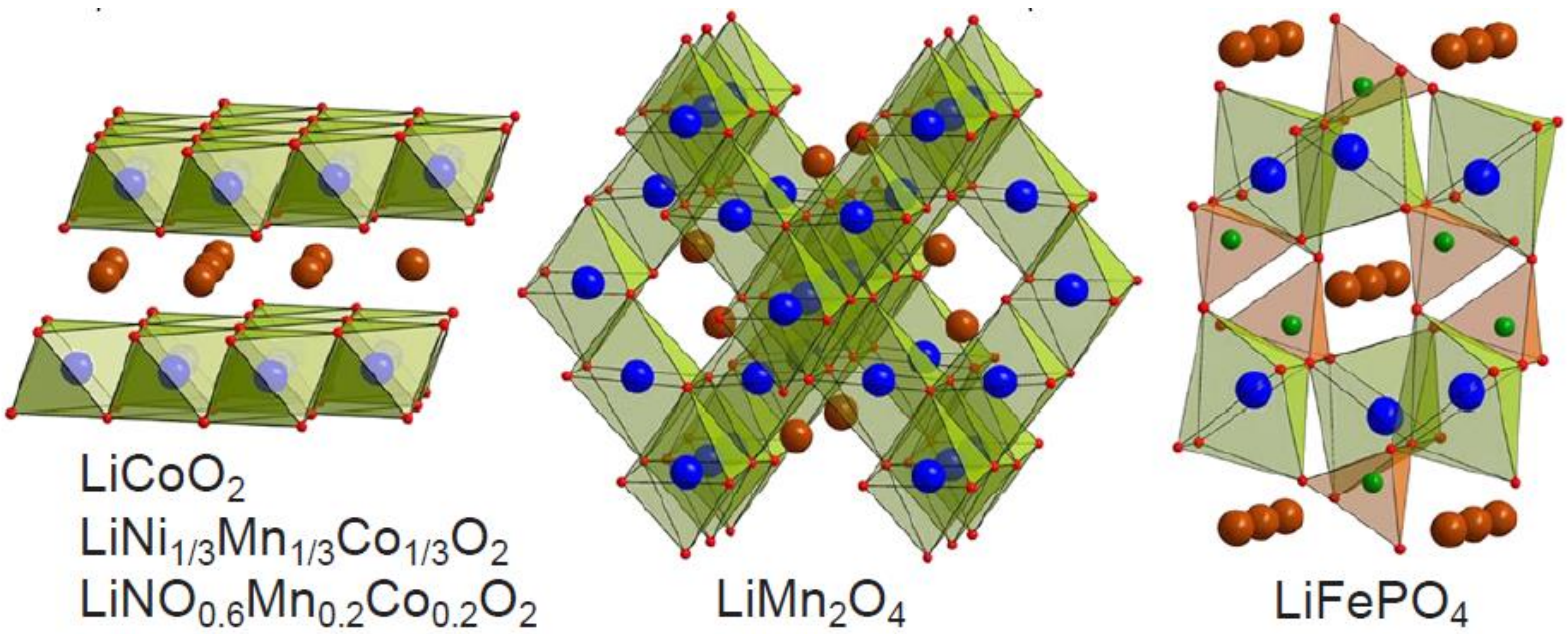
Crystal structures of currently used cathode materials



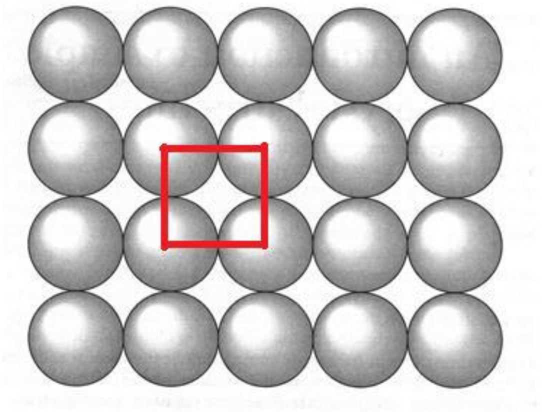
A_xMO_2

2D Li transport

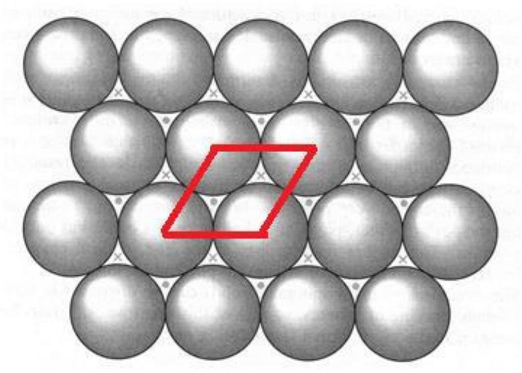
3D Li transport

1D Li transport

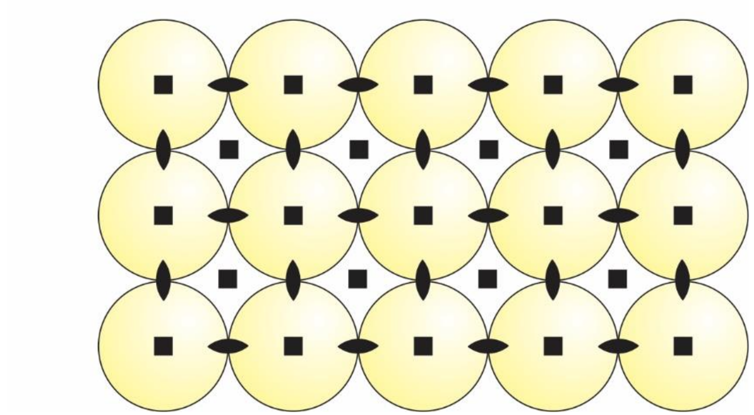
Close-packing of equal spheres



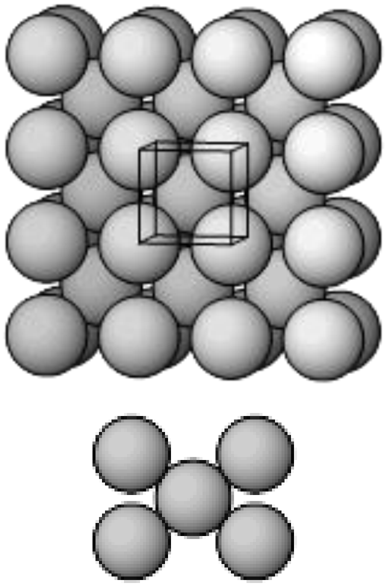
tetragonal



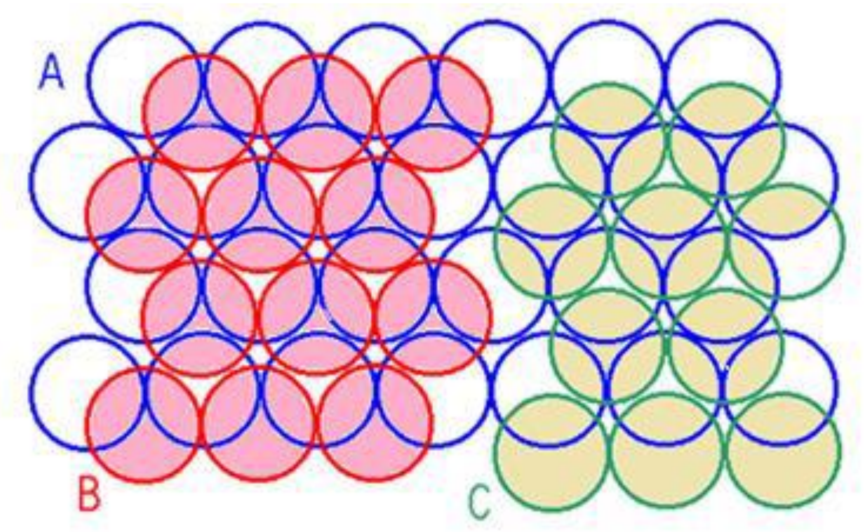
hexagonal



Simple tetragonal or hexagonal packing

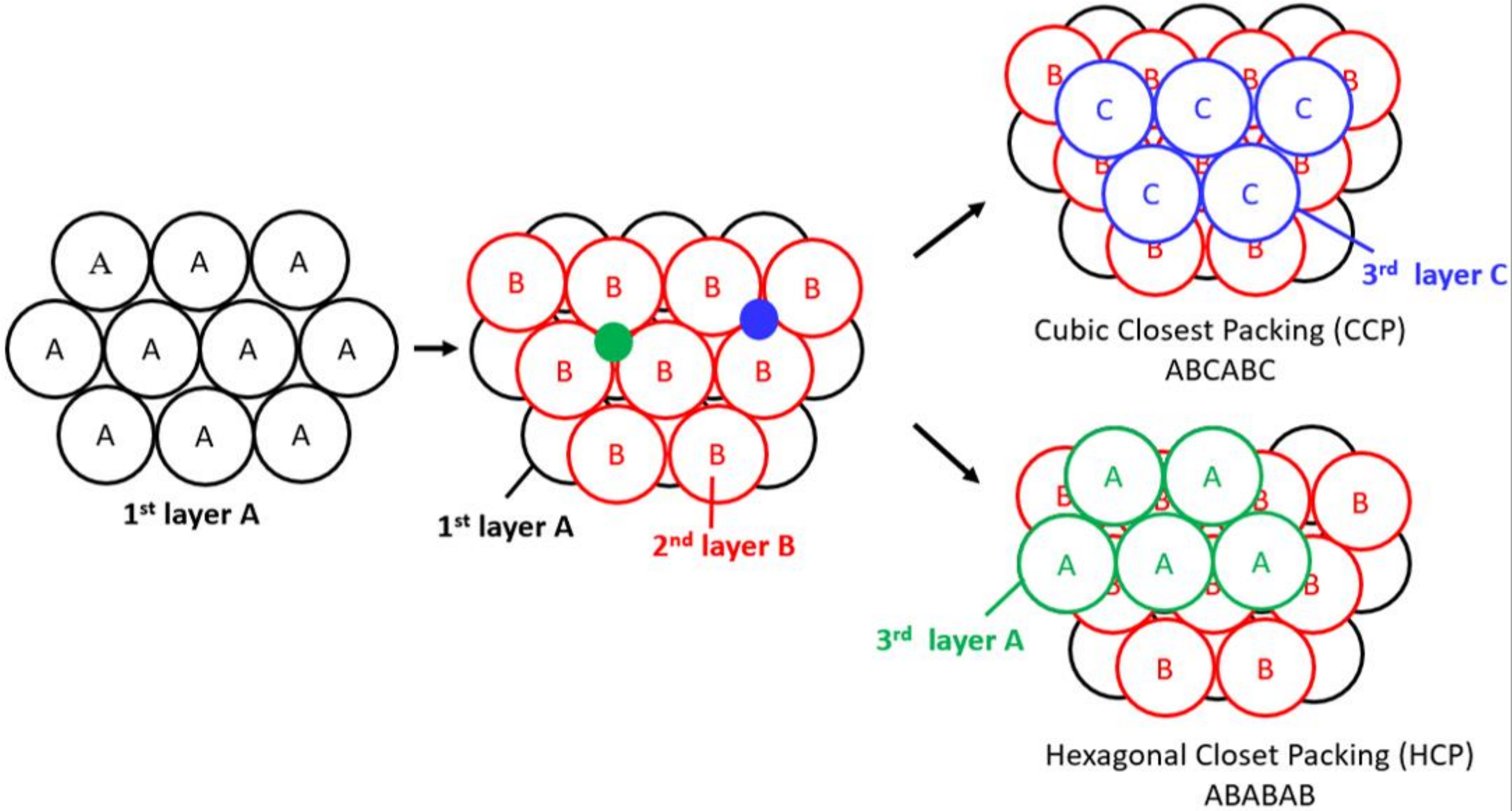


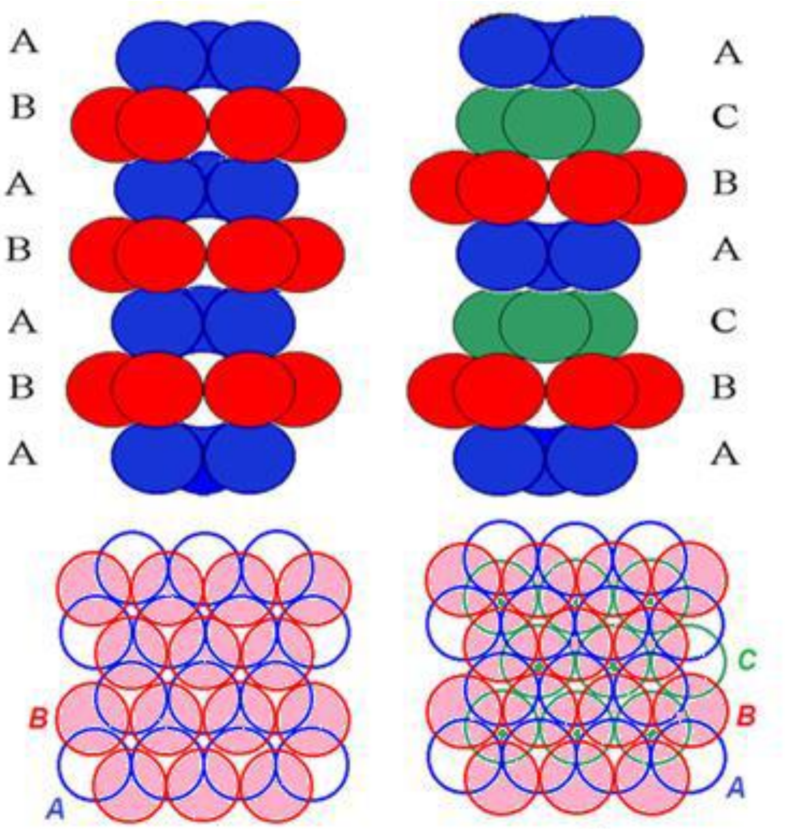
Body-centered cubic packing



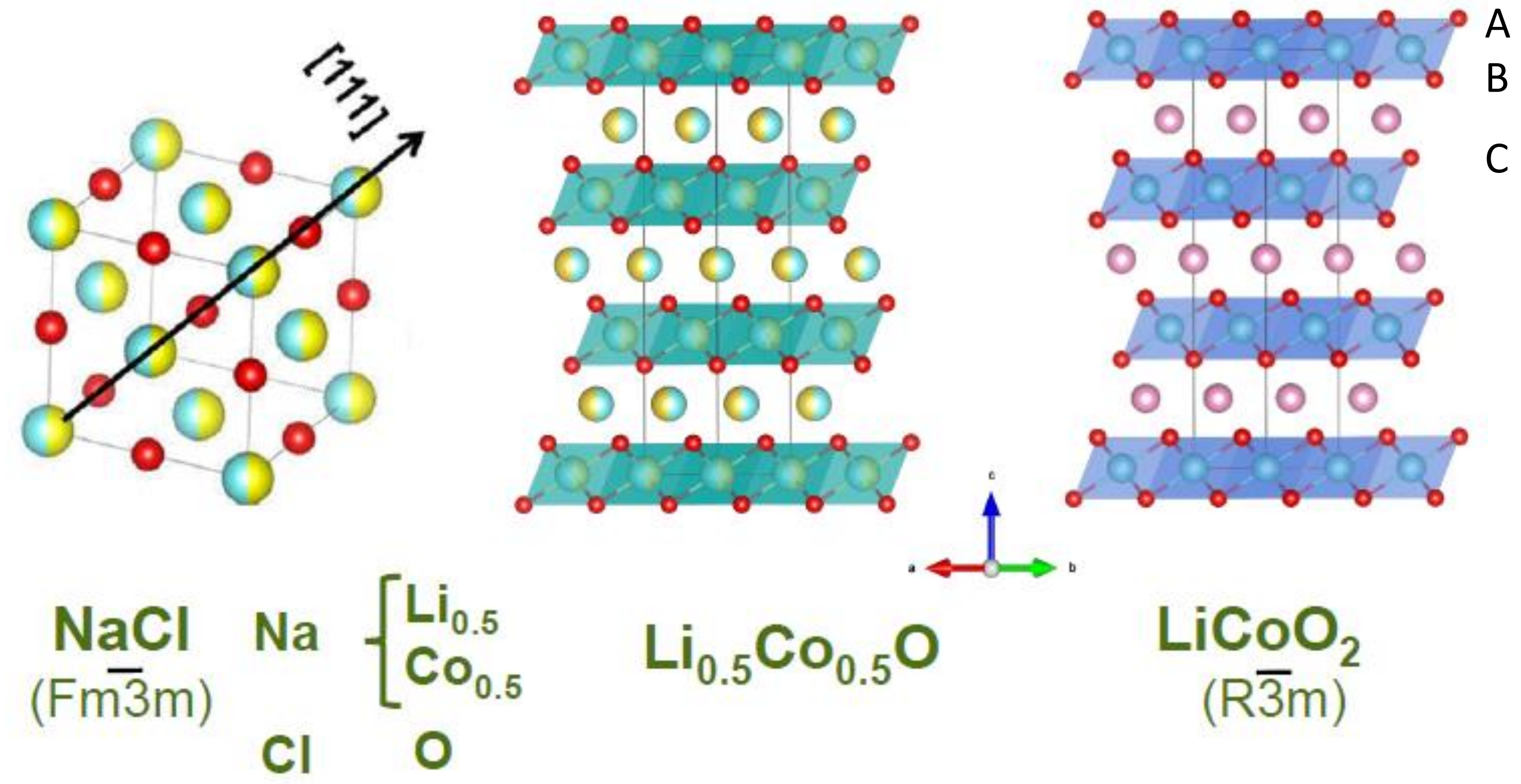
close-packing

Close-packing of equal spheres



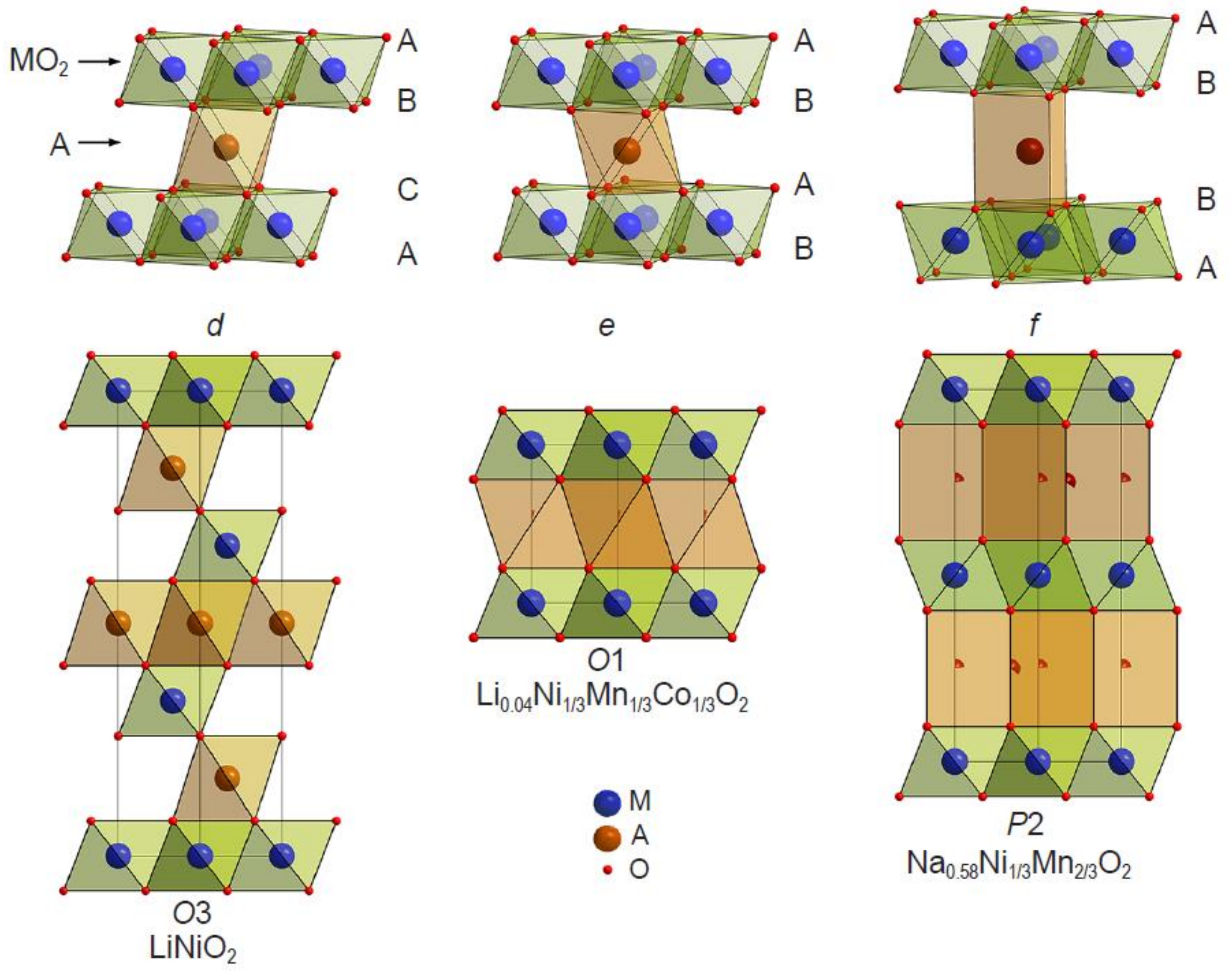


Crystal structure of layered oxides



$$a \approx a_{RS}/\sqrt{2} \approx 2.9\text{Å},\ c \approx a_{RS}2\sqrt{3} \approx 14.2\text{Å}$$

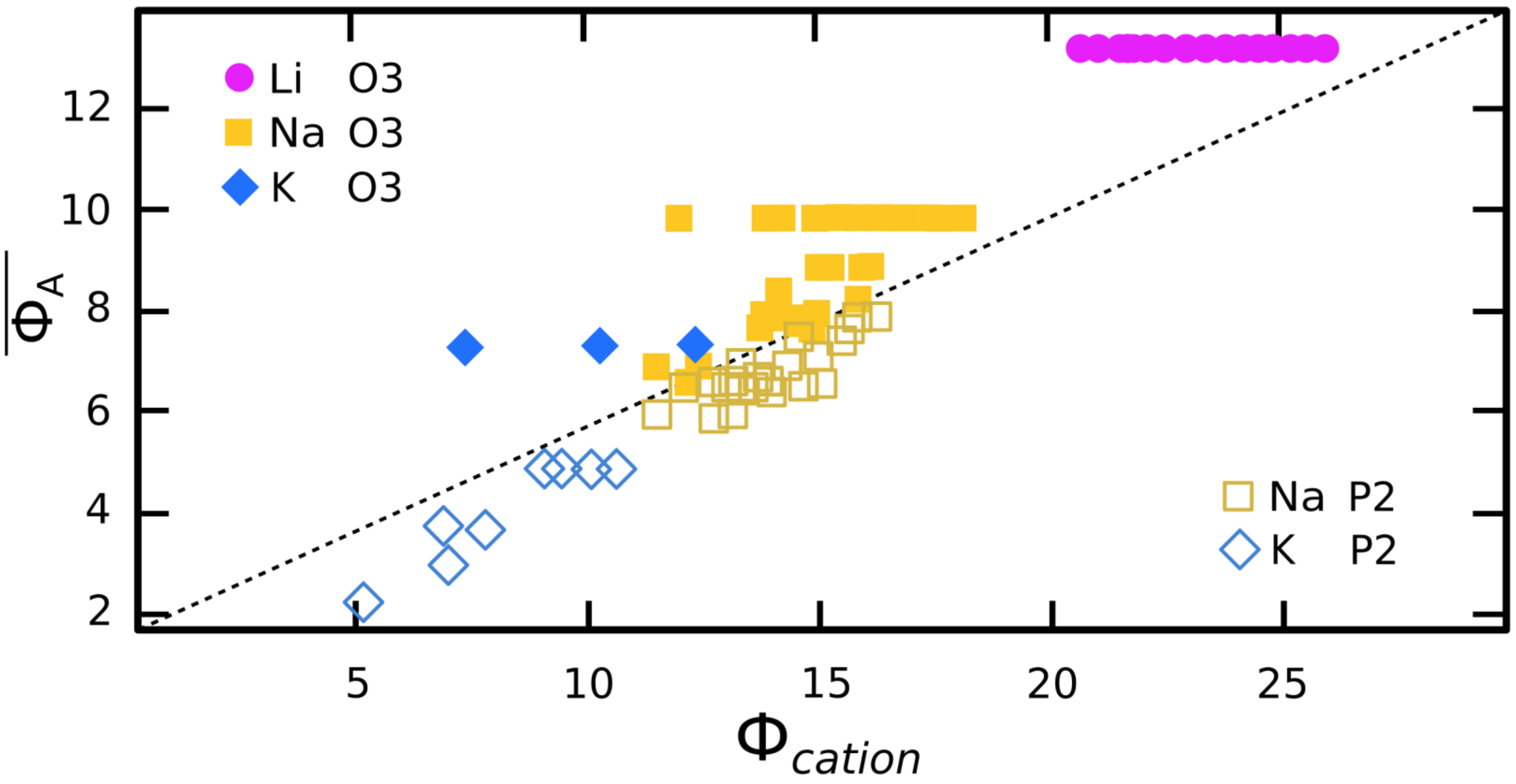
Various types of packings in layered oxides



XI, where
“X” is a capital Latin letter denoting the coordination environment of the alkali metal A (O – octahedral, T – tetrahedral, P – prismatic),
“I” is a value equal to the number of MO_2 layers per one return period along directions of layer alternation.

10.1016/0378-4363(80)90214-4

Crystal structure of layered oxides



Cationic potential phase map for alkali metal layered oxides A_xMO_2

"cationic potential"

$$\Phi_{cation} = \frac{\overline{\Phi_M} \cdot \overline{\Phi_A}}{\overline{\Phi_O}}$$

where $\overline{\Phi_M} = \sum_i w_i \frac{n_i}{r_i}$,

and represents the weighted average ionic potential of TMs

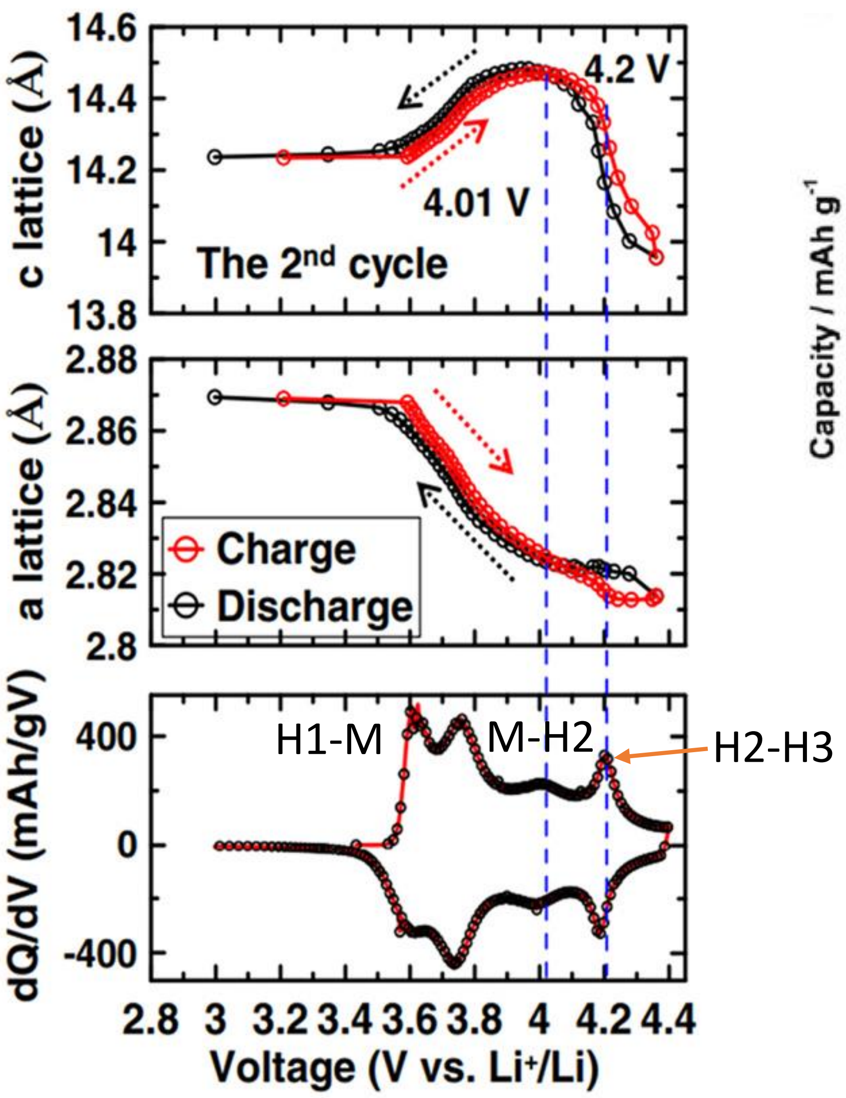
w_i is the content of TM_i having charge number n_i and radius r_i

$$\overline{\Phi_A} = \frac{x}{r_A}$$

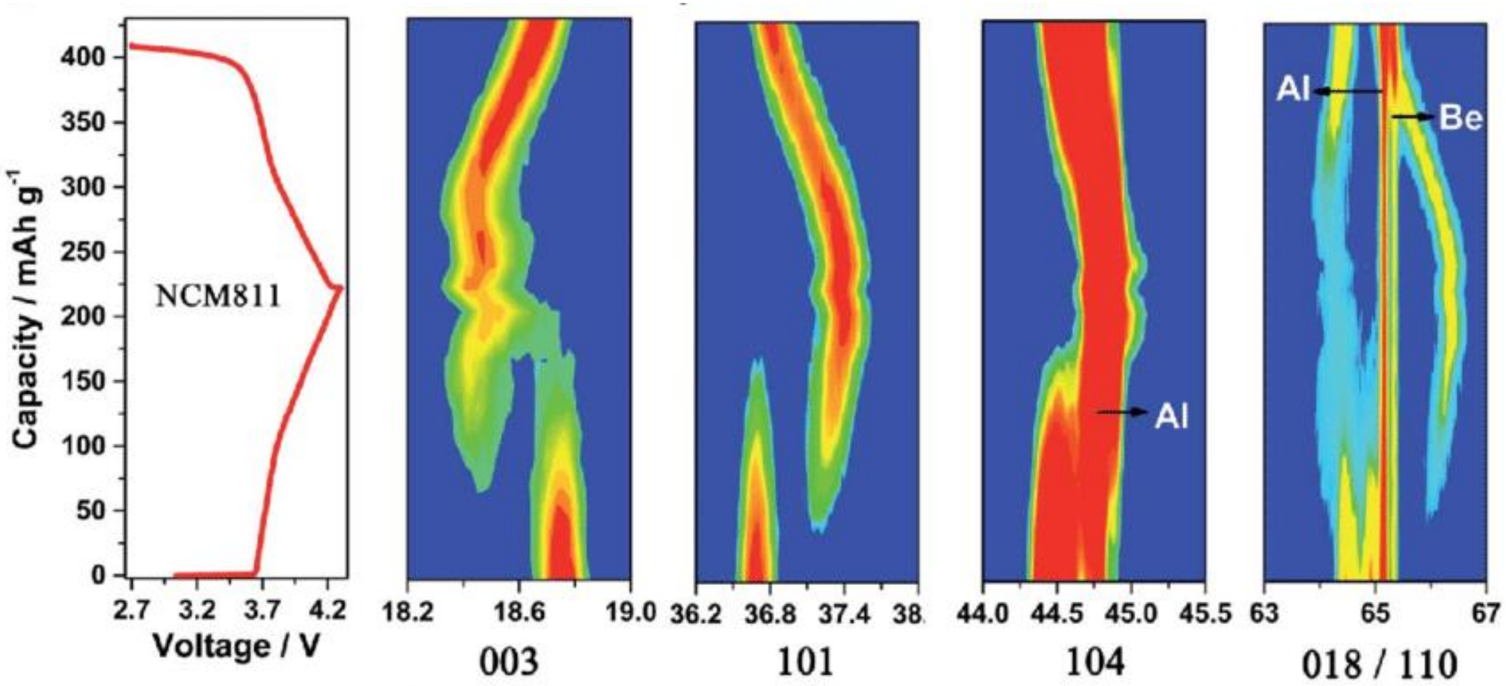
represents the weighted average ionic potential of A

10.1126/science.aay9972

Crystal structure of layered oxides during charge/discharge



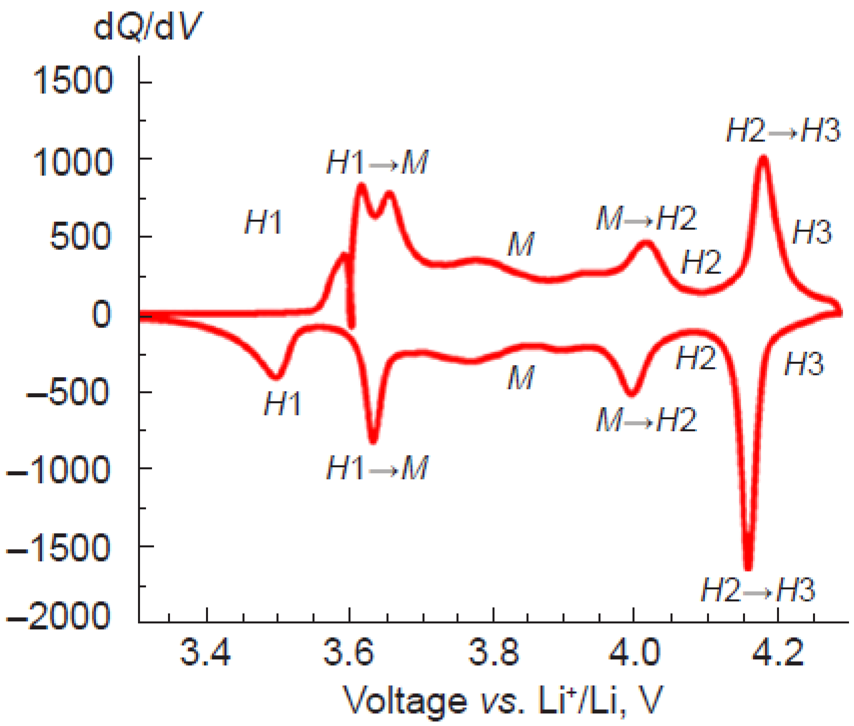
The *c* lattice and *a* lattice of NCM811 and the dQ/dV plot

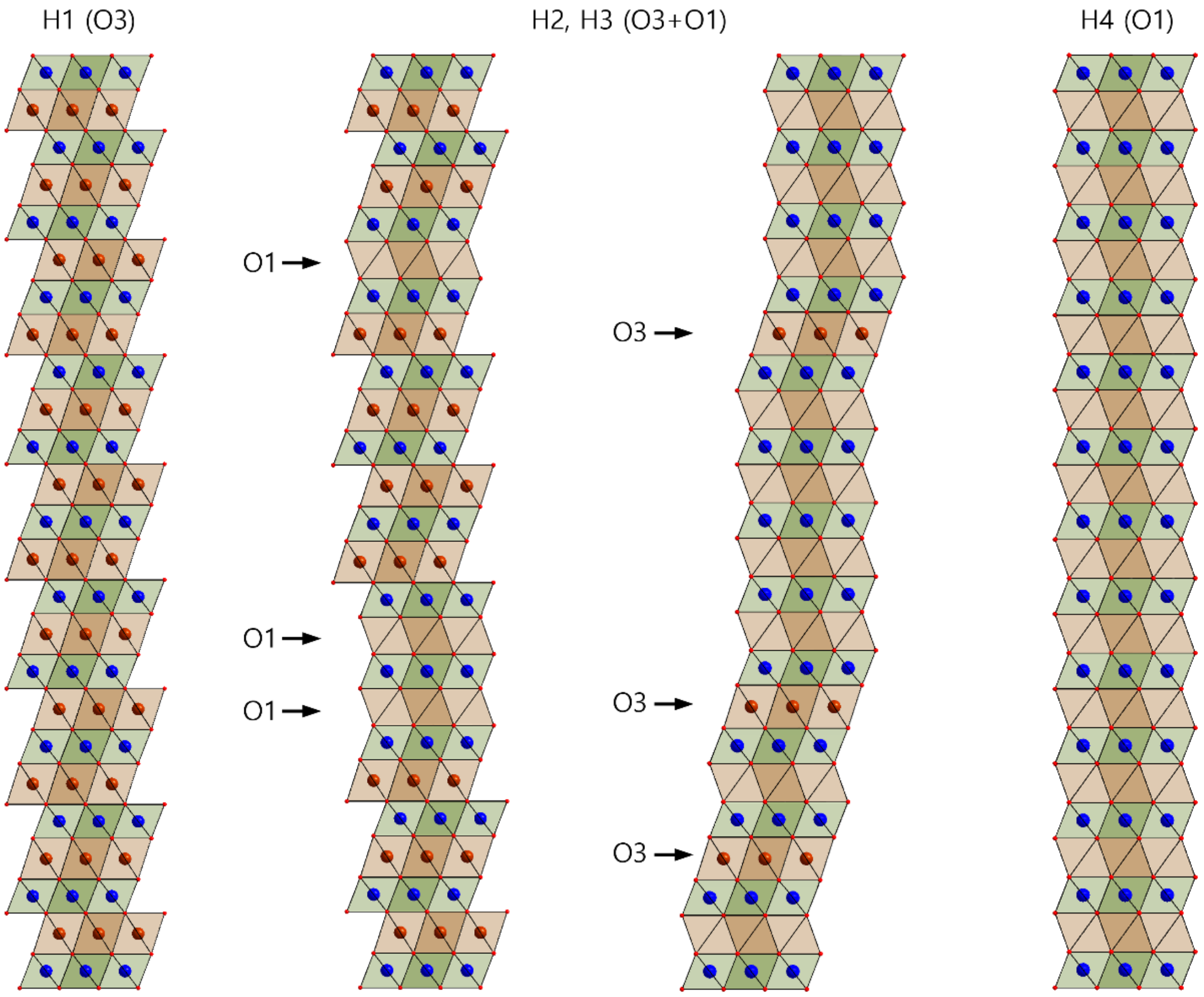


In situ XRD examinations during charging/discharging of NMC811 in the first cycle, showing recorded charge/ discharge curves and contour plots of 003, 101, 104 and 018/110 reflections

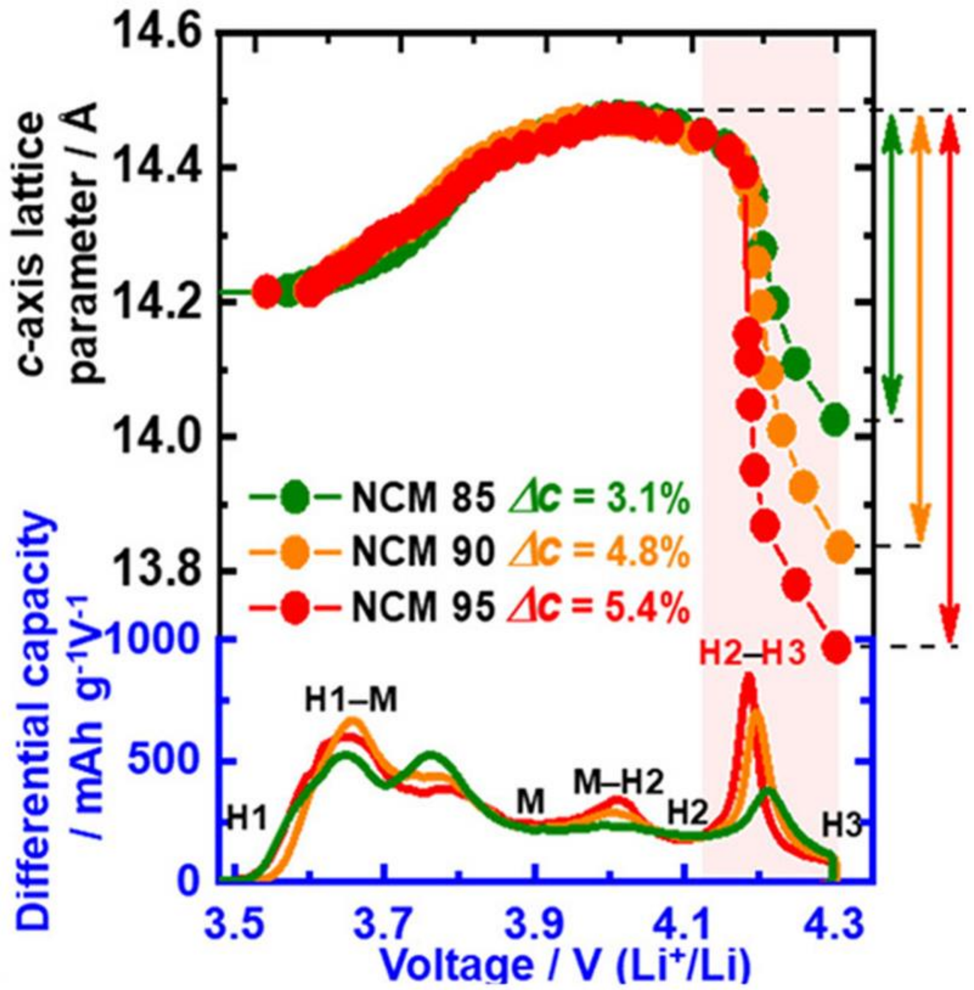
10.1016/j.susmat.2021.e00305

Crystal structure of layered oxides during charge/discharge

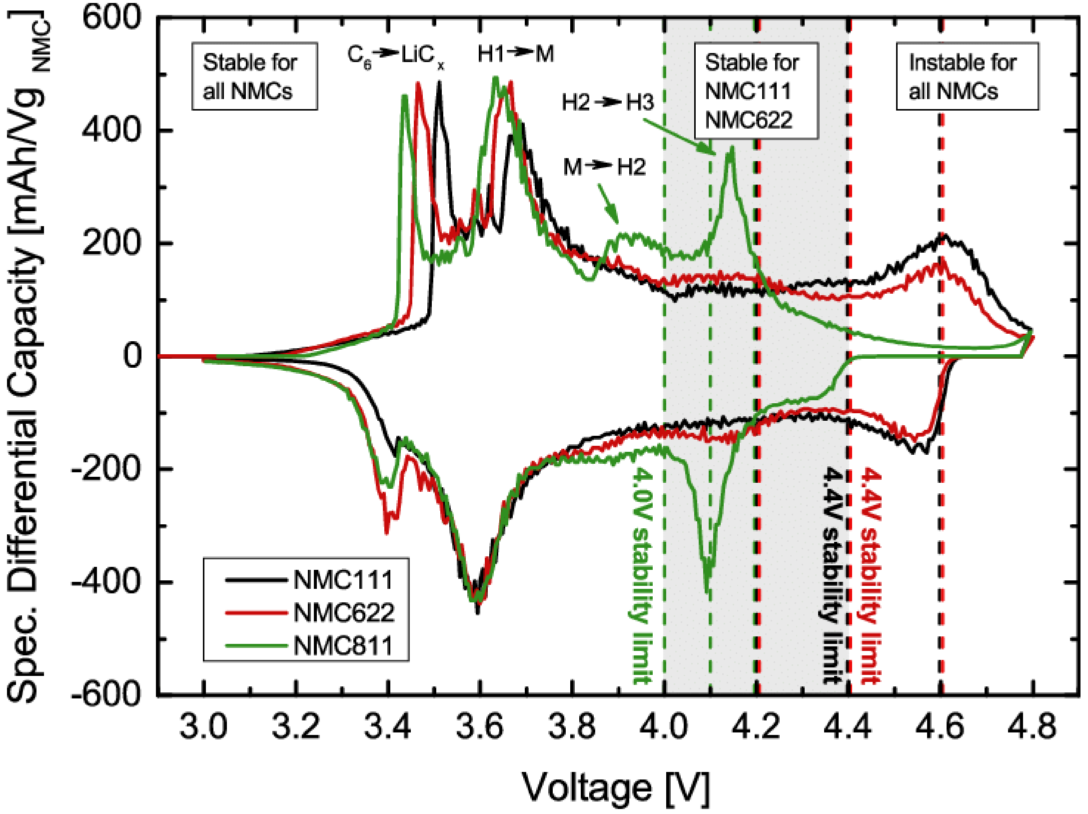




Crystal structure of layered oxides during charge/discharge



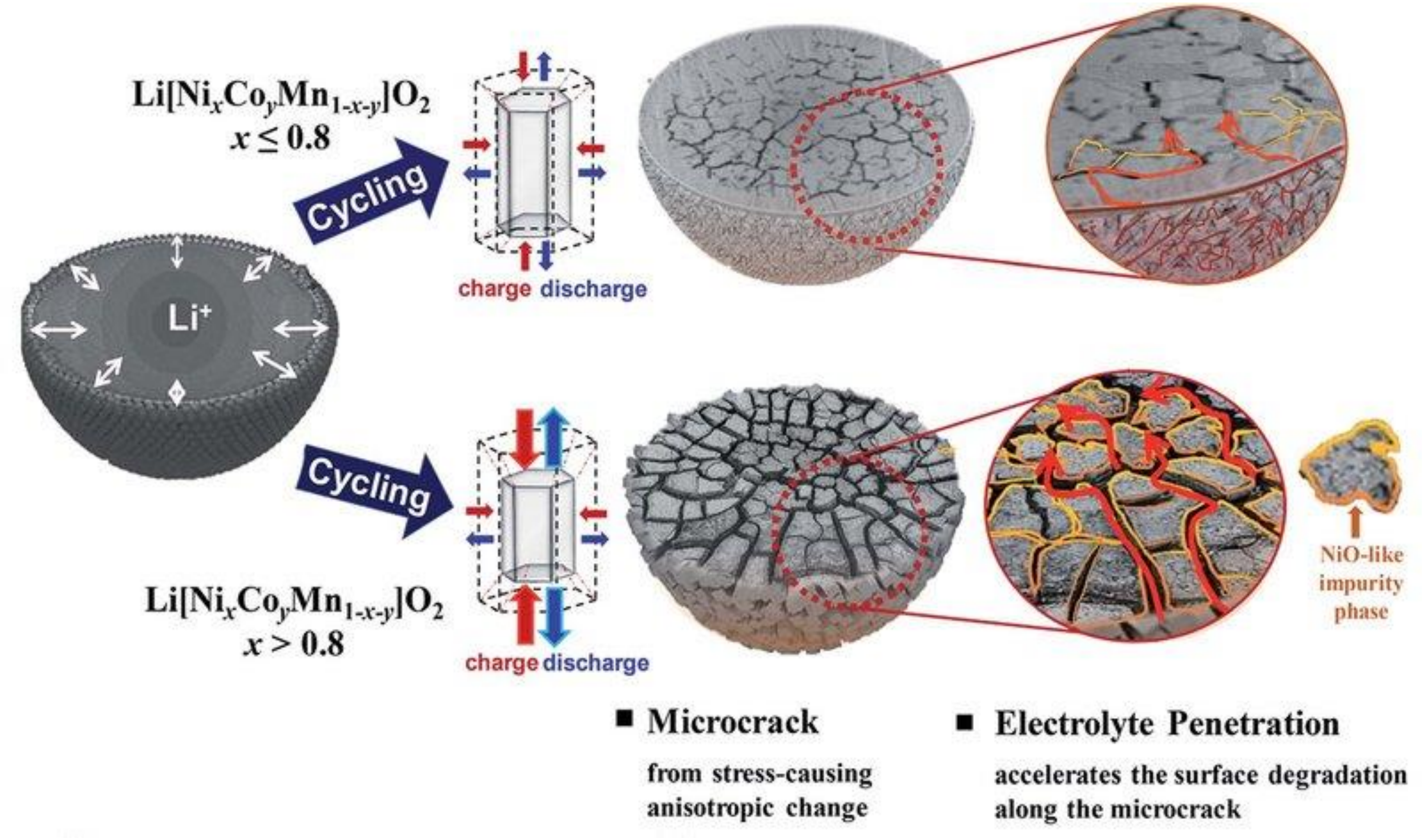
Comparison of the variation in the *c* lattice changes and corresponding differential capacity of the NMC cathodes



The dQ/dV plots for NMC cathodes

10.1016/j.susmat.2021.e00305

Degradation of layered oxides during charge/discharge

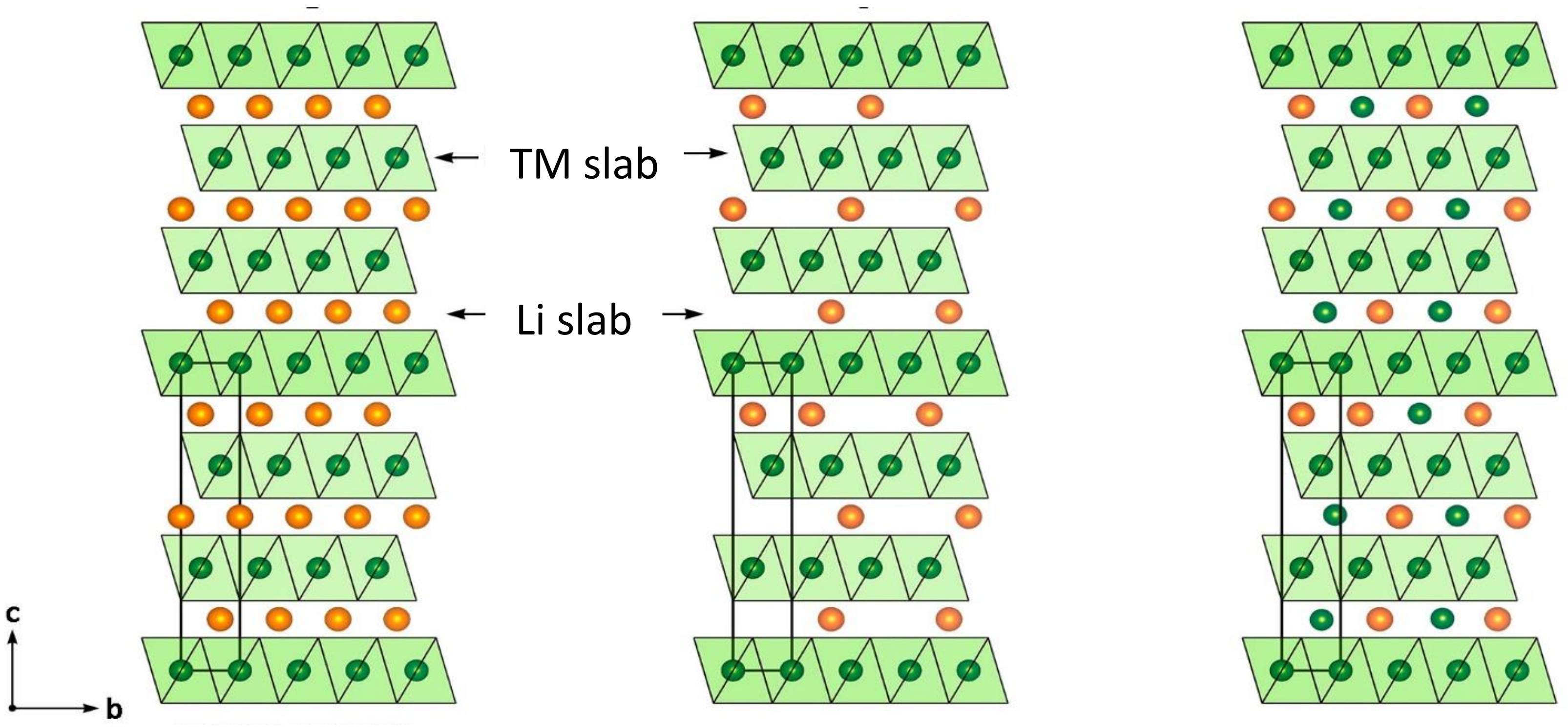


Microcracks and oxygen release are critical for NMC cathode failure

Degradation schematic model of NMC cathodes

10.1016/j.susmat.2021.e00305

Cation migration and oxygen release in layered oxides during charge/discharge



ordered structure

structure with Li vacancies in highly charged state

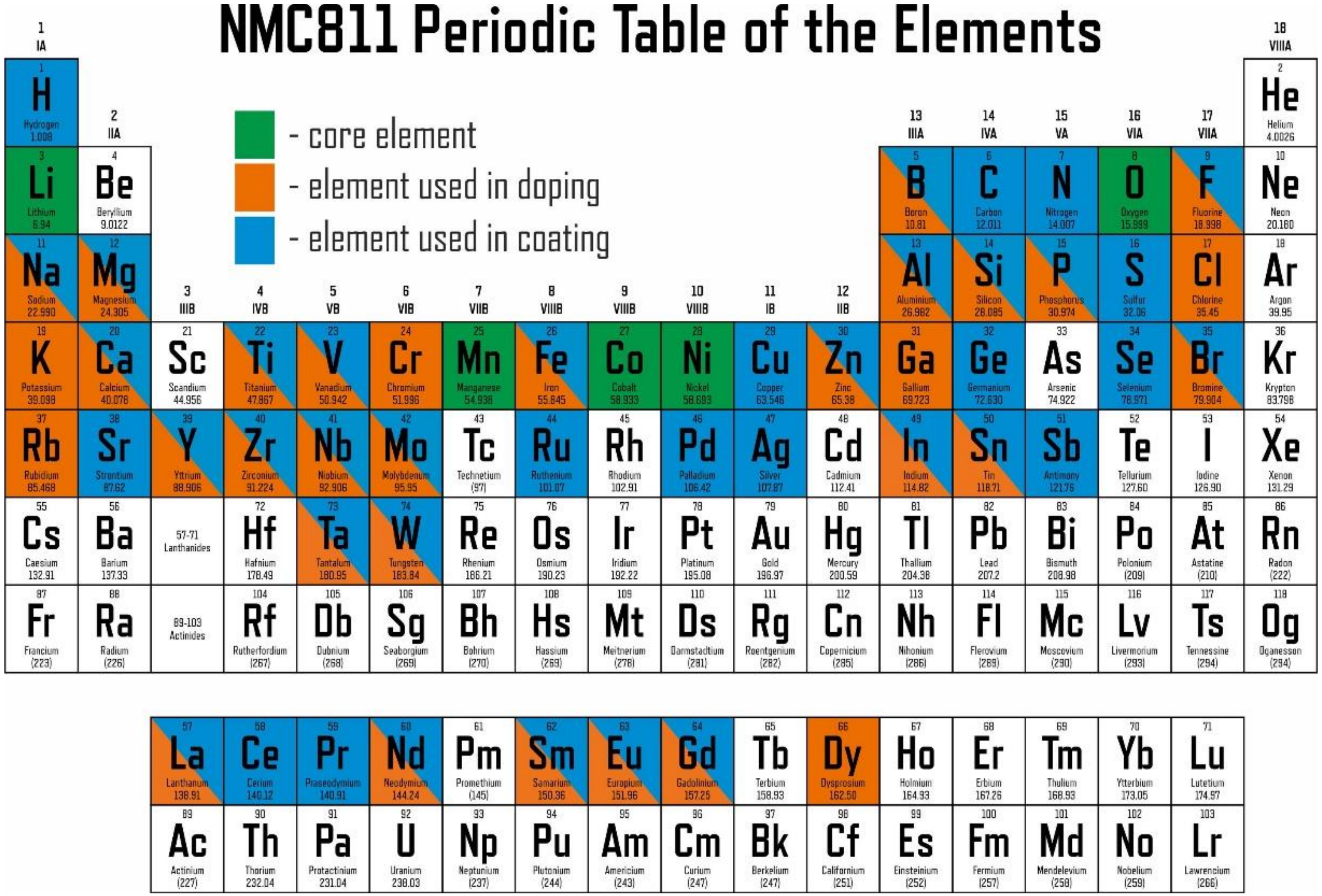
Partially cation mixed phase with TM ions in Li slab (TMO)

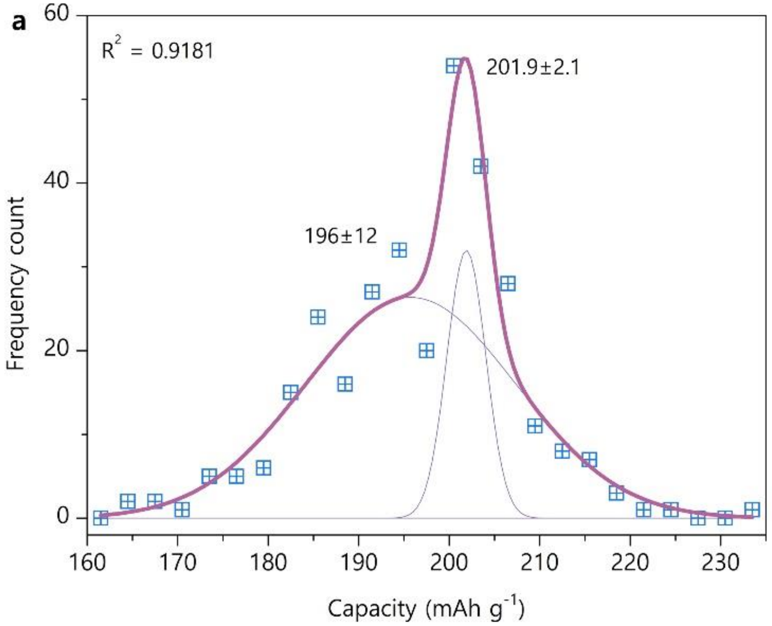
$r(Ni^{2+}) = 0.69$ Å, $r(Li^{+}) = 0.76$ Å

$$2Li_{0.5}NiO_2 \text{ (ordered)} \rightarrow LiNi_2O_4 \text{ (spinel)}$$

$$4Li_{0.5}NiO_2 \text{ (ordered)} \rightarrow 4NiO + \text{“}Li_2O\text{”} + 3/2O_2$$

Modification of layered oxides

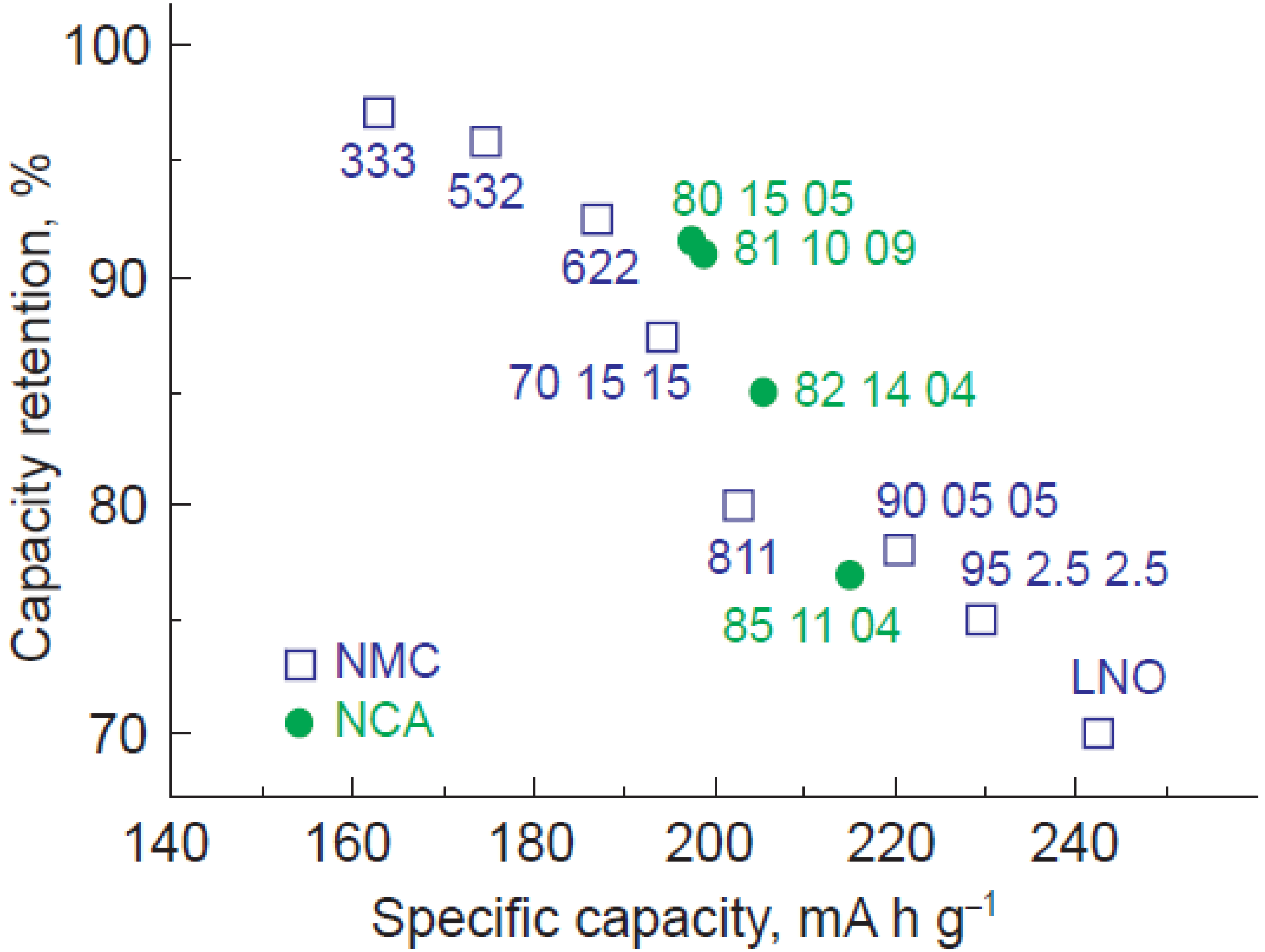


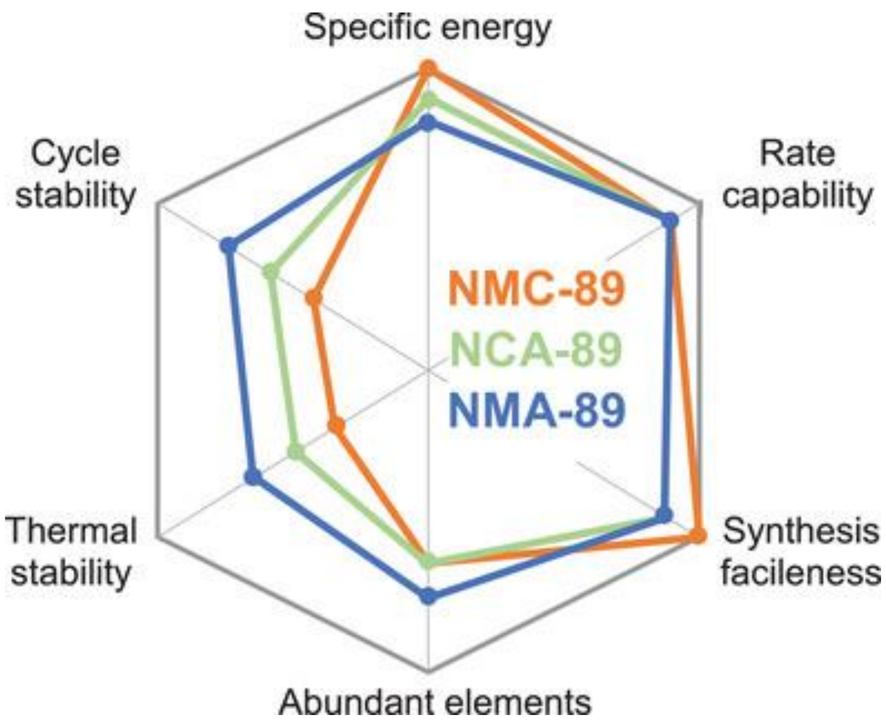


Chemical elements utilized in various doping and coating strategies targeting improvement of the functional properties of NMC811 cathode materials, based on the data from 381 publications from the years of 2009 – 2023.

https://ssrn.com/abstract=4524502

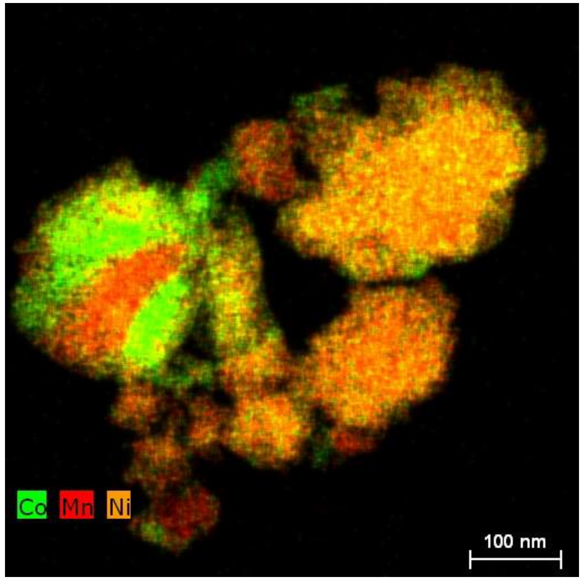
Modification of layered oxides

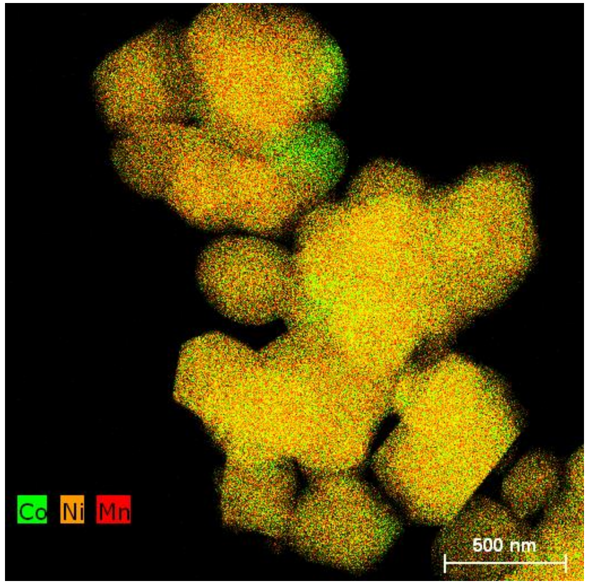


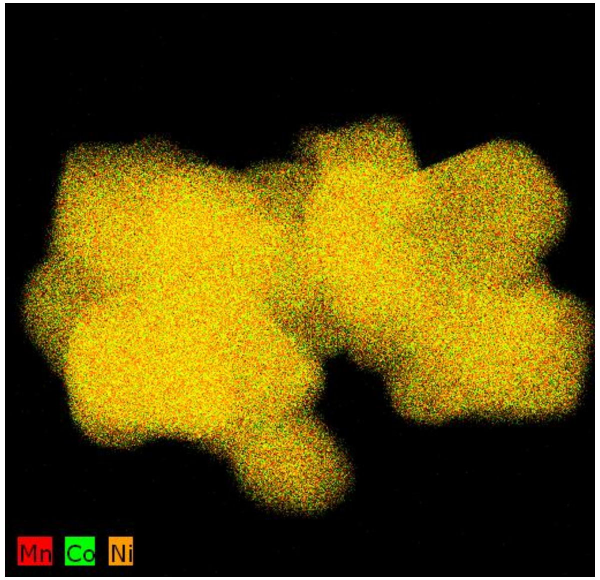


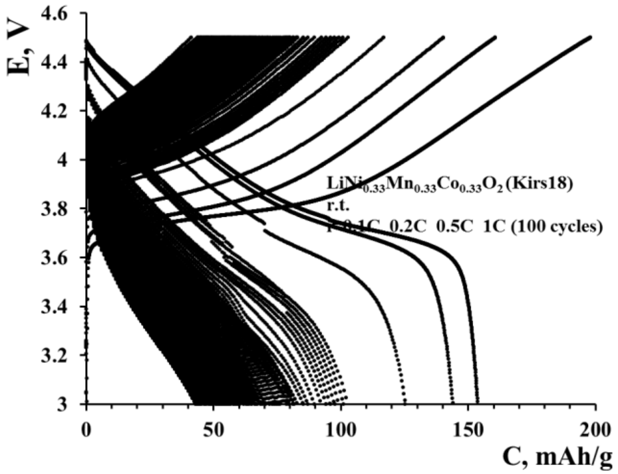
Synthesis of layered oxides

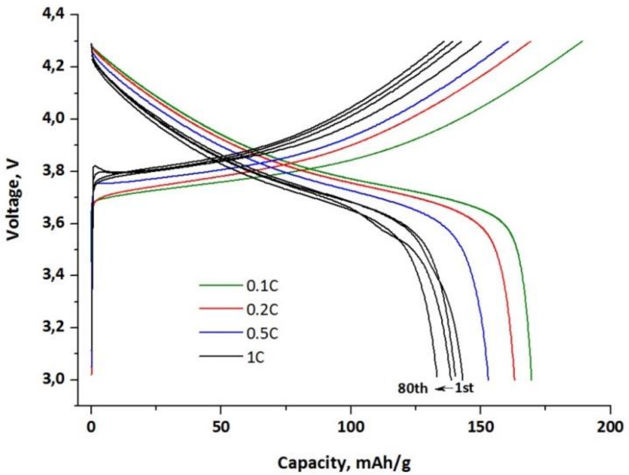
Inhomogeneous TM distribution

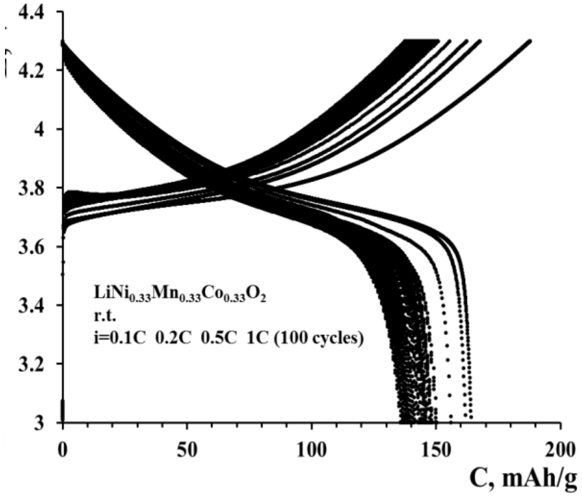




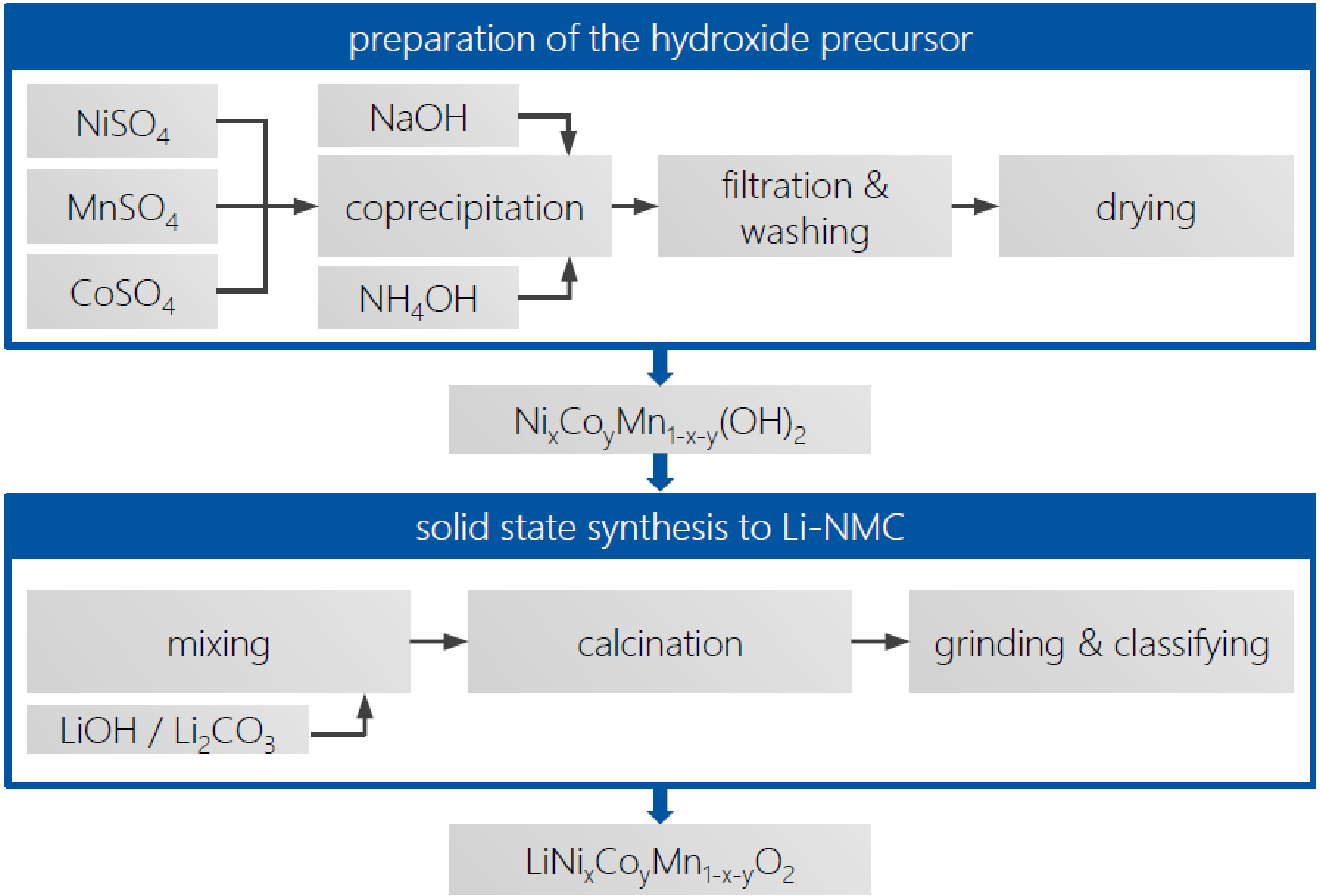


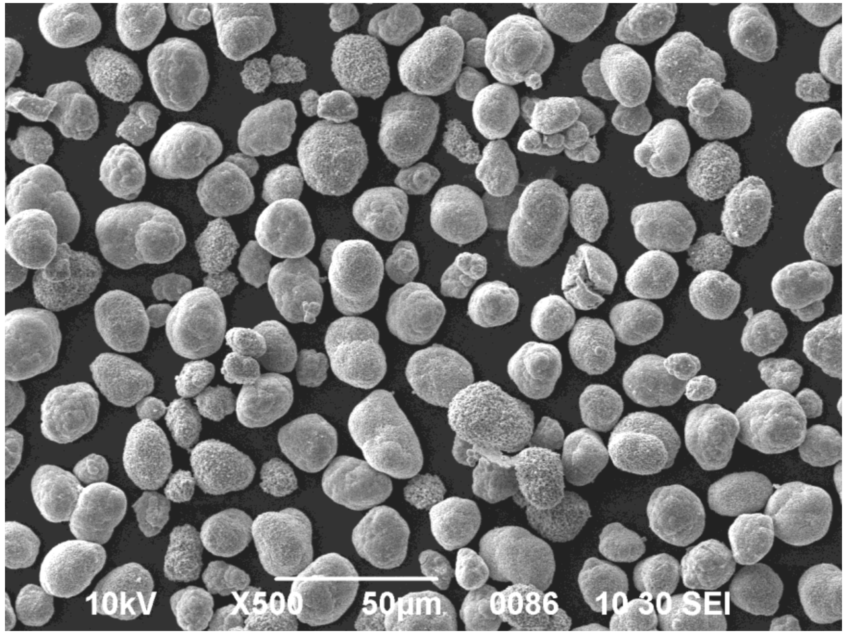






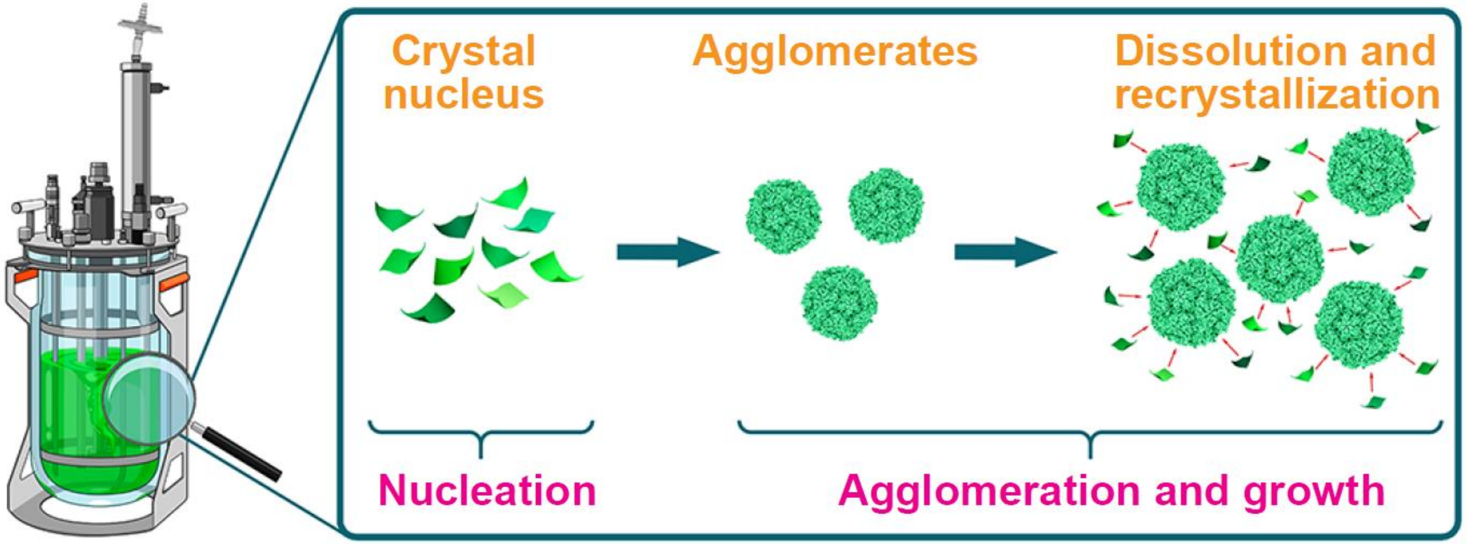
Synthesis of layered oxides





SEM image of NMC cathode

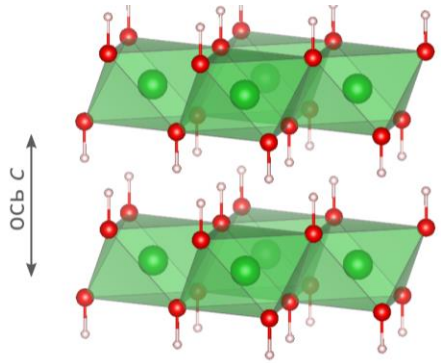
Co-precipitation



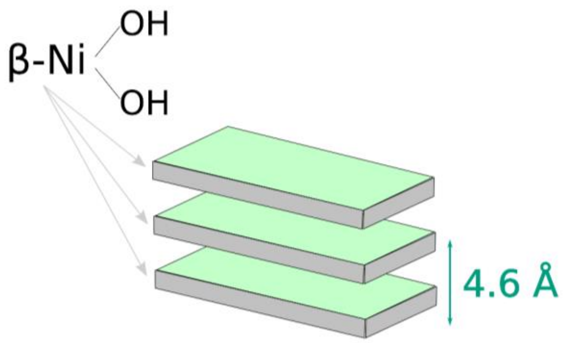
The scheme of co-precipitation of the hydroxide precursor $TM(OH)_2$

$$Me^{2+} + nNH_3 \rightarrow [Me(NH_3)_n]^{2+}$$
$$[Me(NH_3)_n]^{2+} + 2OH^- \rightarrow Me(OH)_2 + nNH_3$$

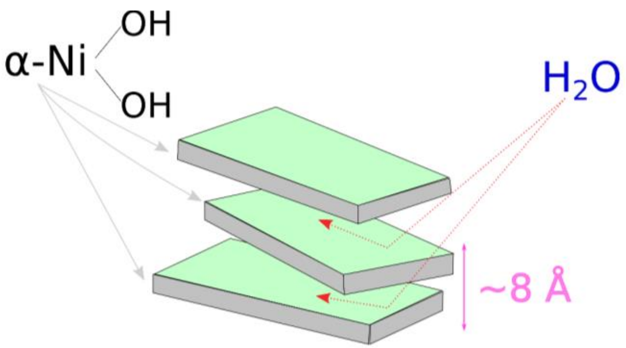
P-3*m*1



ordered



disordered



Defects in layered oxides

1. The anti-site disorder of Li and TM
(exchange Ni ↔ Li, r(Ni^{2+}) = 0.69 Å, r(Li^{+}) = 0.76 Å):

$$Ni_{Ni}^{\times} + Li_{Li}^{\times} \rightarrow Li_{Ni}^{'} + Ni_{Li}^{\bullet}$$

2. Excess Ni in Li positions (low p(O_2)):

$$V_{Li}^{'} + Ni_{Ni}^{\bullet} + O_O^{\times} \rightarrow Ni_{Li}^{\bullet} + V_{Ni}^{'''} + V_O^{\bullet\bullet} + 1/2O_2$$

3. Excess Li in Ni positions (high p(O_2)):

$$Ni_{Ni}^{\times} + 2Li_{(s)} + O_2 \rightarrow Li_{Ni}^{'} + Ni_{Ni}^{\bullet} + Li_{Li}^{\times} + 2O_O^{\times}$$

$LiCoO_2$
NMC111
NMC532
NMC622
(↕ air)

NMC811
NMC952525
$LiNiO_2$
(↕ oxygen)

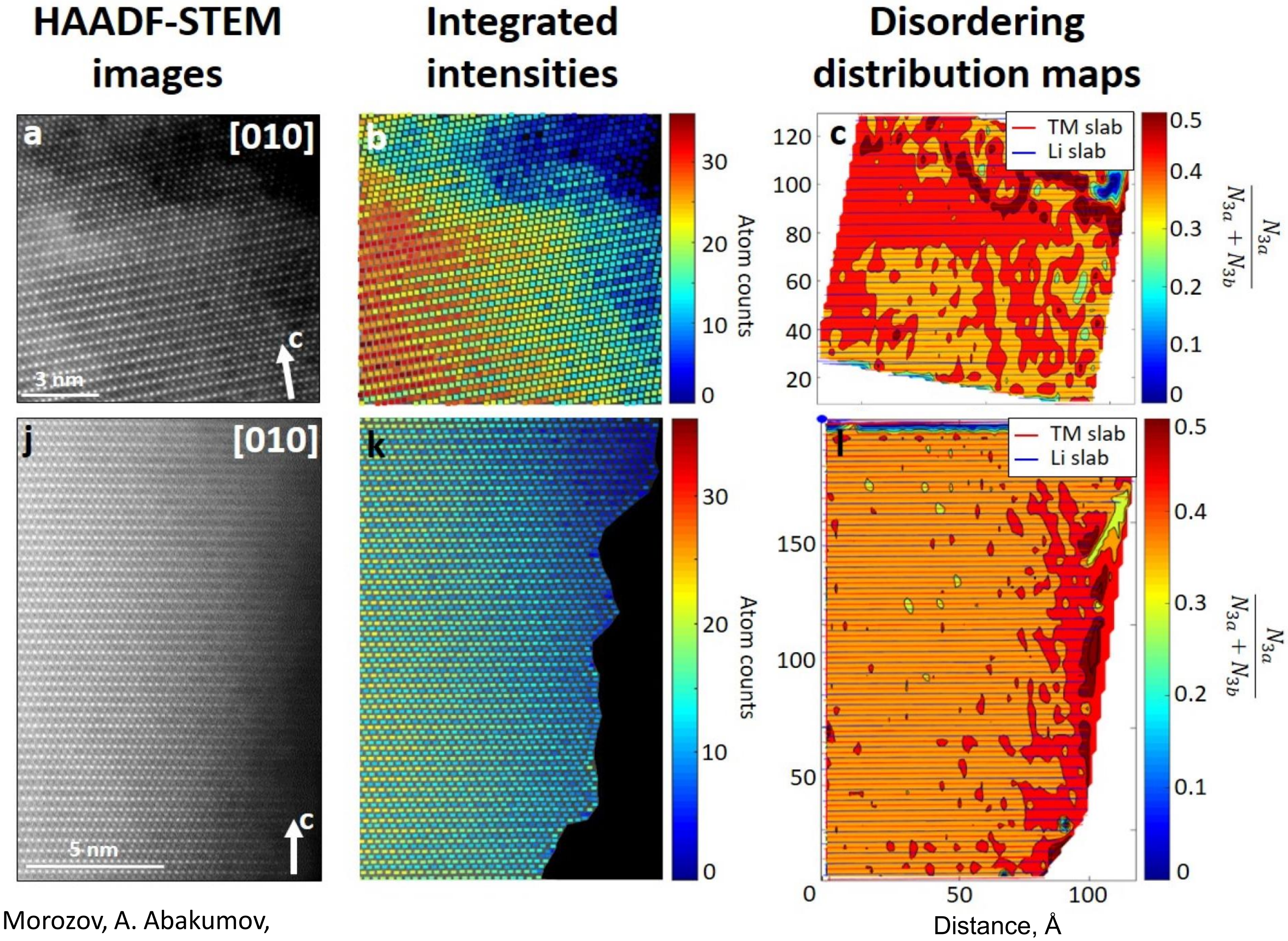
Kröger-Wink notation X^Z_Y

X – element symbol for an atom, V for vacancy;
Y – type of the site occupied by X: (i for an interstitial, element symbol for site normally occupied by this element);
Z – charge relative to the normal ion charge on the site
′ negative relative charge
• positive relative charge
x zero relative charge (x is often omitted)

Defects in layered oxides

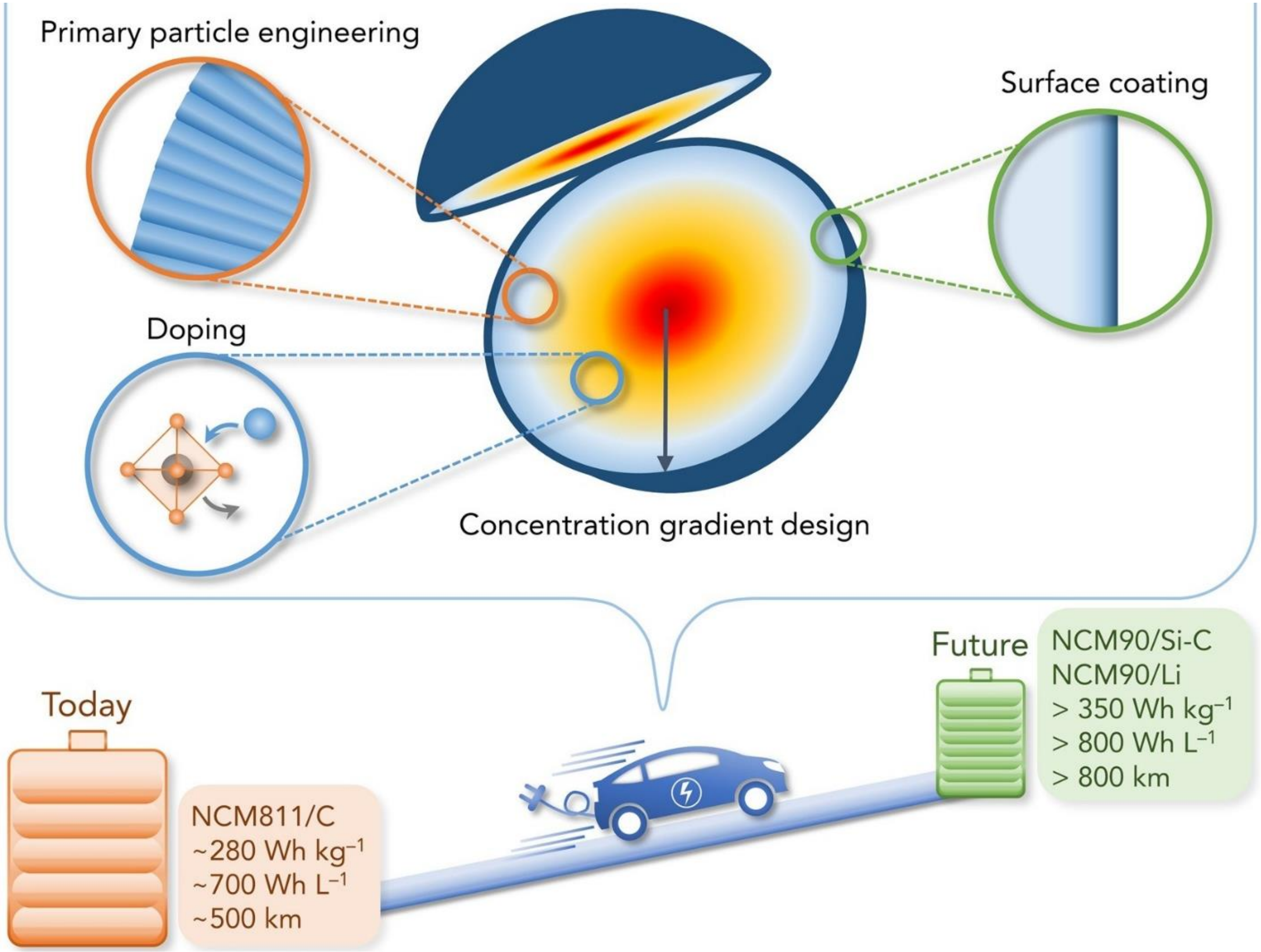
Air-annealed

Oxygen-annealed

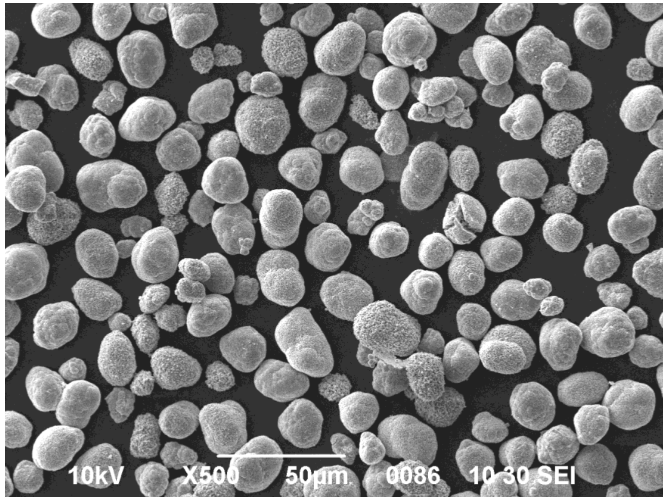


Orlova, Savina, S. Abakumov, Morozov, A. Abakumov, *Symmetry*, 13, 1628 (2021).

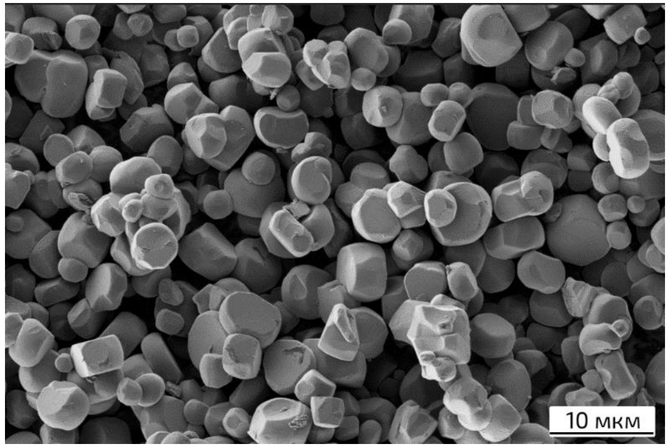
Modification strategies



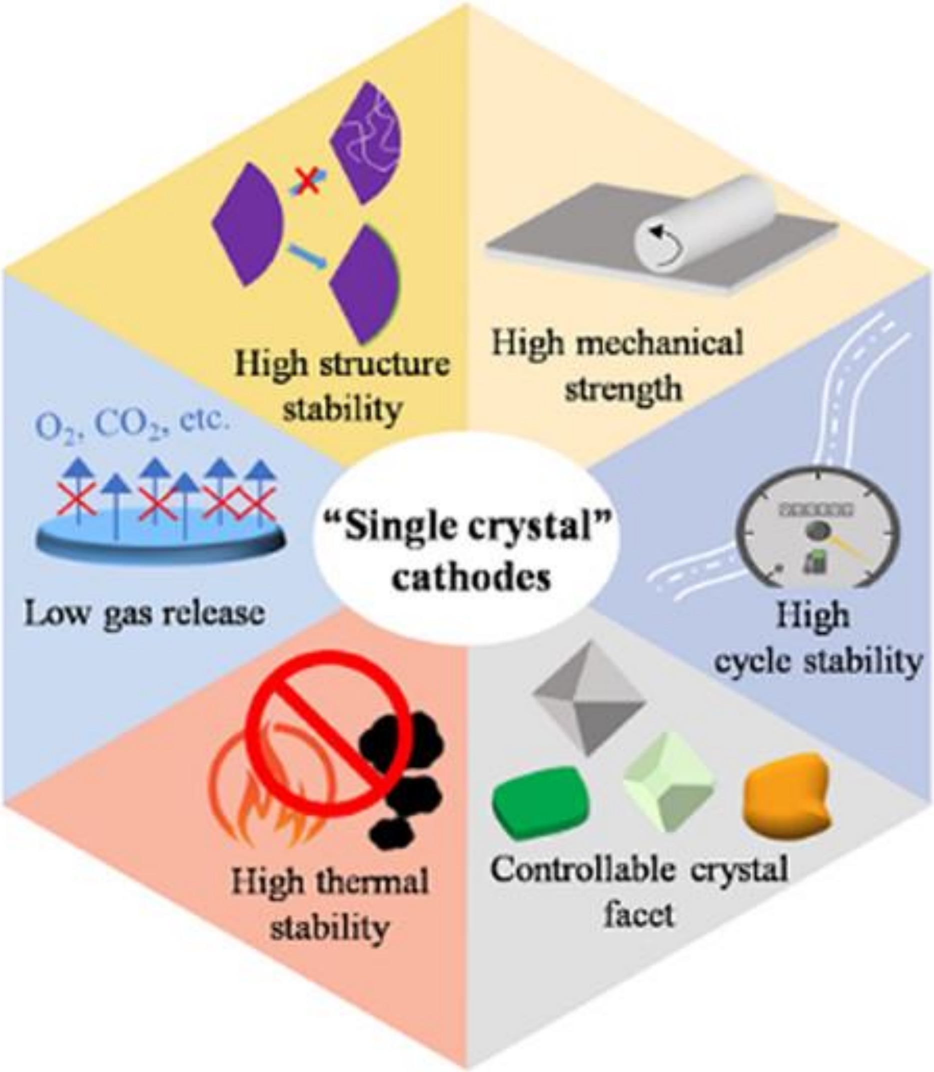
Single crystal layered oxides



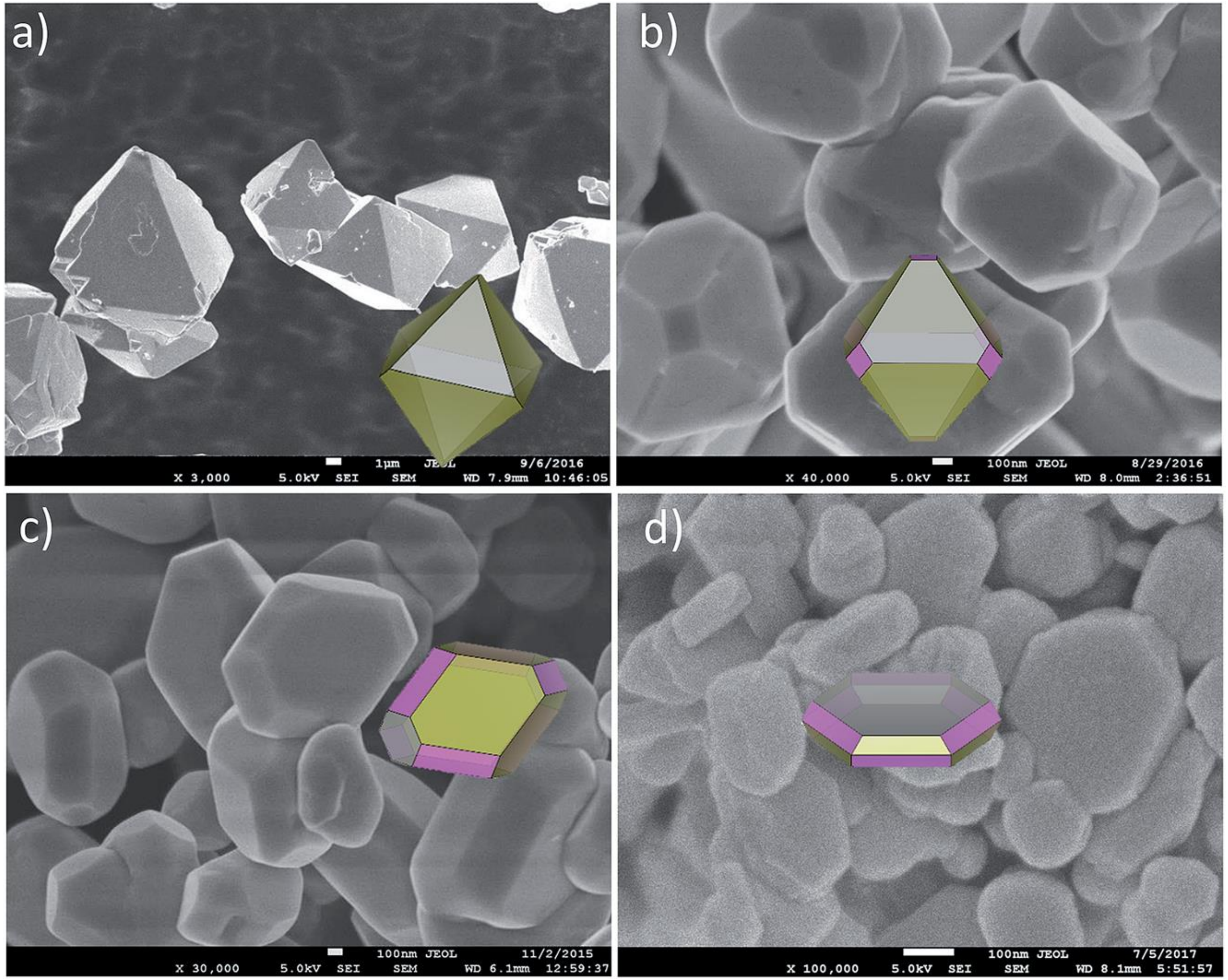
Spherical-like agglomerates

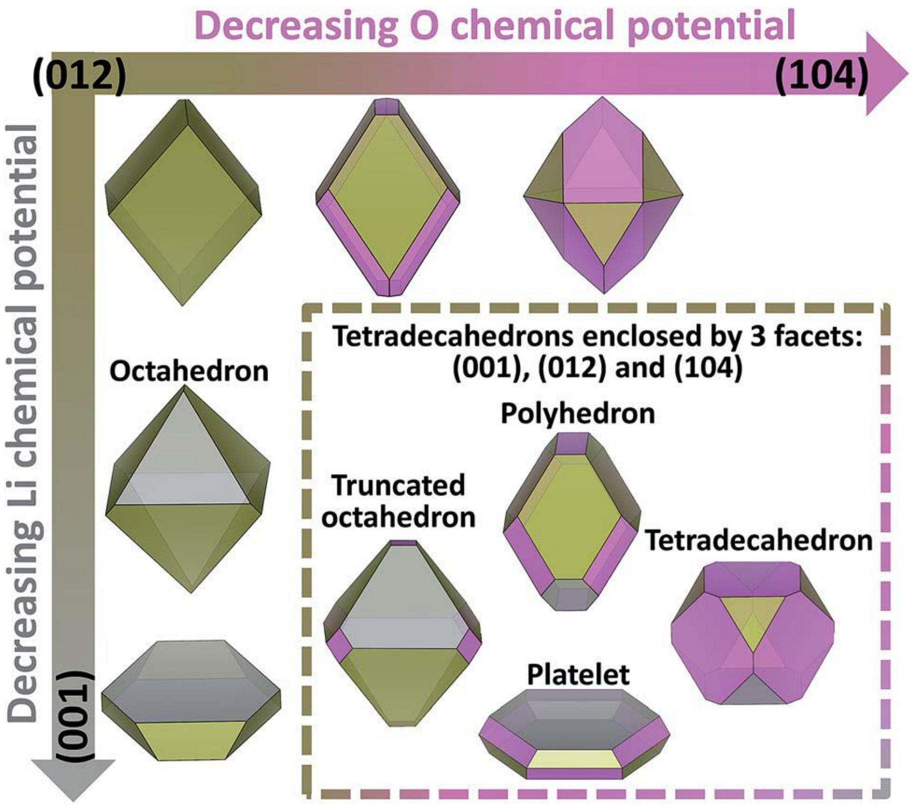


Single crystal

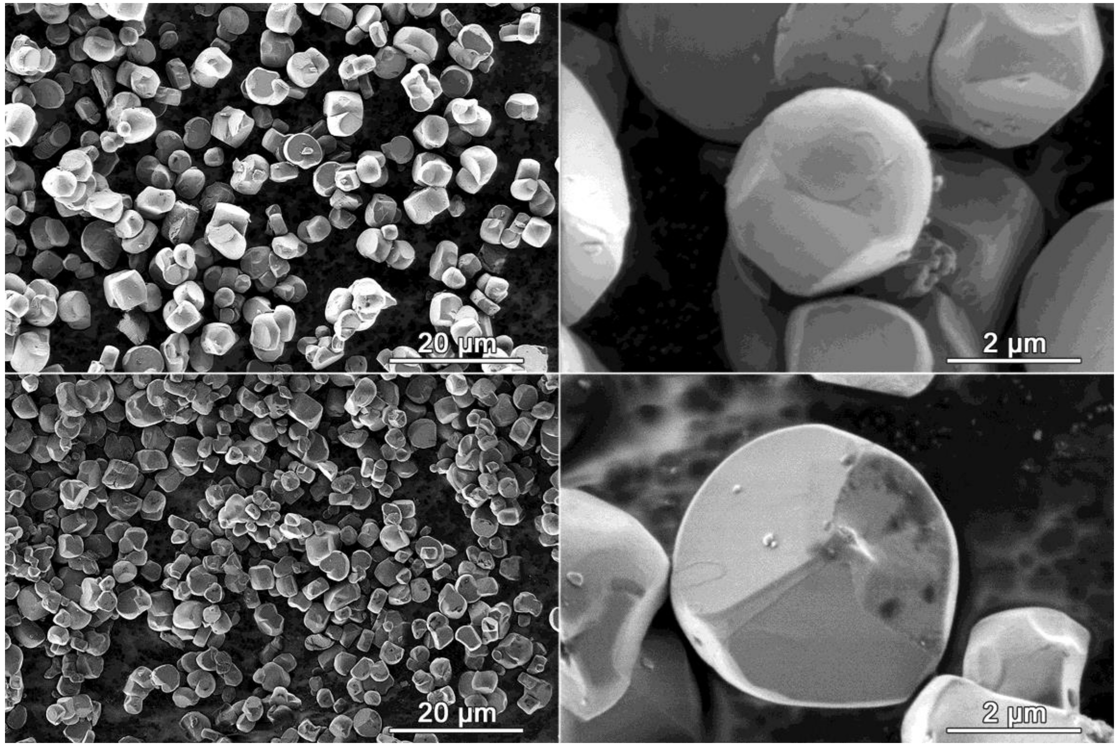


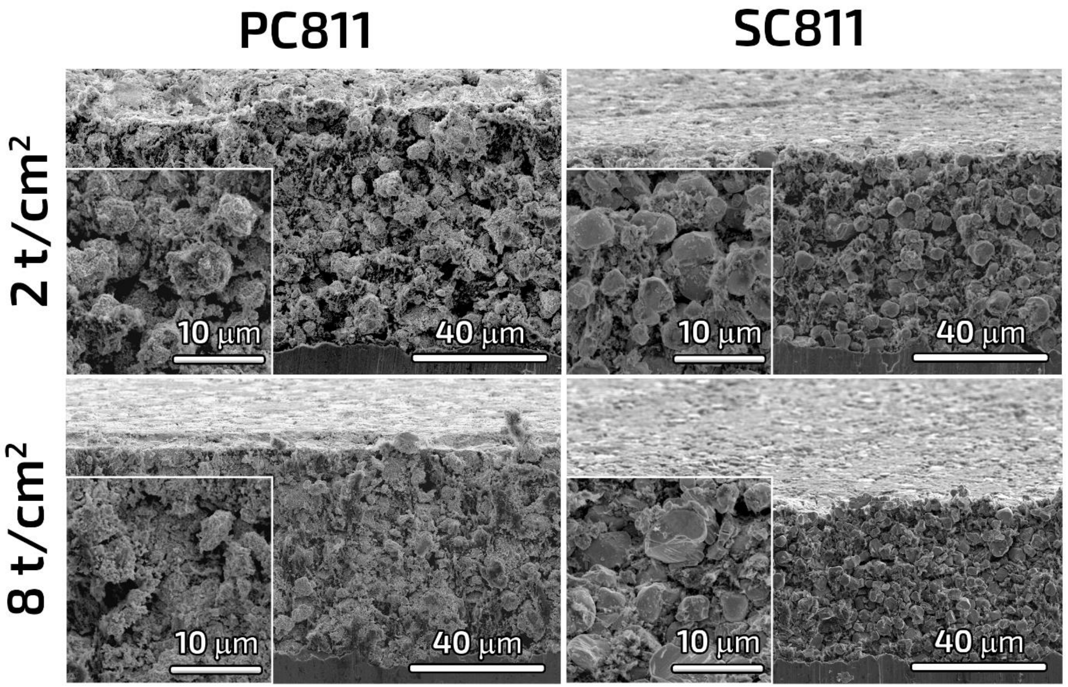
Single crystal layered oxides

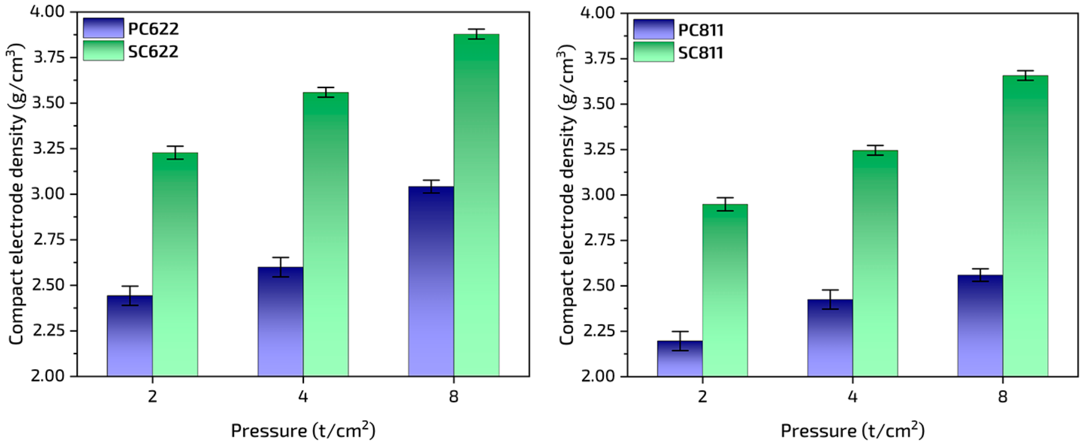




Single crystal layered oxides

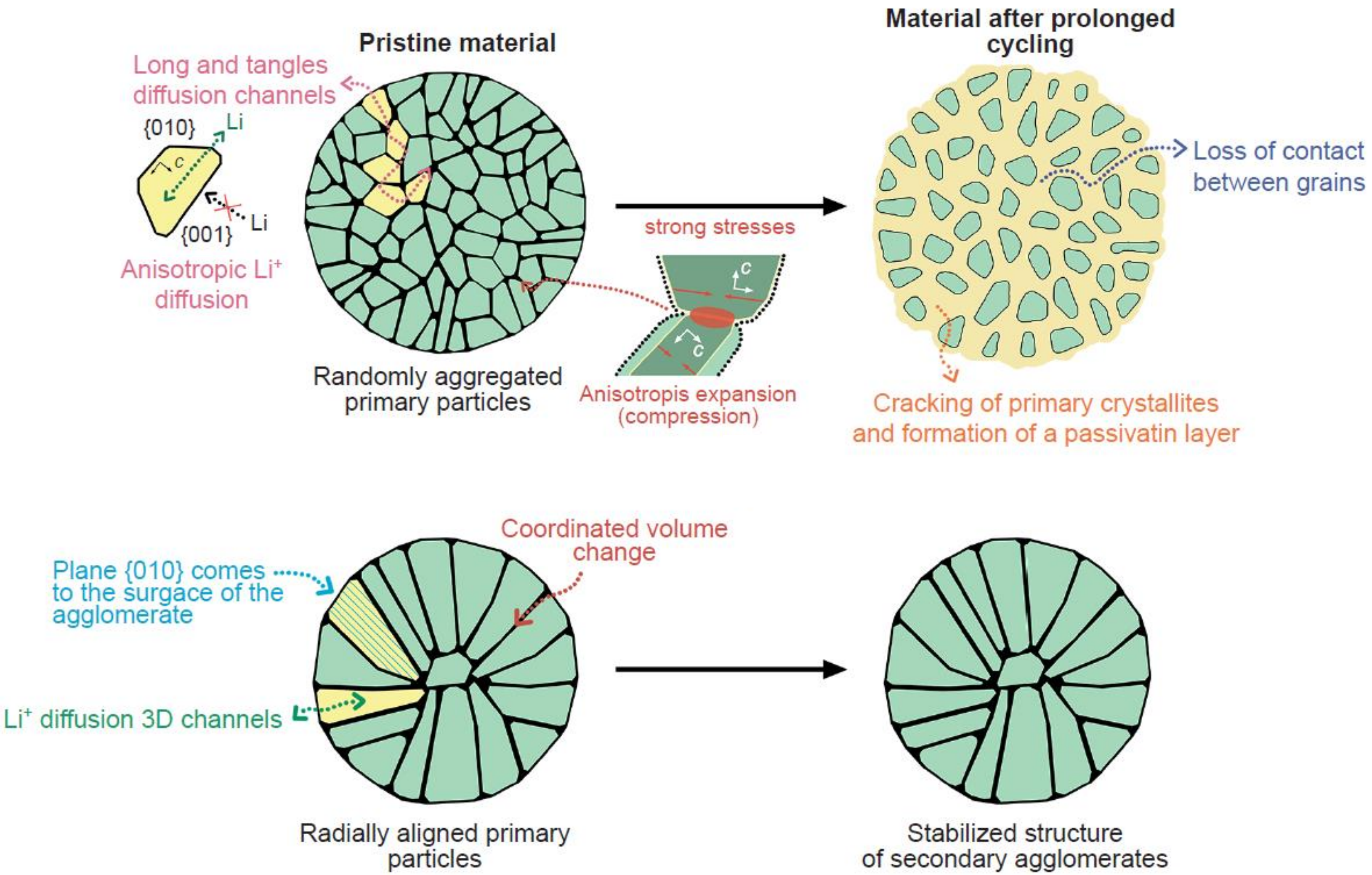




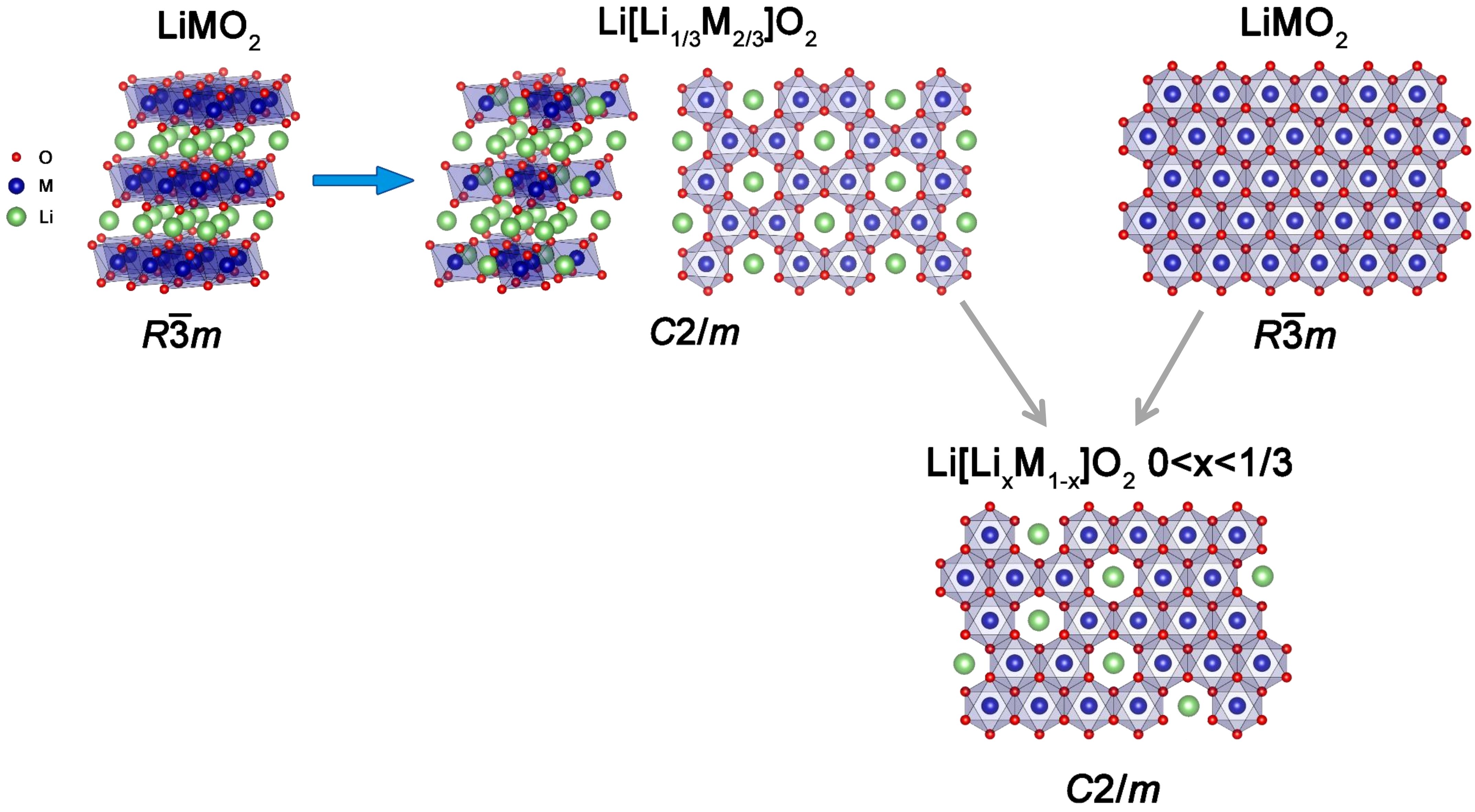


Moiseev, Savina, Pavlova, Abakumova, Pazhetnov, Abakumov, Energy Adv., 1, 677–681 (2022), patent RU 2 776 156, 14.07.2022

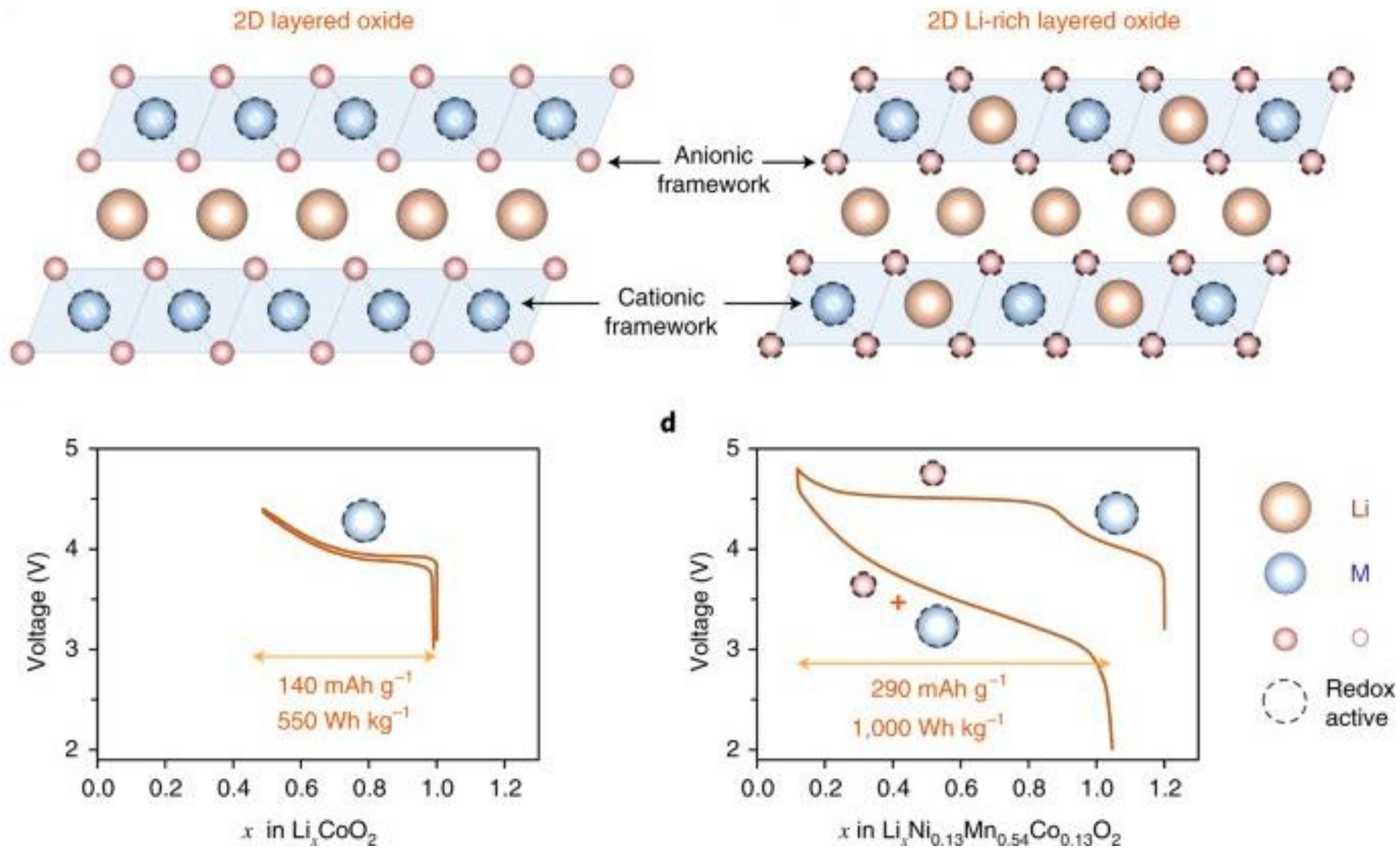
Microstructure organization of layered oxides



Crystal structure of Li-rich layered oxides



Electrochemical performance of Li-rich layered oxides

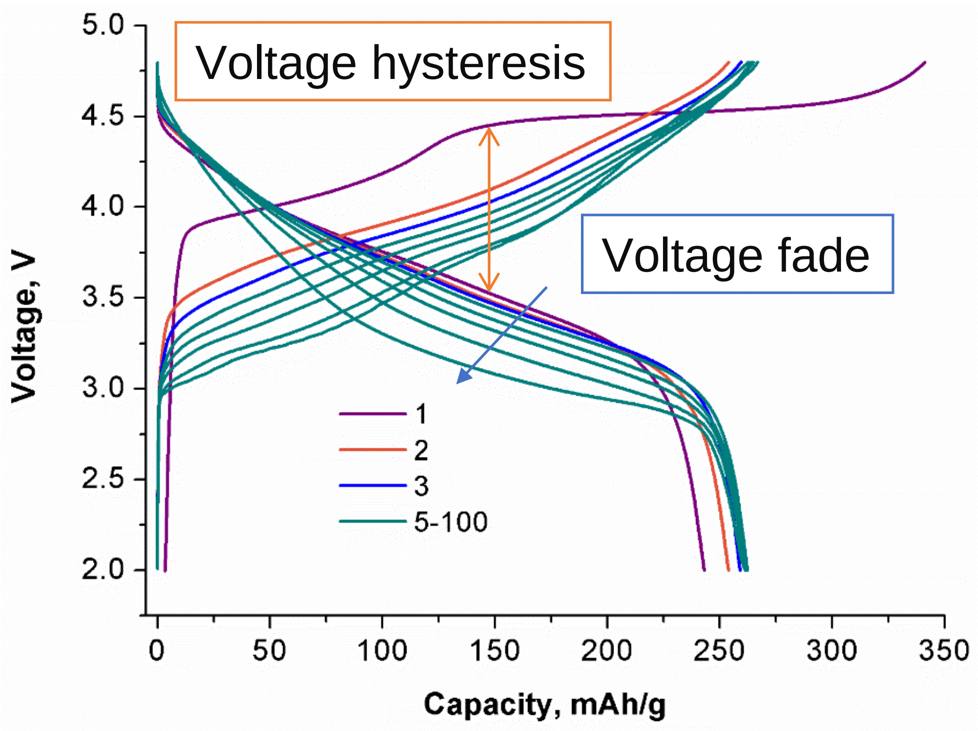


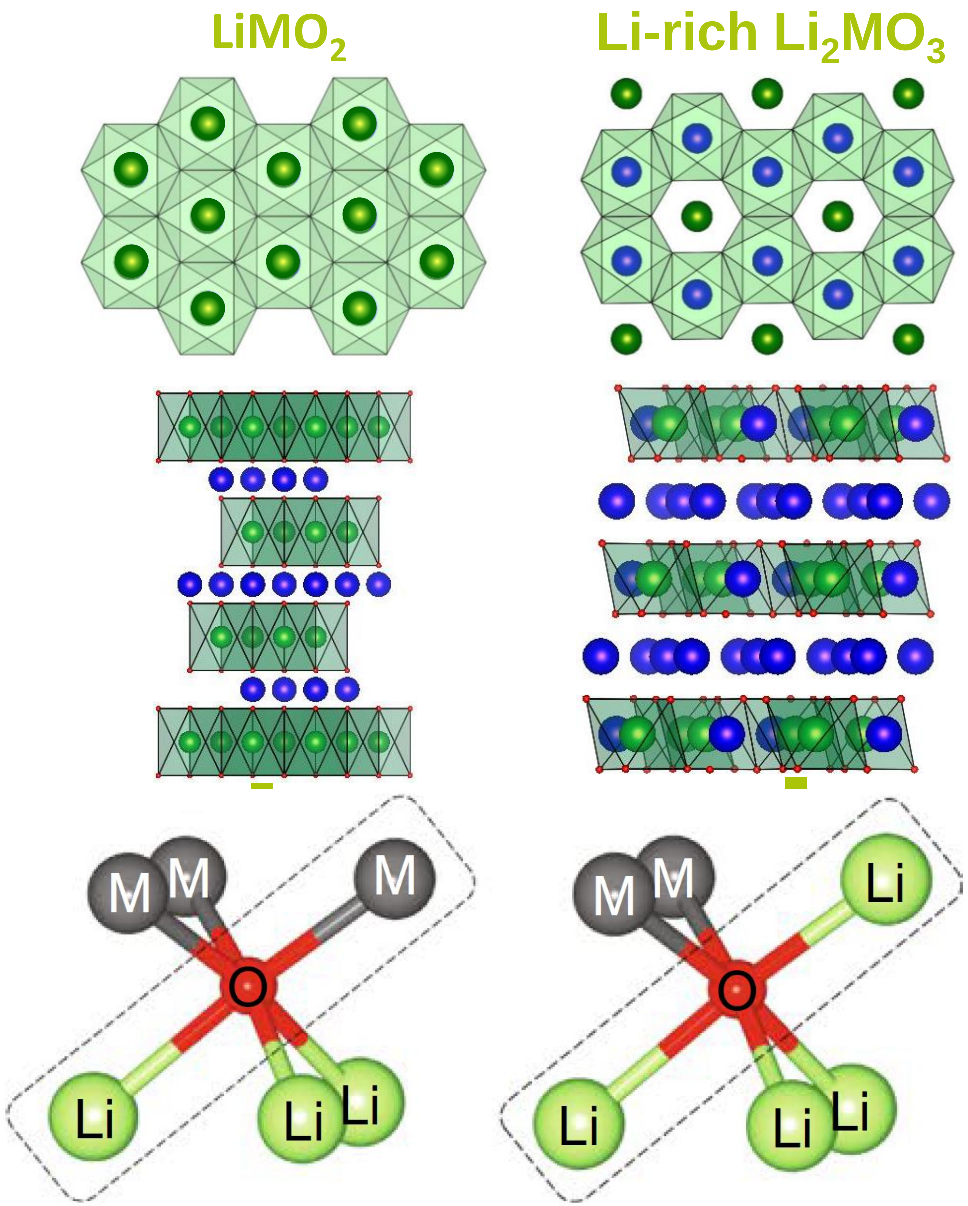
Negative side of Li-rich NMC

Drawbacks:

1. Slow kinetics
2. Voltage hysteresis
3. Voltage fade
4. Irreversible oxygen oxidation (gaseous O_2 evolution)

Li-rich NMC (*$Li_{4/3-x}Ni_xMn_{2/3-x}Co_xO_2$*)





Assat G., Tarascon J. M., *Nature Energy*, *3*(5), 373-386, 2018.

Thx!