



LOMONOSOV MOSCOW
STATE UNIVERSITY

Skoltech



Russian Science
Foundation

Crystallography and Crystal Chemistry
VIII International School-Conference of
Young Scientists 2023

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



Dr. Aleksandra A. Savina

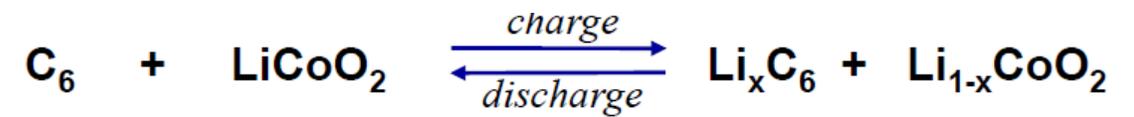
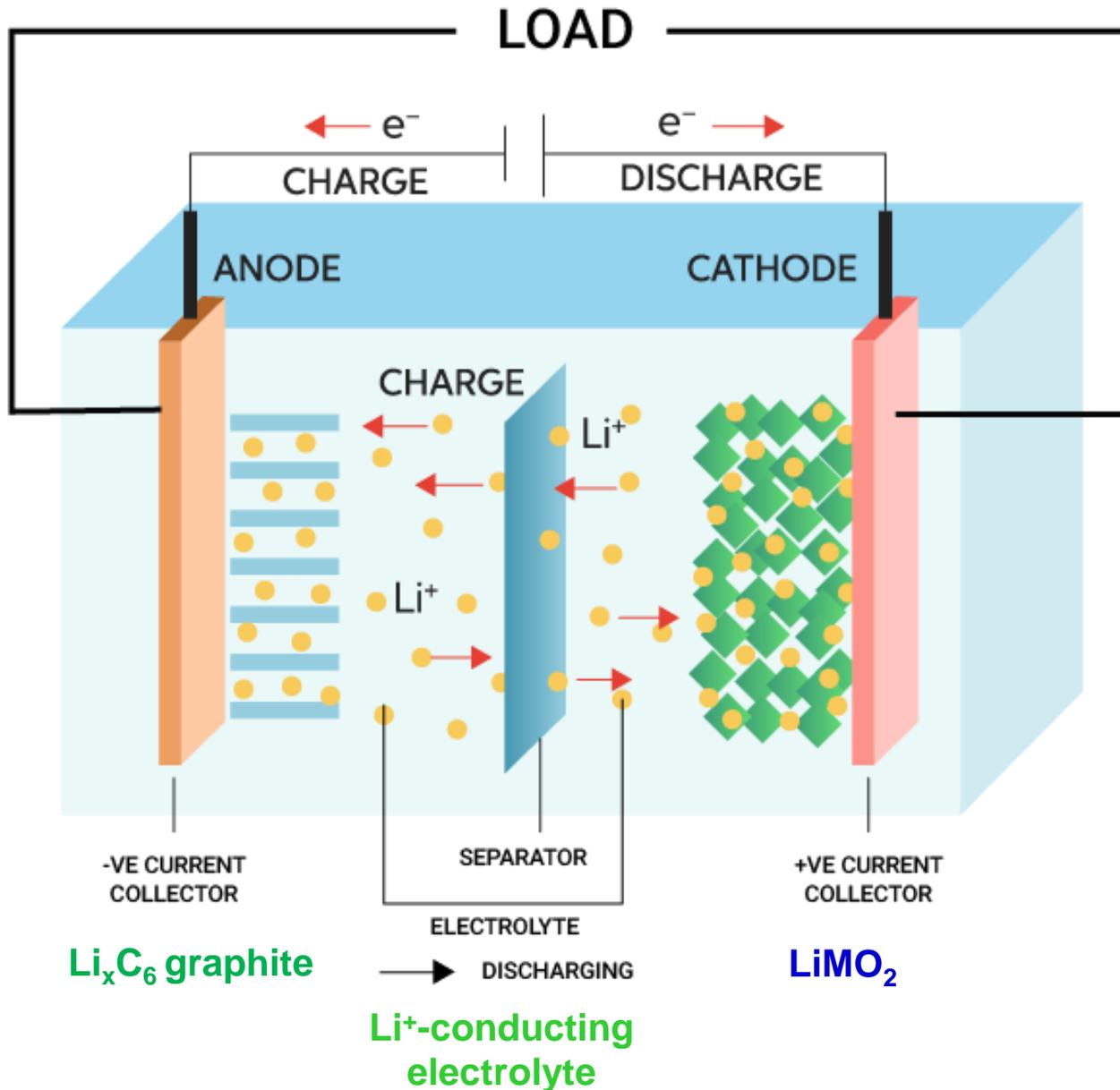
PhD in Chemistry, Senior Research Scientist

Center for Energy Science and Technology

Skoltech, Moscow, Russian Federation

November 11th, 2023

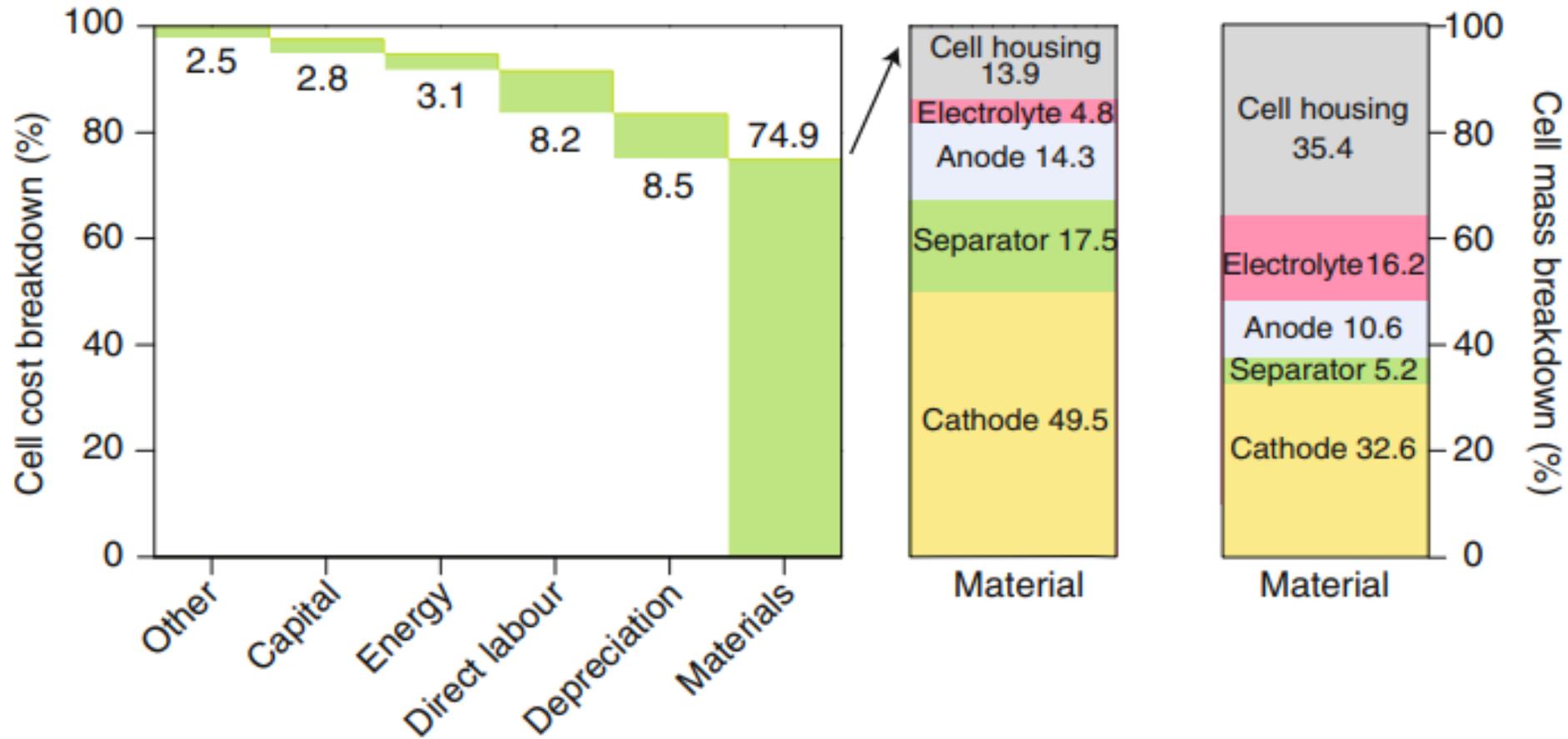
Li-ion batteries



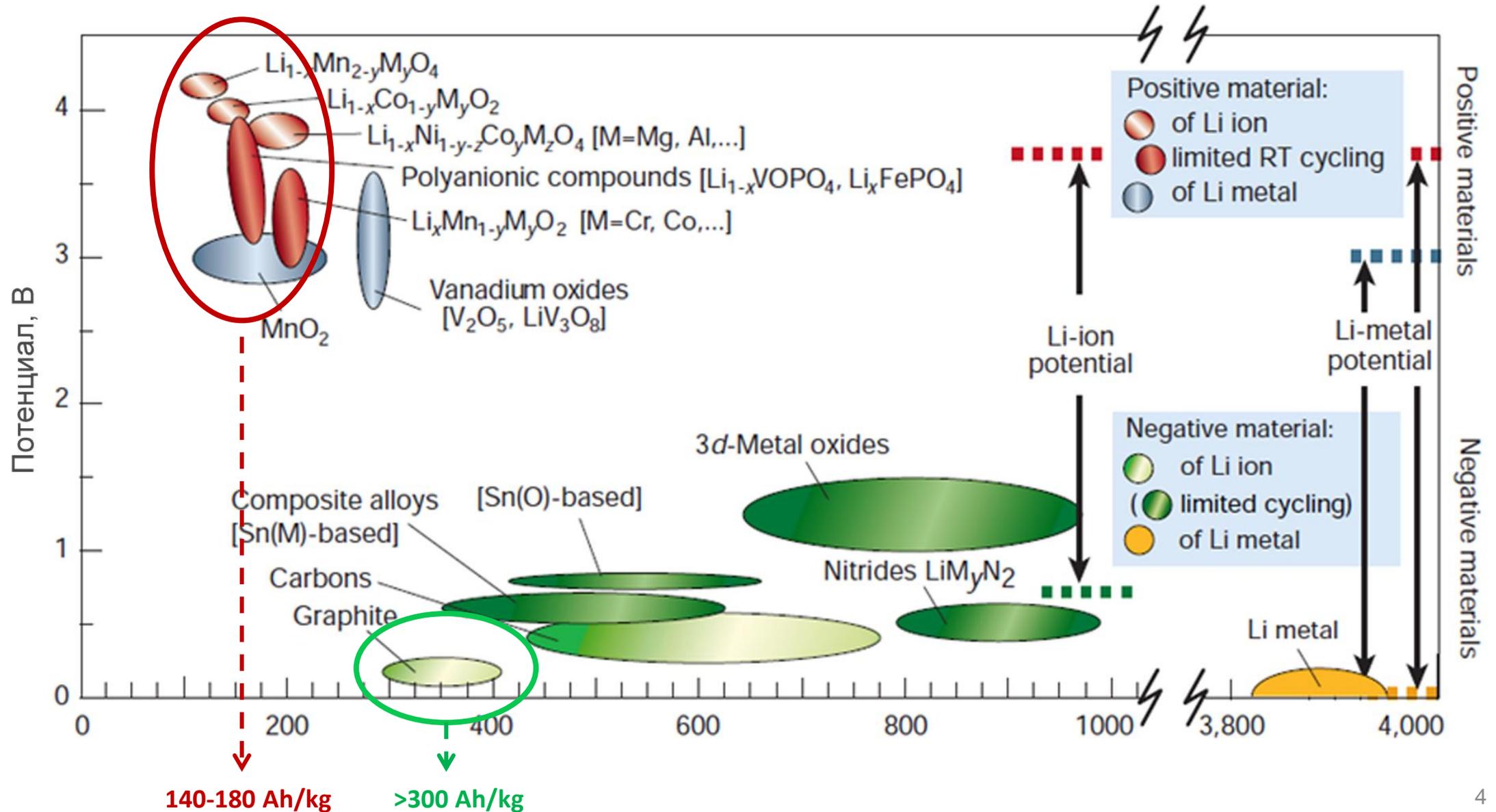
Electrolyte:

Li-salt -LiPF₆, LiBF₄(LiClO₄, LiAsF₆), LiCF₃SO₃
 Solvent-ethylene carbonate(CH₂O)₂C, dimethyl carbonate(CH₃O)₂CO

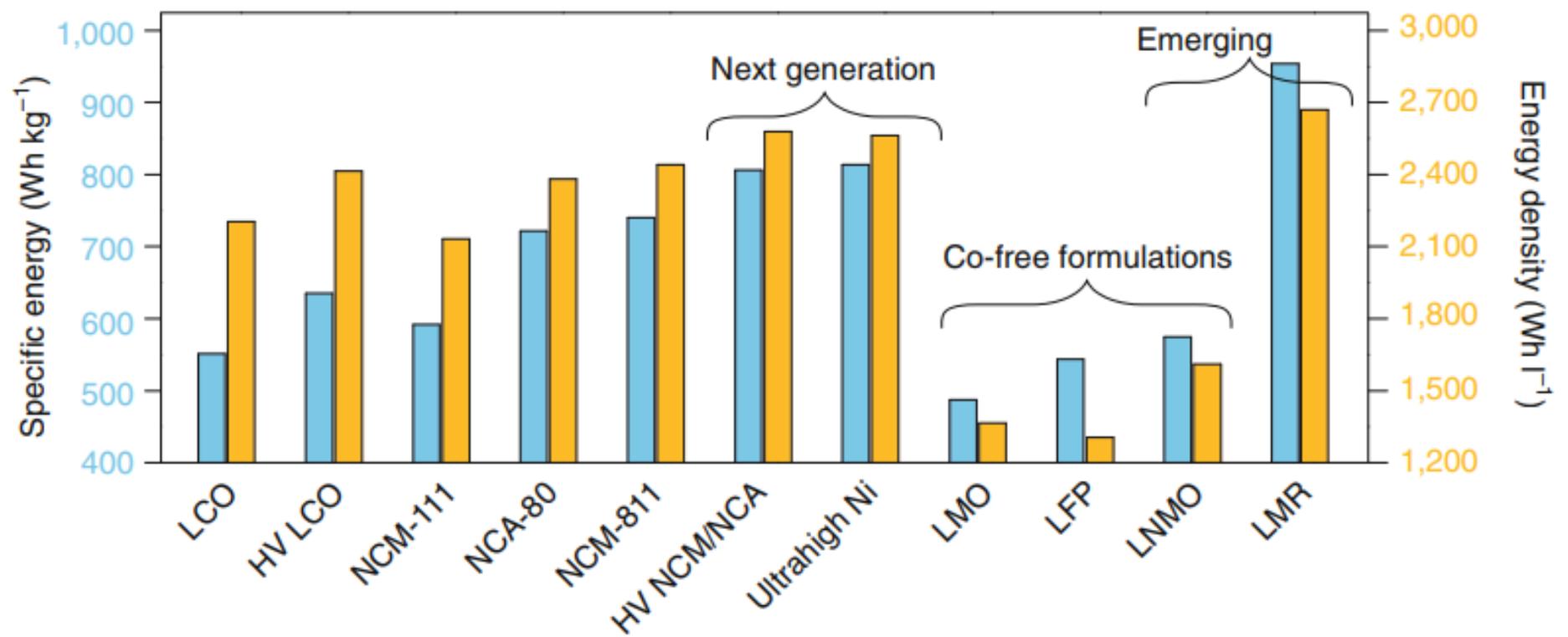
Li-ion batteries



Materials for LIBs



Cathode materials for LIBs



LCO - LiCoO₂

NCA - LiNi_{0.84}Co_{0.12}Al_{0.04}O₂

LFP - LiFePO₄

LMO - LiMn₂O₄

LNMO - LiMn_{1.5}Ni_{0.5}O₄

NMC - Li(Ni_xMn_yCo_z)O₂, x + y + z = 1

NMC111 - LiNi_{1/3}Mn_{1/3}Co_{1/3}O₂

NMC811 - LiNi_{0.8}Mn_{0.1}Co_{0.1}O₂

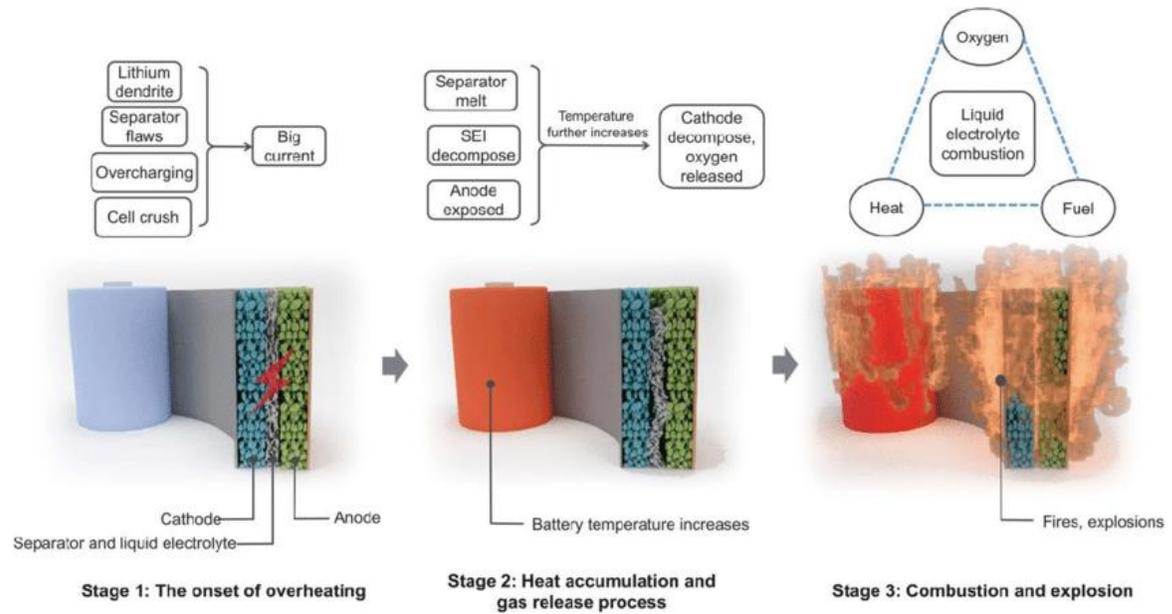
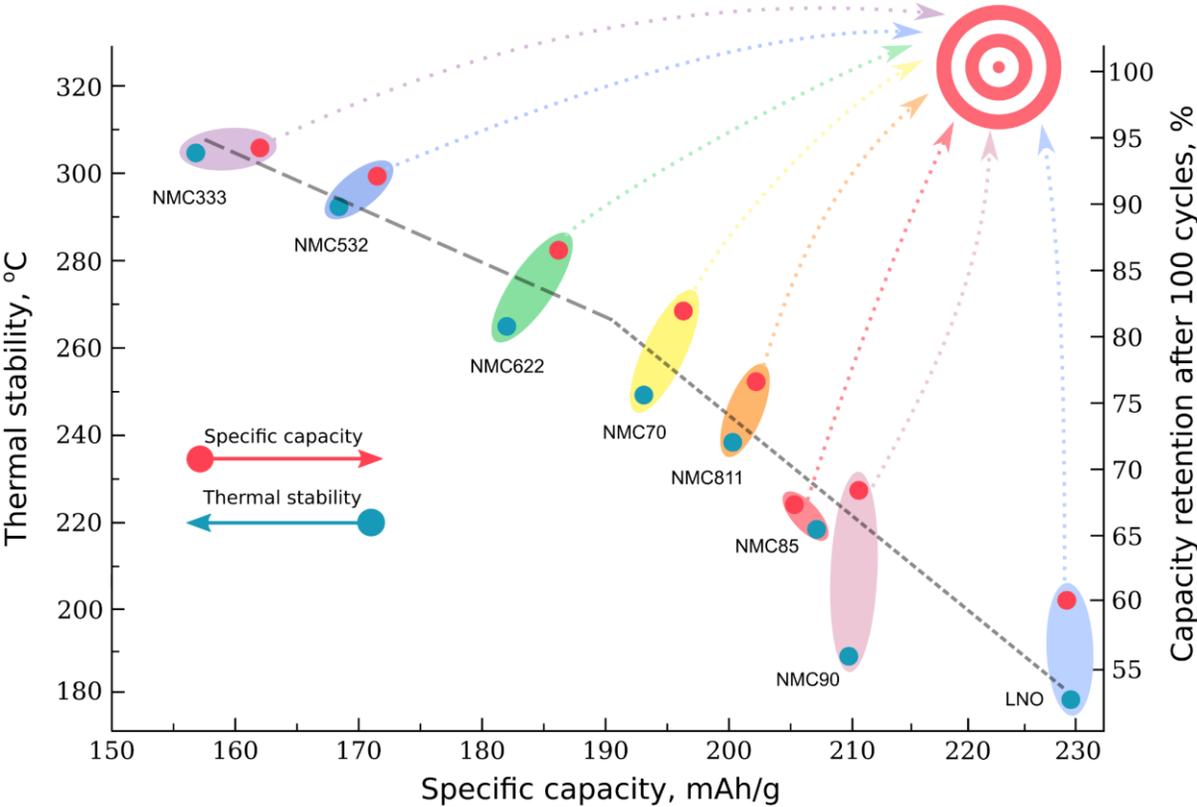
LMR - Li-rich NMC



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 |
| $\text{LiNi}_{1/3}\text{Mn}_{1/3}\text{Co}_{1/3}\text{O}_2$ (NMC111) | 600 | 160 | High stability | Low energy density |
| $\text{LiNi}_{0.6}\text{Mn}_{0.2}\text{Co}_{0.2}\text{O}_2$ (NMC622) | 685 | 180 | Relatively high energy density | Relatively low stability |
| $\text{LiNi}_{0.8}\text{Mn}_{0.1}\text{Co}_{0.1}\text{O}_2$ (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 |

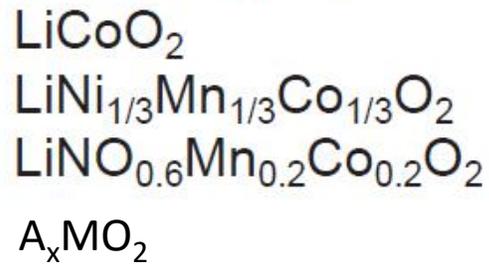
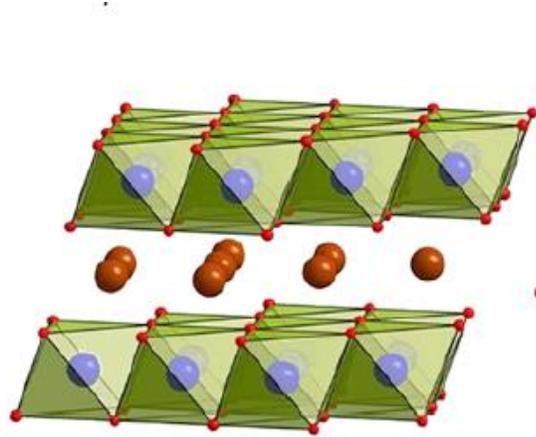
Cathode materials



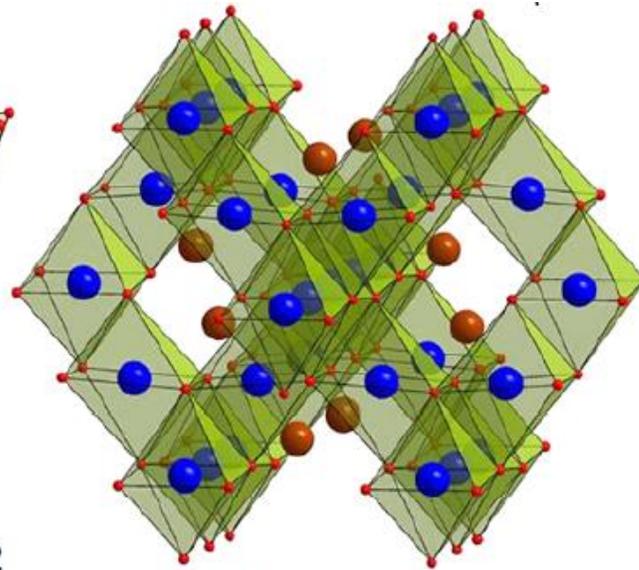
Key characteristics of cathode materials

| 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 |
| $\text{LiNi}_{1/3}\text{Mn}_{1/3}\text{Co}_{1/3}\text{O}_2$ (NMC111) | 600 | 160 | High stability | Low energy density |
| $\text{LiNi}_{0.6}\text{Mn}_{0.2}\text{Co}_{0.2}\text{O}_2$ (NMC622) | 685 | 180 | Relatively high energy density | Relatively low stability |
| $\text{LiNi}_{0.8}\text{Mn}_{0.1}\text{Co}_{0.1}\text{O}_2$ (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 |

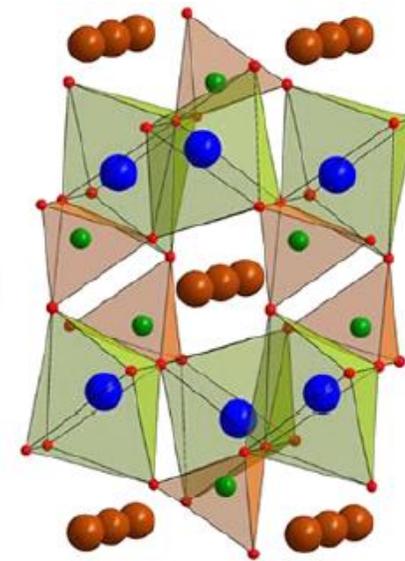
Crystal structures of currently used cathode materials



2D Li transport

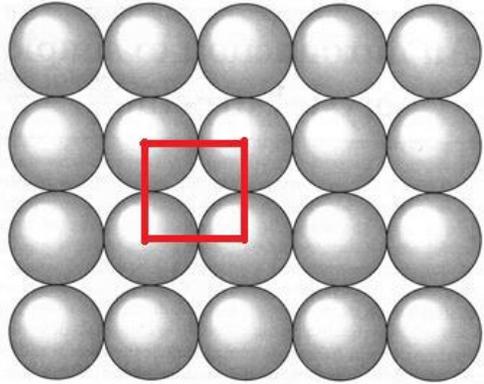


3D Li transport

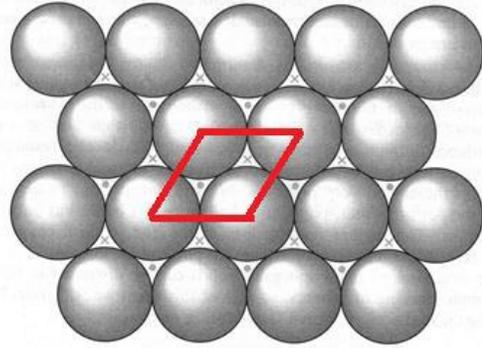


1D Li transport

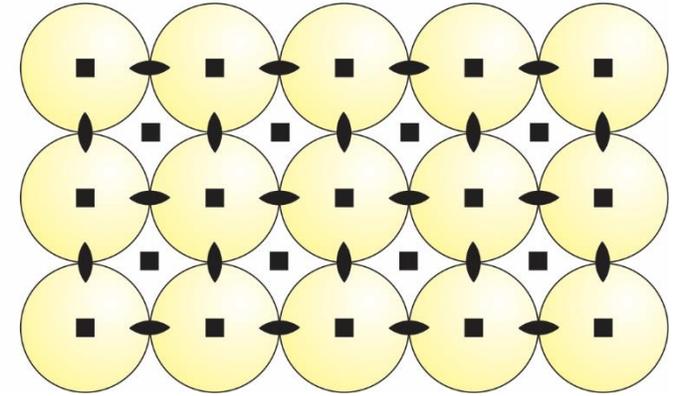
Close-packing of equal spheres



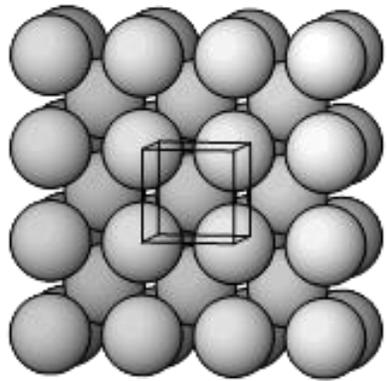
tetragonal



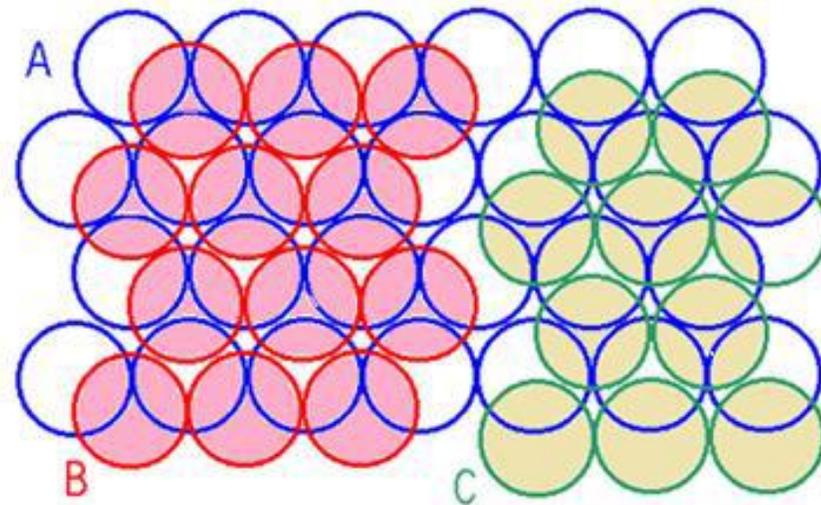
hexagonal



Simple tetragonal or hexagonal packing

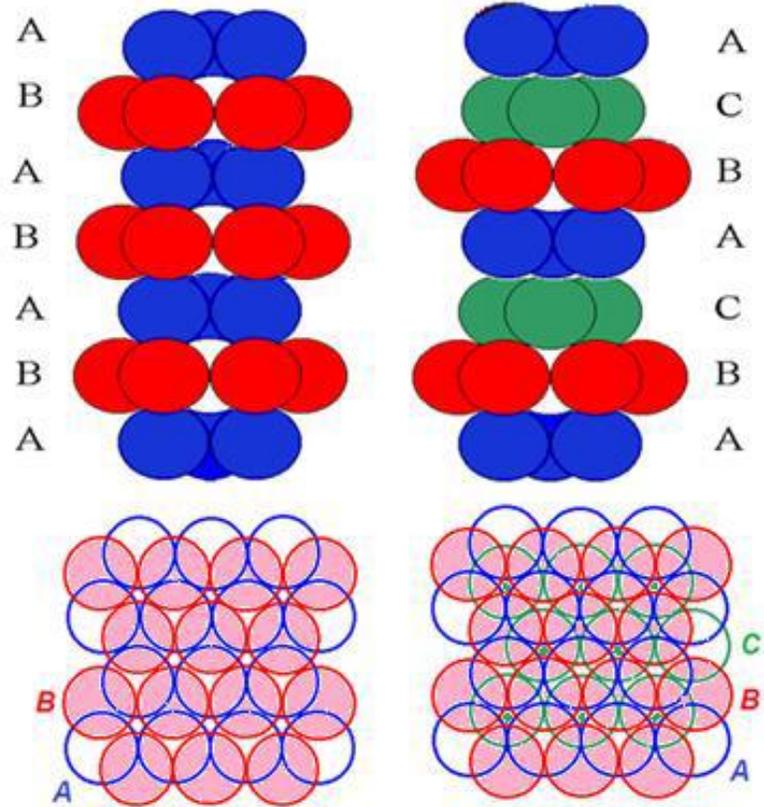
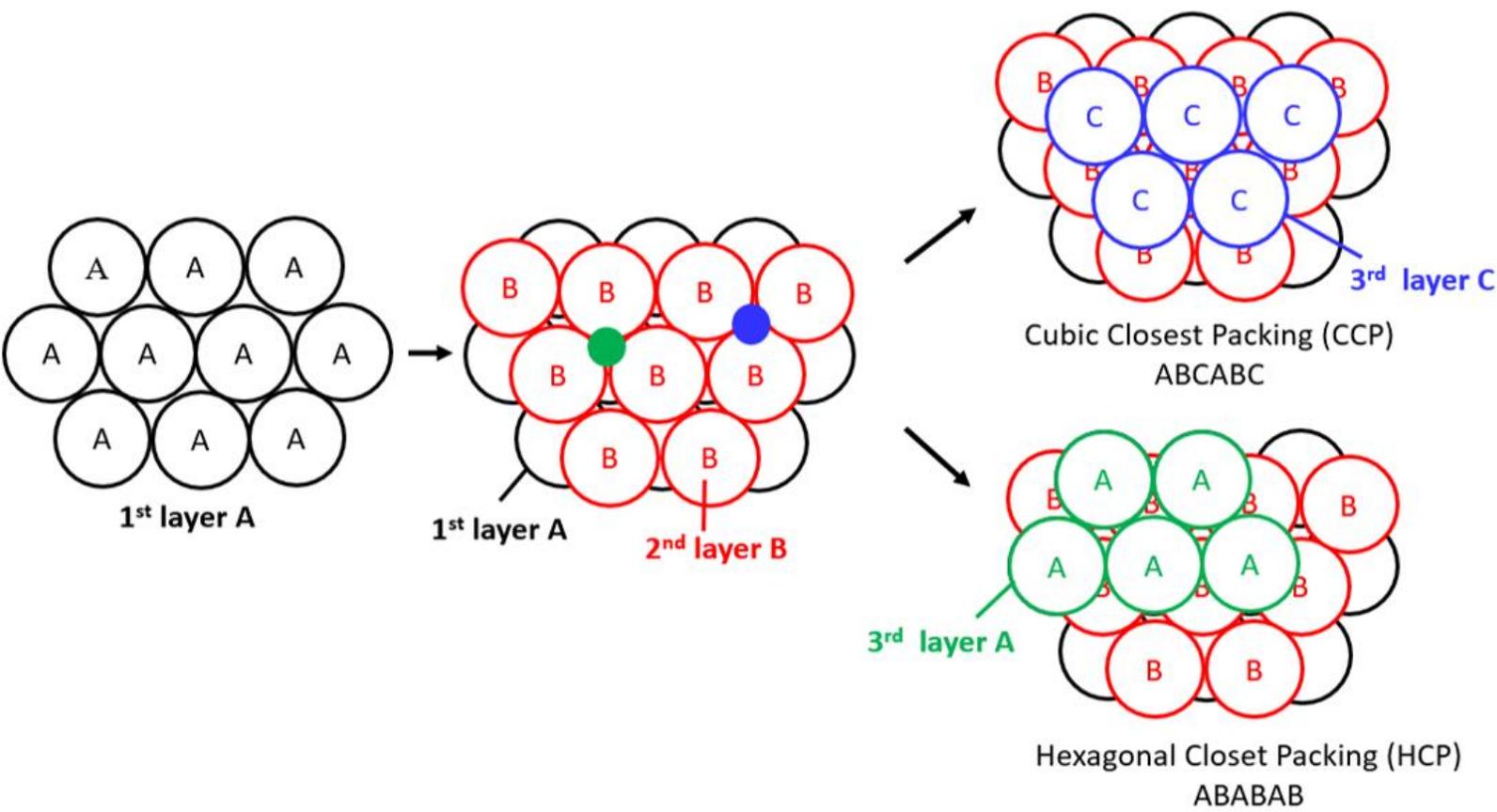


Body-centered cubic packing

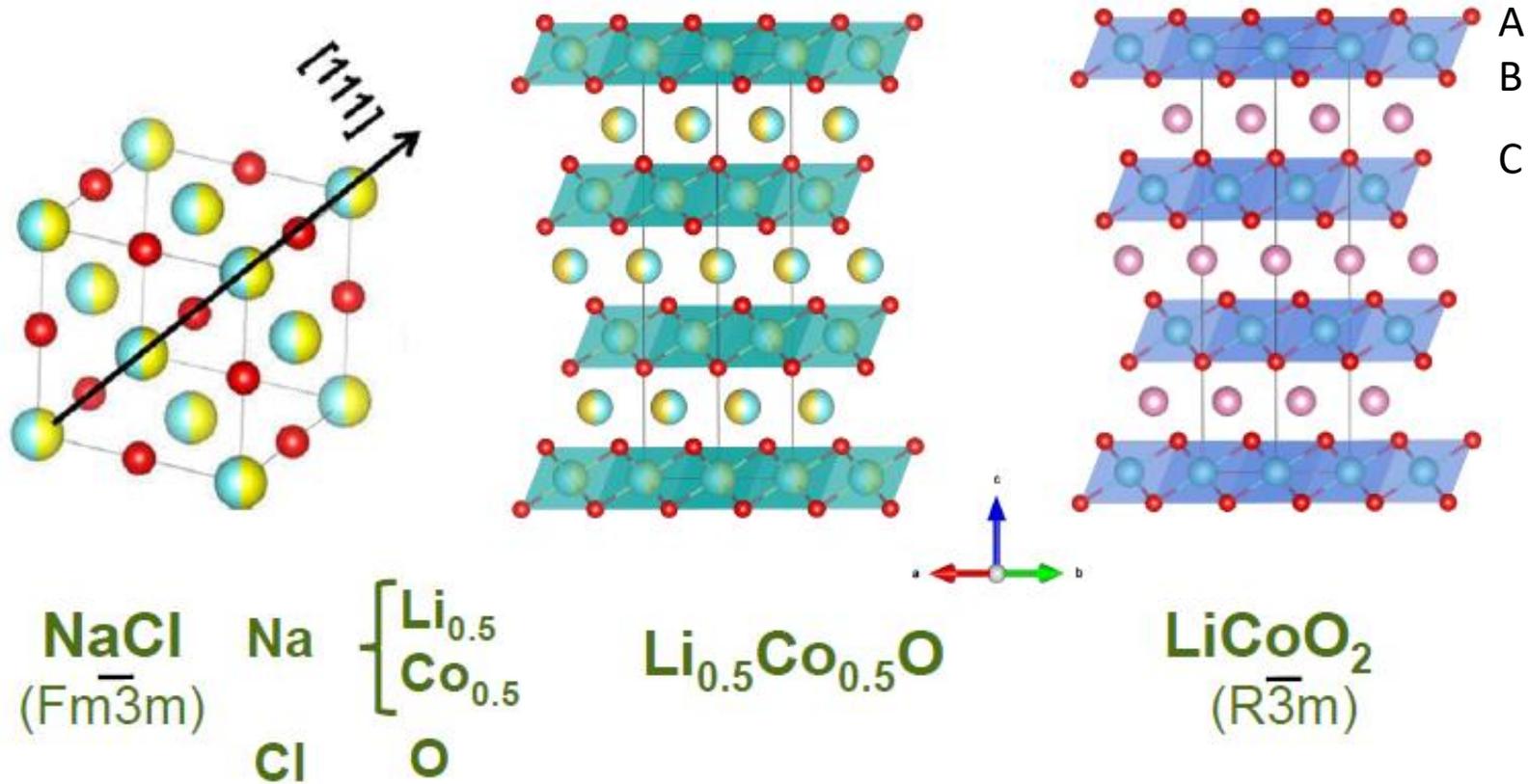


close-packing

Close-packing of equal spheres

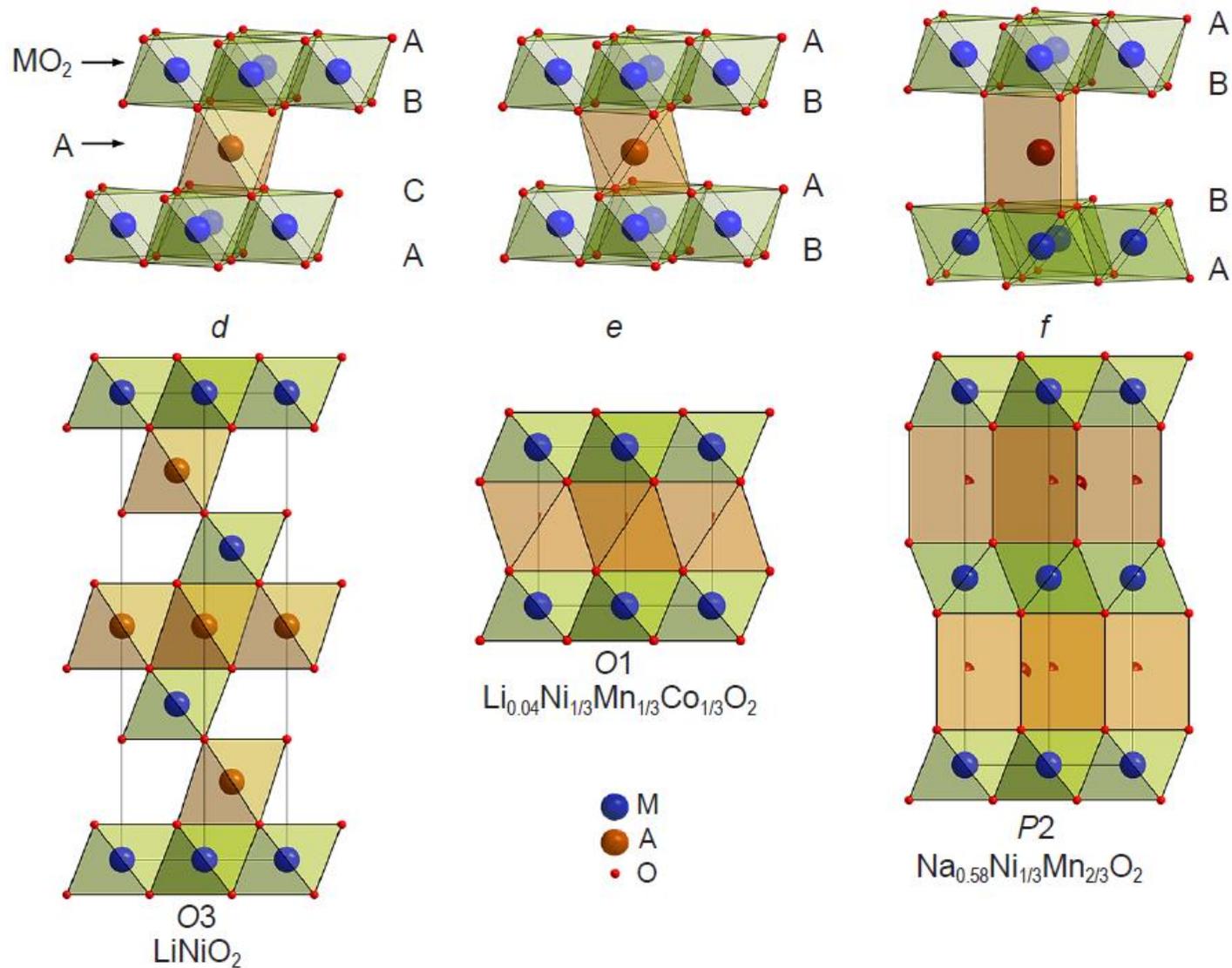


Crystal structure of layered oxides



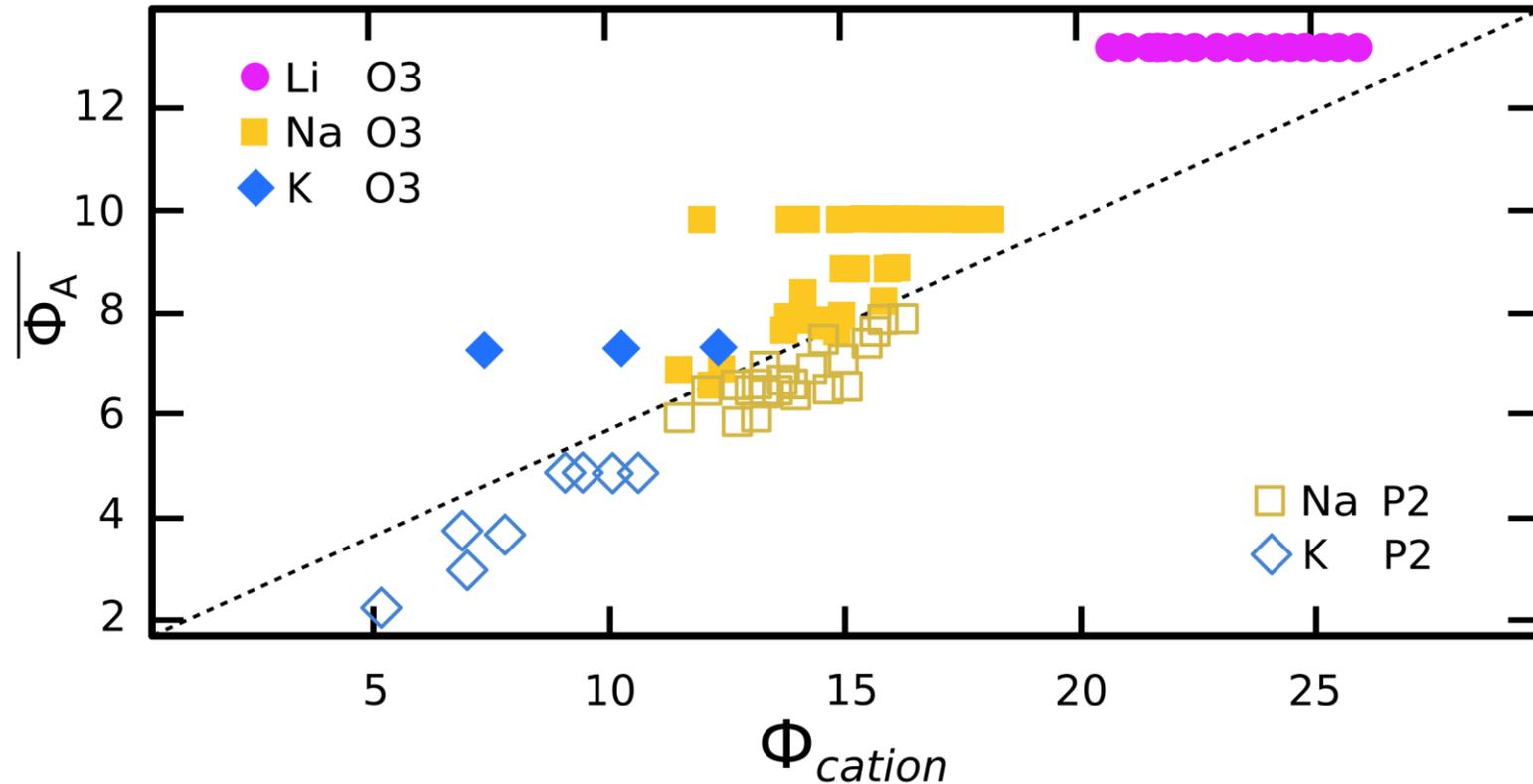
$$a \approx a_{\text{RS}}/\sqrt{2} \approx 2.9\text{\AA}, \quad c \approx a_{\text{RS}}2\sqrt{3} \approx 14.2\text{\AA}$$

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.

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

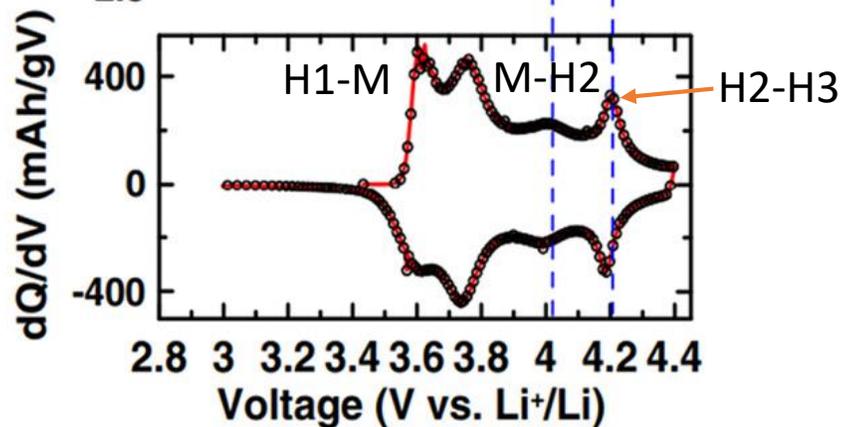
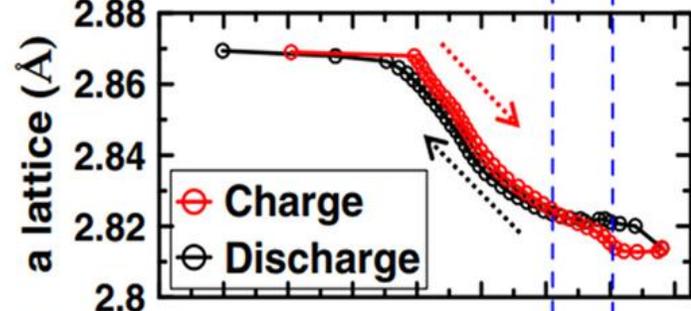
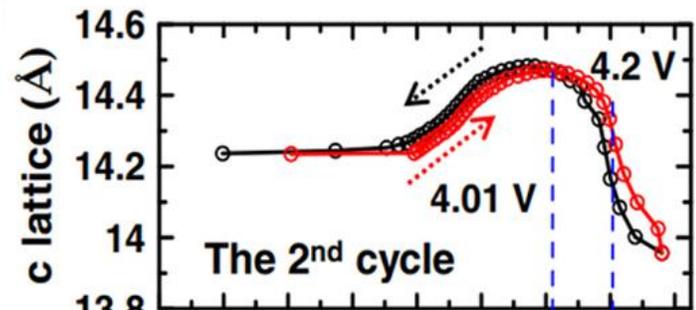
and represents the weighted average ionic potential of TMs

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

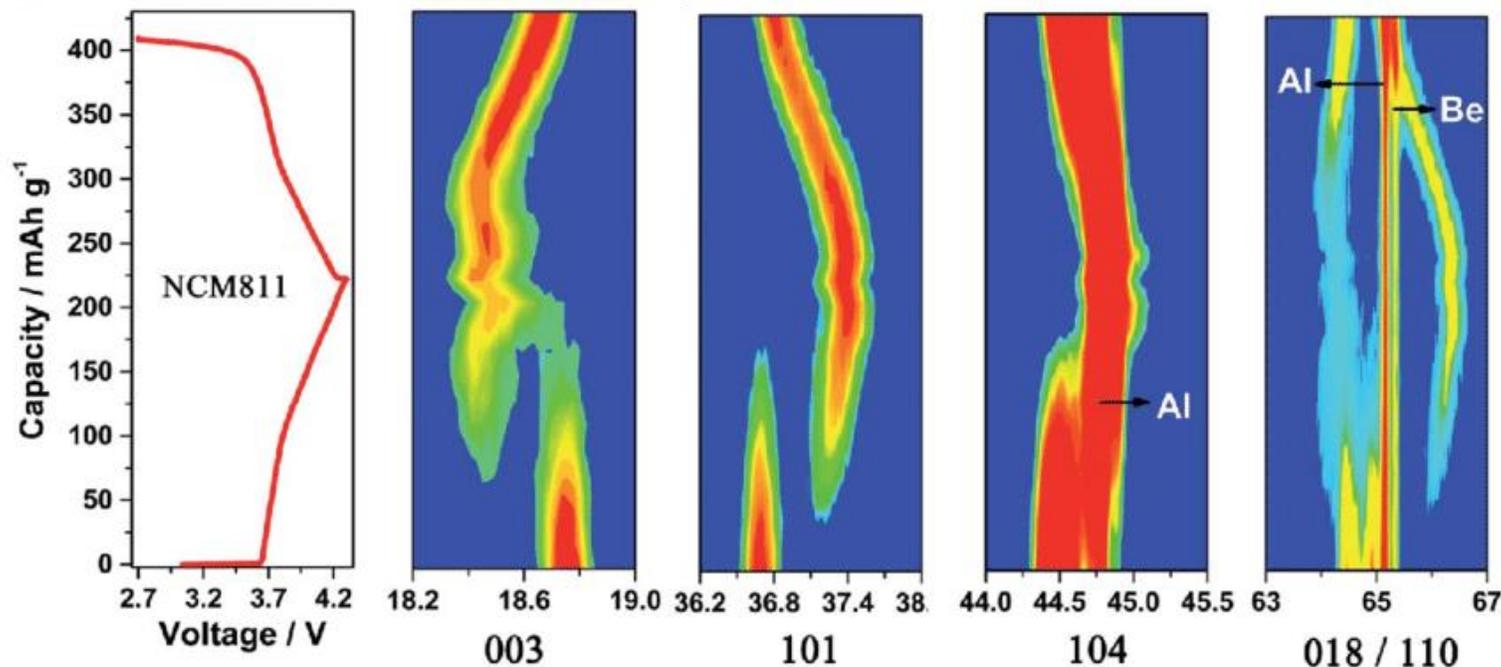
$$\overline{\Phi_A} = \frac{x}{r_A}$$

represents the weighted average ionic potential of A

Crystal structure of layered oxides during charge/discharge

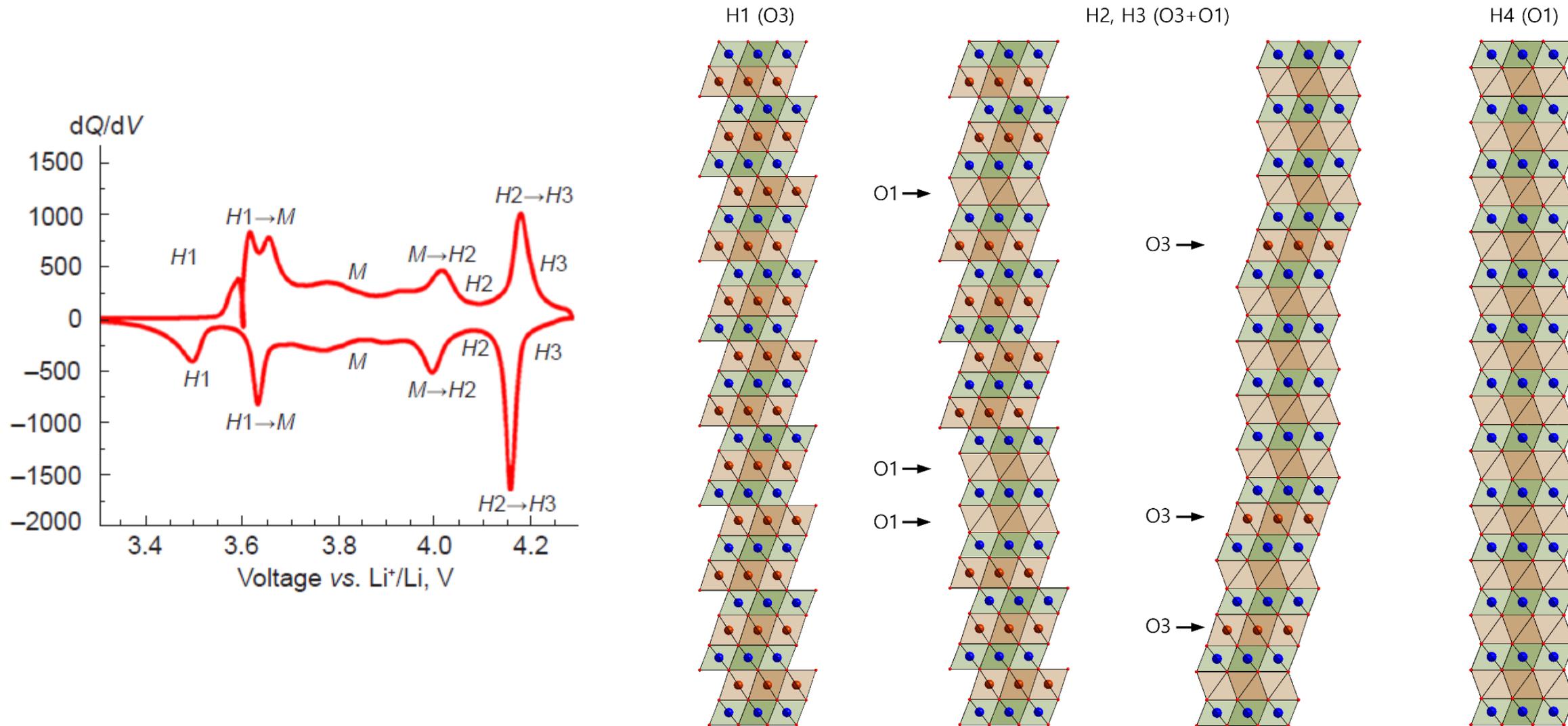


The c lattice and a lattice of NCM811 and the dQ/dV plot

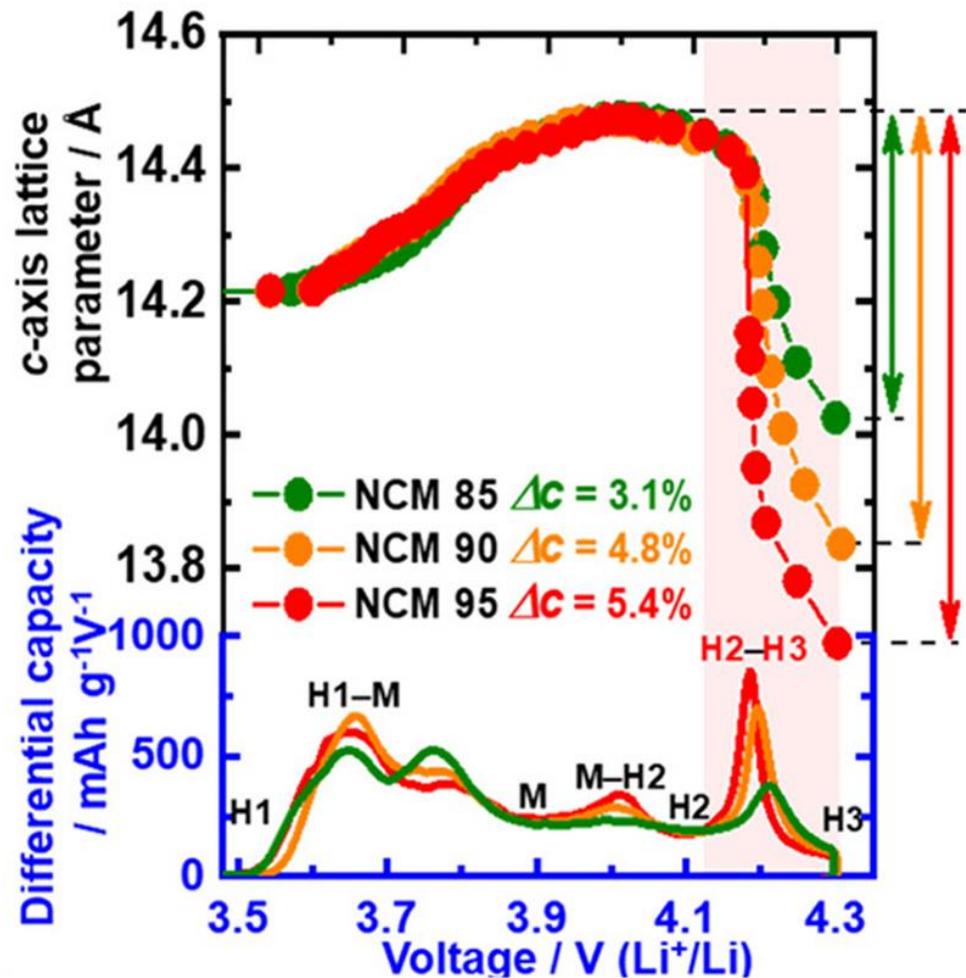


In situ XRD examinations during charging/discharging of NMC811 in the first cycle, showing recorded charge/ discharge curves and contour plots of 003, 101, 104 and 018/110 reflections

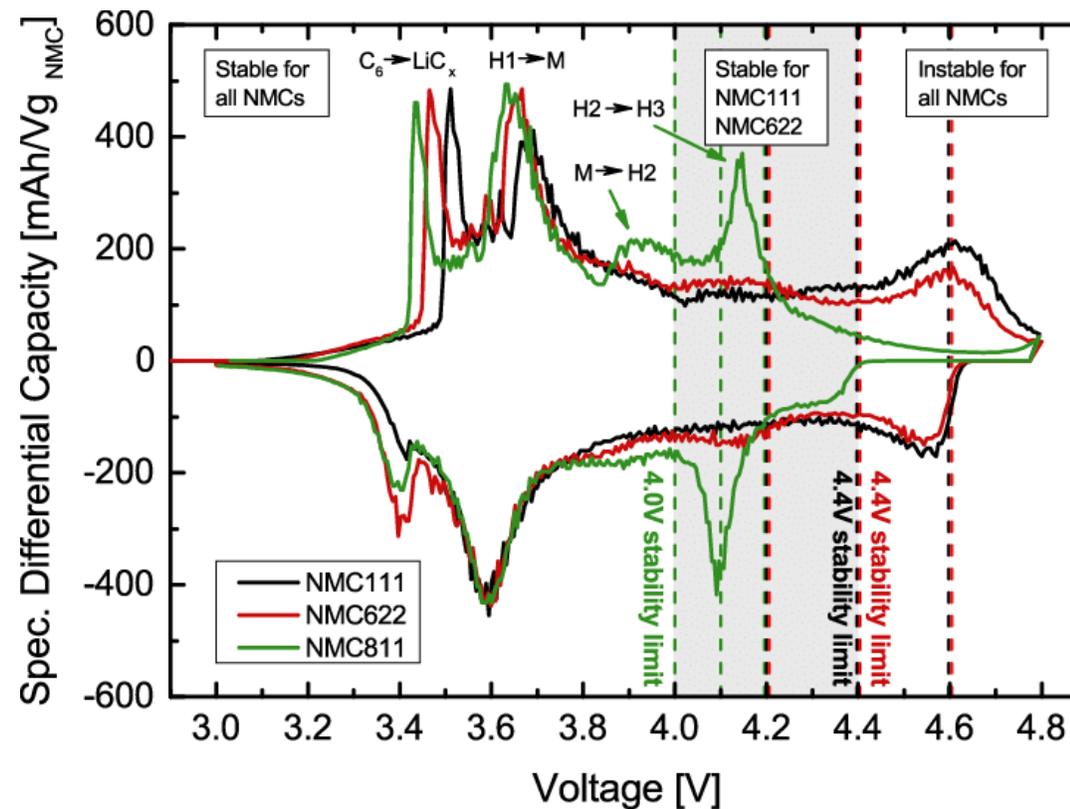
Crystal structure of layered oxides during charge/discharge



Crystal structure of layered oxides during charge/discharge

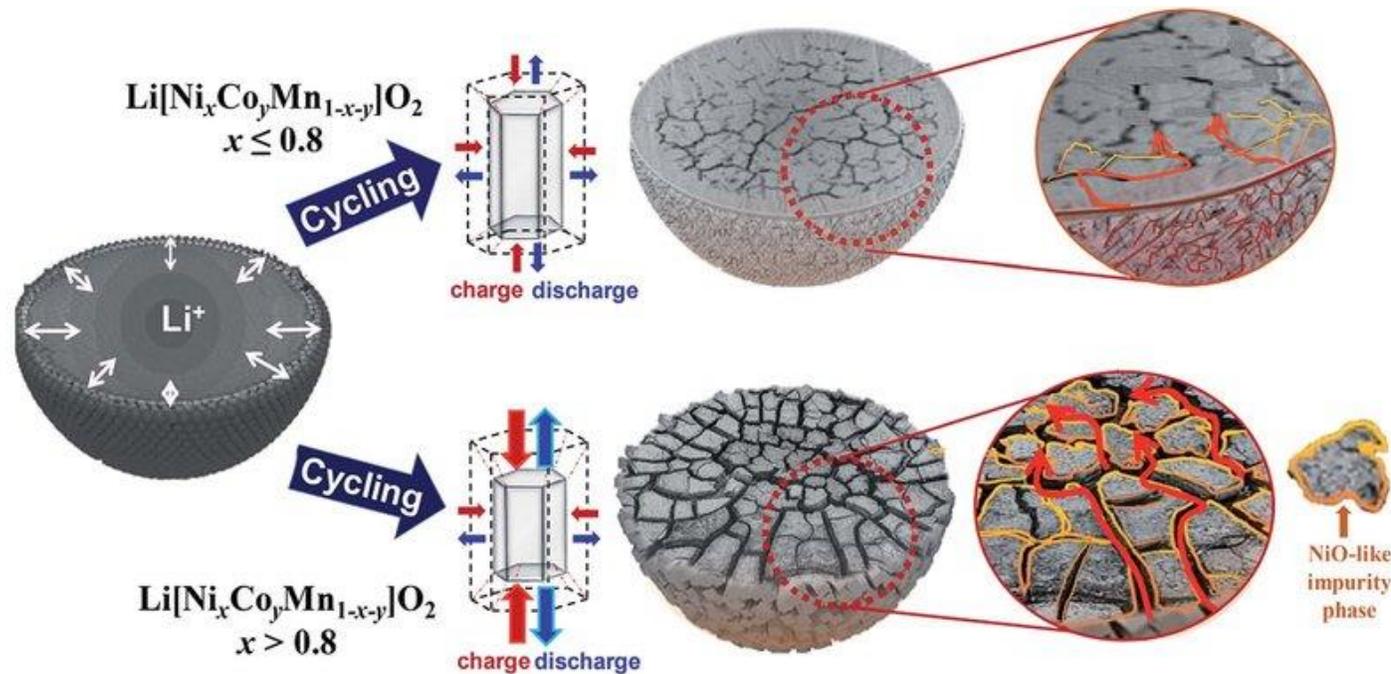


Comparison of the variation in the c lattice changes and corresponding differential capacity of the NMC cathodes



The dQ/dV plots for NMC cathodes

Degradation of layered oxides during charge/discharge

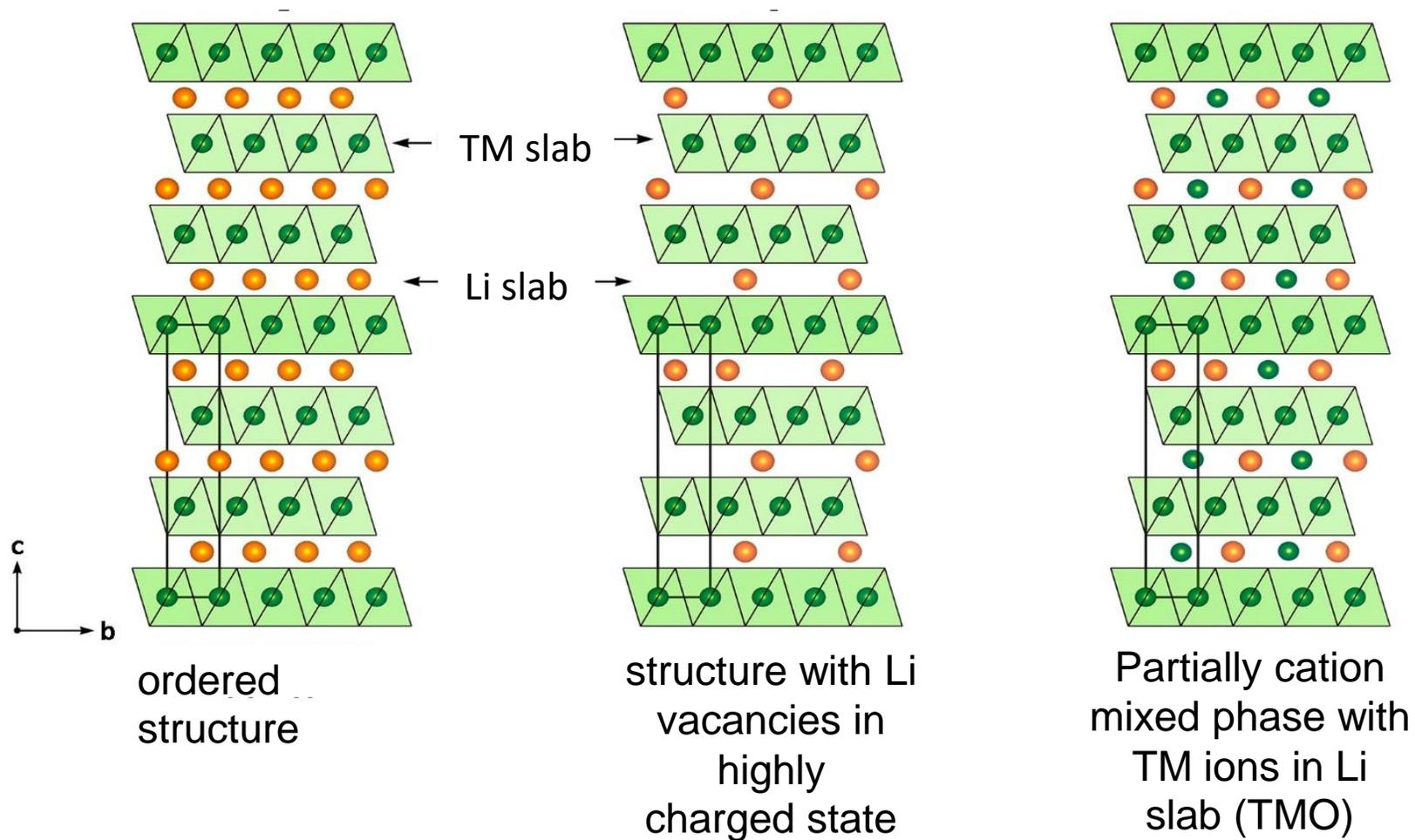


Microcracks and oxygen release are critical for NMC cathode failure

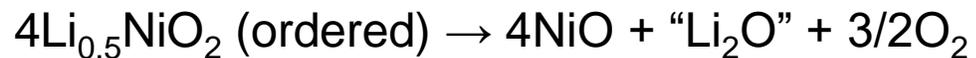
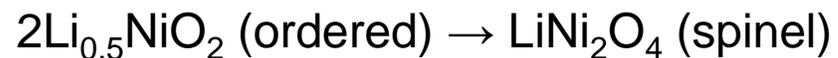
- **Microcrack**
from stress-causing anisotropic change
- **Electrolyte Penetration**
accelerates the surface degradation along the microcrack

Degradation schematic model of NMC cathodes

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



$$r(\text{Ni}^{2+}) = 0.69 \text{ \AA}, r(\text{Li}^+) = 0.76 \text{ \AA}$$



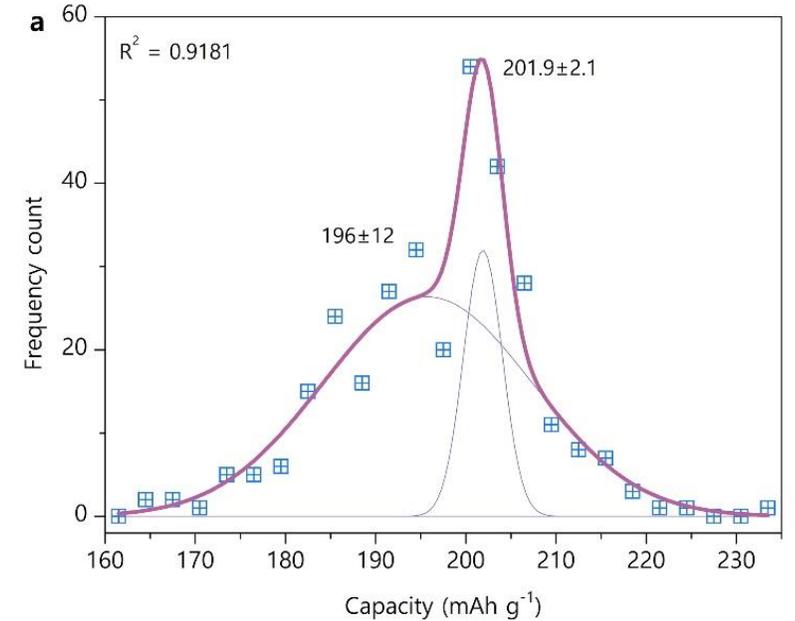
Modification of layered oxides

NMC811 Periodic Table of the Elements

| | | | | | | | | | | | | | | | | | |
|--------------------------------|---------------------------------|--------------------------------|-------------------------------------|--------------------------------|----------------------------------|---------------------------------|---------------------------------|----------------------------------|------------------------------------|-----------------------------------|-----------------------------------|---------------------------------|---------------------------------|---------------------------------|-----------------------------------|----------------------------------|---------------------------------|
| 1 IA | | | | | | | | | | | | | | | | | 18 VIIIA |
| 1 H Hydrogen 1.008 | | | | | | | | | | | | | | | | | 2 He Helium 4.0026 |
| 3 Li Lithium 6.94 | 4 Be Beryllium 9.0122 | | | | | | | | | | | 5 B Boron 10.81 | 6 C Carbon 12.011 | 7 N Nitrogen 14.007 | 8 O Oxygen 15.999 | 9 F Fluorine 18.998 | 10 Ne Neon 20.180 |
| 11 Na Sodium 22.990 | 12 Mg Magnesium 24.305 | | | | | | | | | | | 13 Al Aluminium 26.982 | 14 Si Silicon 28.085 | 15 P Phosphorus 30.974 | 16 S Sulfur 32.06 | 17 Cl Chlorine 35.45 | 18 Ar Argon 39.95 |
| 19 K Potassium 39.098 | 20 Ca Calcium 40.078 | 21 Sc Scandium 44.956 | 22 Ti Titanium 47.867 | 23 V Vanadium 50.942 | 24 Cr Chromium 51.996 | 25 Mn Manganese 54.938 | 26 Fe Iron 55.845 | 27 Co Cobalt 58.933 | 28 Ni Nickel 58.693 | 29 Cu Copper 63.546 | 30 Zn Zinc 65.38 | 31 Ga Gallium 69.723 | 32 Ge Germanium 72.630 | 33 As Arsenic 74.922 | 34 Se Selenium 76.971 | 35 Br Bromine 79.904 | 36 Kr Krypton 83.798 |
| 37 Rb Rubidium 85.468 | 38 Sr Strontium 87.62 | 39 Y Yttrium 88.906 | 40 Zr Zirconium 91.224 | 41 Nb Niobium 92.906 | 42 Mo Molybdenum 95.95 | 43 Tc Technetium (97) | 44 Ru Ruthenium 101.07 | 45 Rh Rhodium 102.91 | 46 Pd Palladium 106.42 | 47 Ag Silver 107.87 | 48 Cd Cadmium 112.41 | 49 In Indium 114.82 | 50 Sn Tin 118.71 | 51 Sb Antimony 121.75 | 52 Te Tellurium 127.60 | 53 I Iodine 126.90 | 54 Xe Xenon 131.29 |
| 55 Cs Caesium 132.91 | 56 Ba Barium 137.33 | 57-71 Lanthanides | 72 Hf Hafnium 178.49 | 73 Ta Tantalum 180.95 | 74 W Tungsten 183.84 | 75 Re Rhenium 186.21 | 76 Os Osmium 190.23 | 77 Ir Iridium 192.22 | 78 Pt Platinum 195.08 | 79 Au Gold 196.97 | 80 Hg Mercury 200.59 | 81 Tl Thallium 204.38 | 82 Pb Lead 207.2 | 83 Bi Bismuth 208.98 | 84 Po Polonium (209) | 85 At Astatine (210) | 86 Rn Radon (222) |
| 87 Fr Francium (223) | 88 Ra Radium (226) | 89-103 Actinides | 104 Rf Rutherfordium (261) | 105 Db Dubnium (269) | 106 Sg Seaborgium (269) | 107 Bh Bohrium (270) | 108 Hs Hassium (269) | 109 Mt Meitnerium (276) | 110 Ds Darmstadtium (281) | 111 Rg Roentgenium (282) | 112 Cn Copernicium (285) | 113 Nh Nihonium (286) | 114 Fl Flerovium (289) | 115 Mc Moscovium (290) | 116 Lv Livermorium (293) | 117 Ts Tennessine (294) | 118 Og Oganesson (294) |

- - core element
- - element used in doping
- - element used in coating

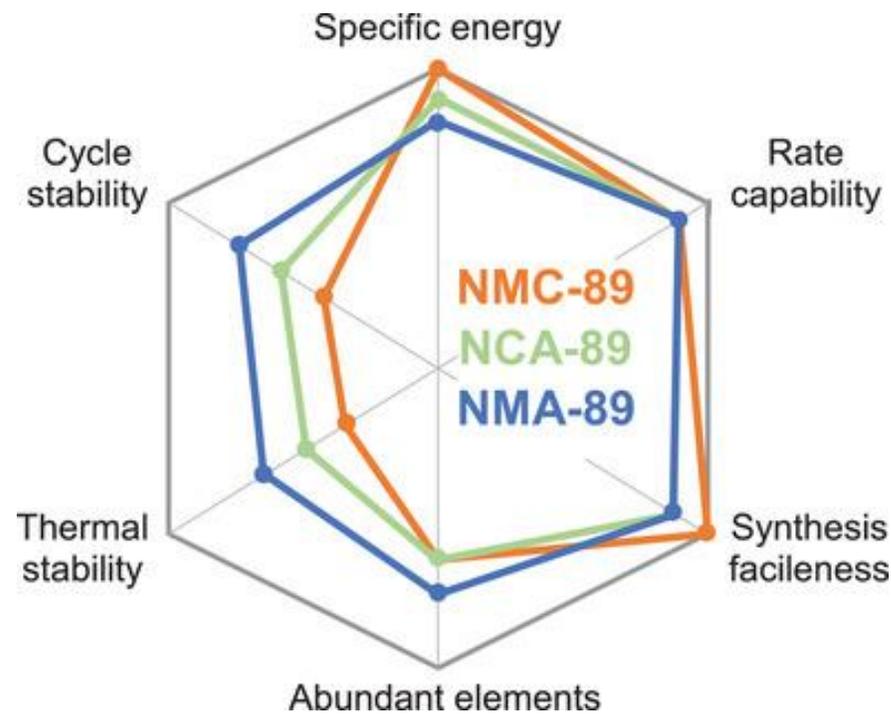
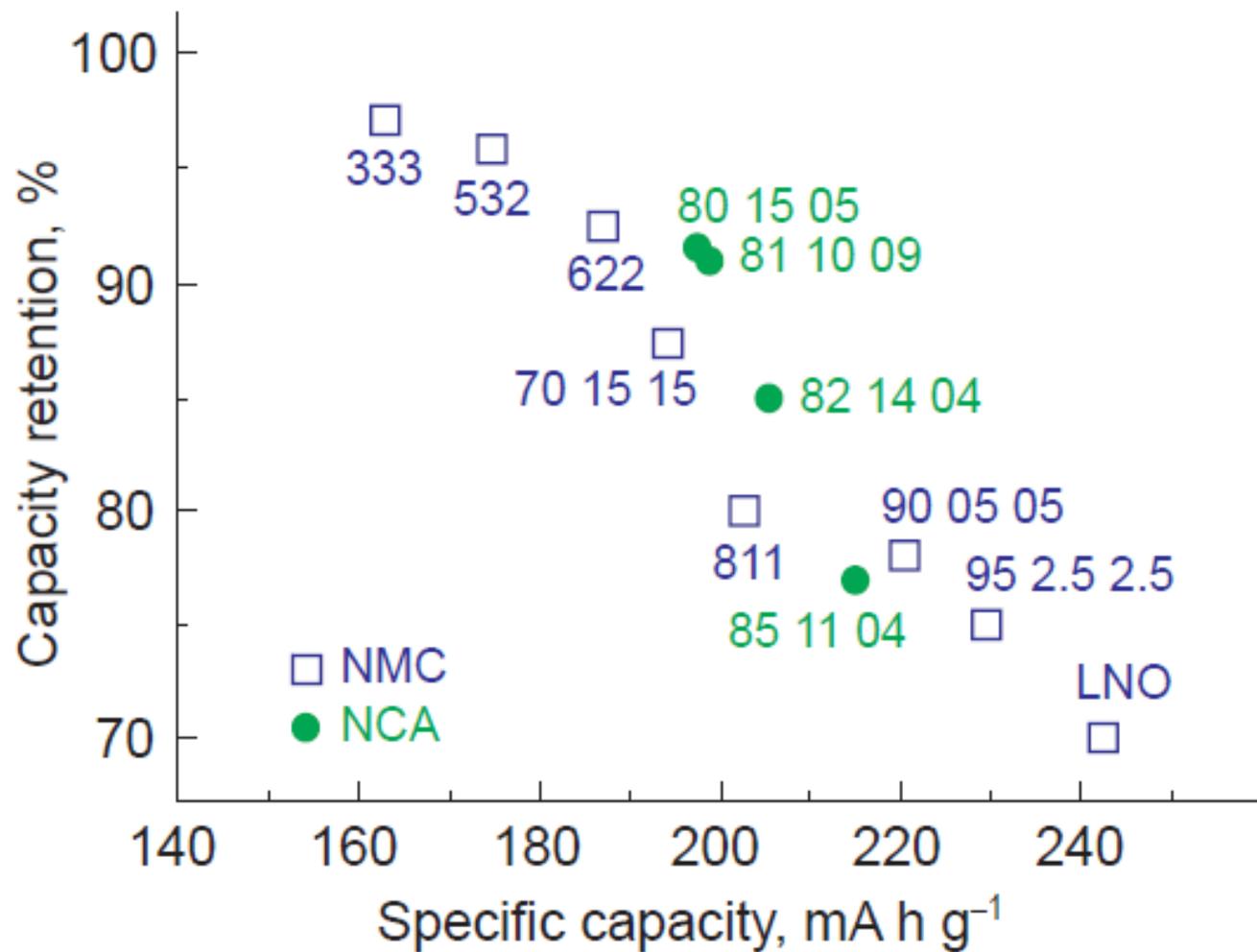
| | | | | | | | | | | | | | | |
|---------------------------------|-------------------------------|------------------------------------|---------------------------------|---------------------------------|--------------------------------|--------------------------------|----------------------------------|--------------------------------|----------------------------------|----------------------------------|-------------------------------|-----------------------------------|---------------------------------|----------------------------------|
| 57 La Lanthanum 138.91 | 58 Ce Cerium 140.12 | 59 Pr Praseodymium 140.91 | 60 Nd Neodymium 144.24 | 61 Pm Promethium (145) | 62 Sm Samarium 150.36 | 63 Eu Europium 151.96 | 64 Gd Gadolinium 157.25 | 65 Tb Terbium 158.93 | 66 Dy Dysprosium 162.50 | 67 Ho Holmium 164.93 | 68 Er Erbium 167.26 | 69 Tm Thulium 168.93 | 70 Yb Ytterbium 173.05 | 71 Lu Lutetium 174.97 |
| 89 Ac Actinium (227) | 90 Th Thorium 232.04 | 91 Pa Protactinium 231.04 | 92 U Uranium 238.03 | 93 Np Neptunium (237) | 94 Pu Plutonium (244) | 95 Am Americium (243) | 96 Cm Curium (247) | 97 Bk Berkelium (247) | 98 Cf Californium (251) | 99 Es Einsteinium (252) | 100 Fm Fermium (257) | 101 Md Mendelevium (258) | 102 No Nobelium (259) | 103 Lr Lawrencium (266) |



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.

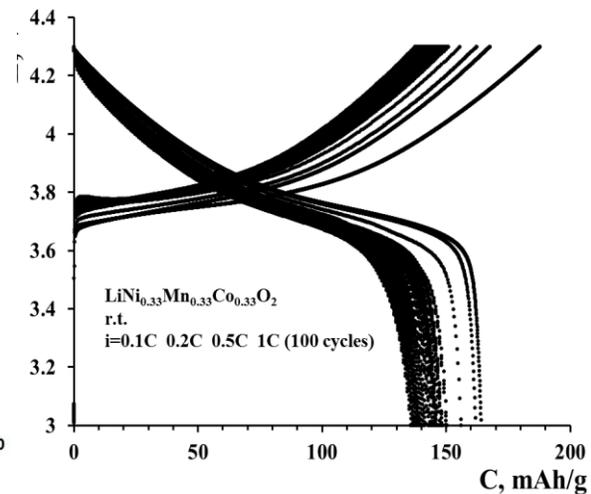
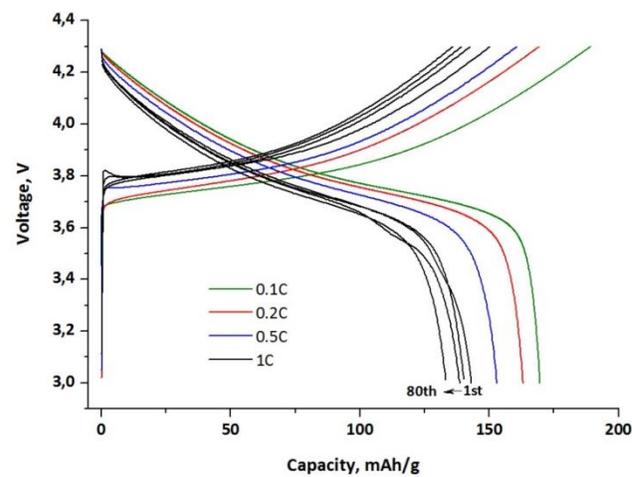
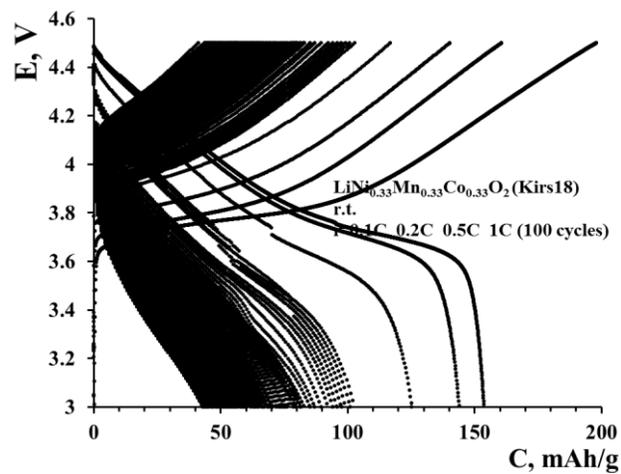
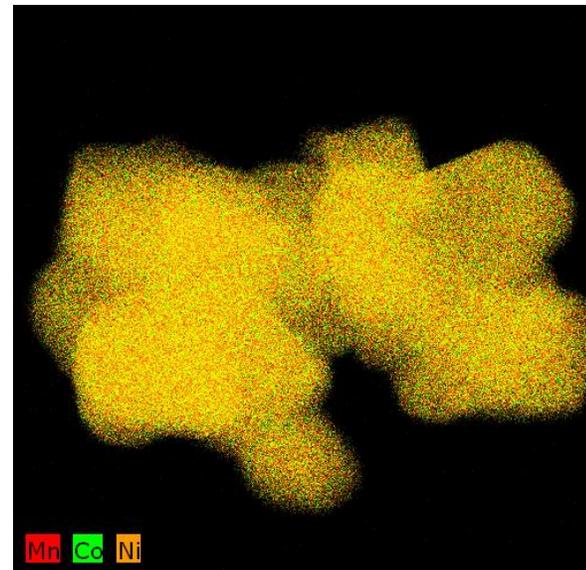
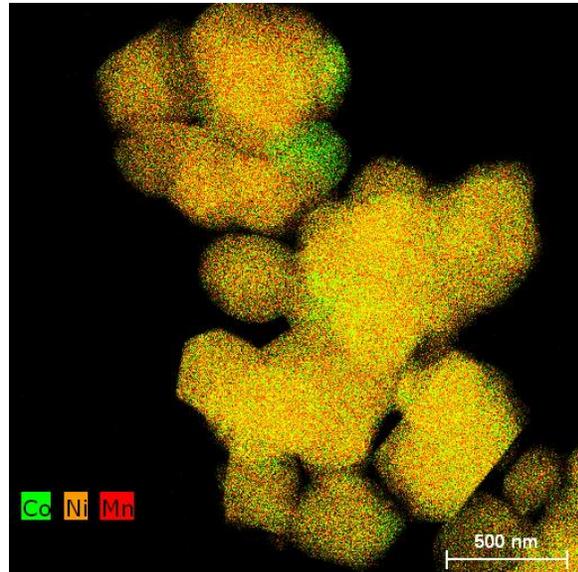
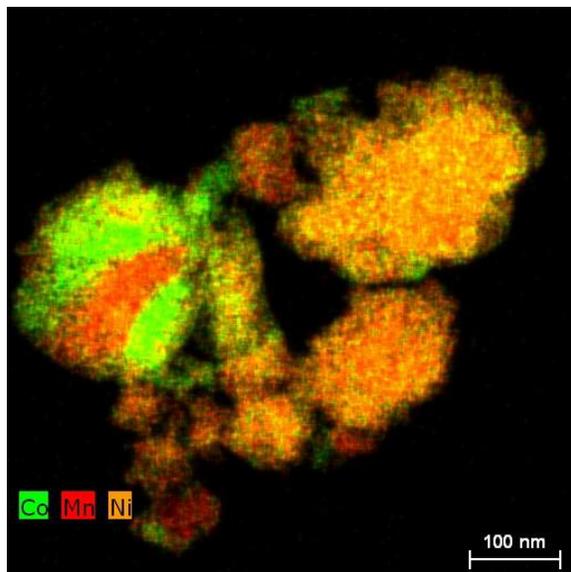
<https://ssrn.com/abstract=4524502>

Modification of layered oxides

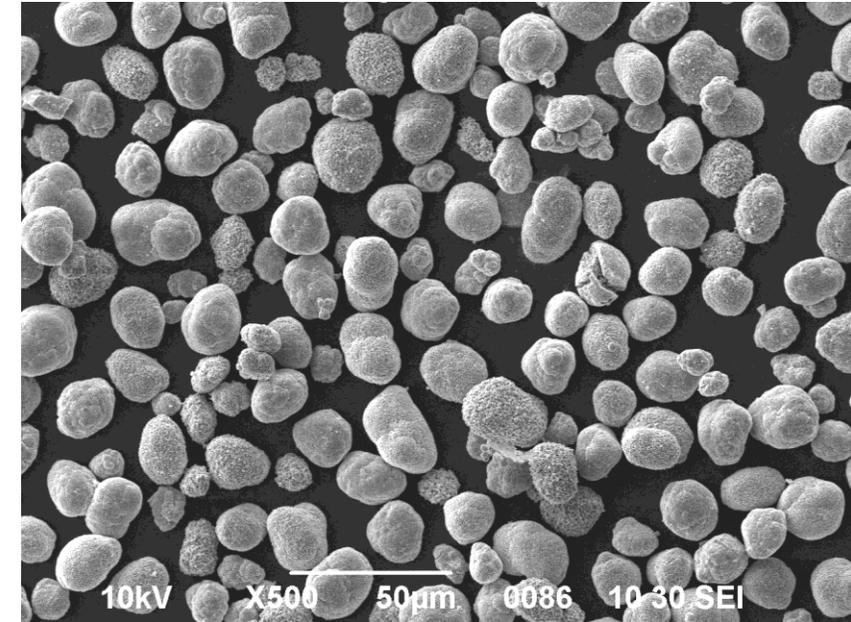
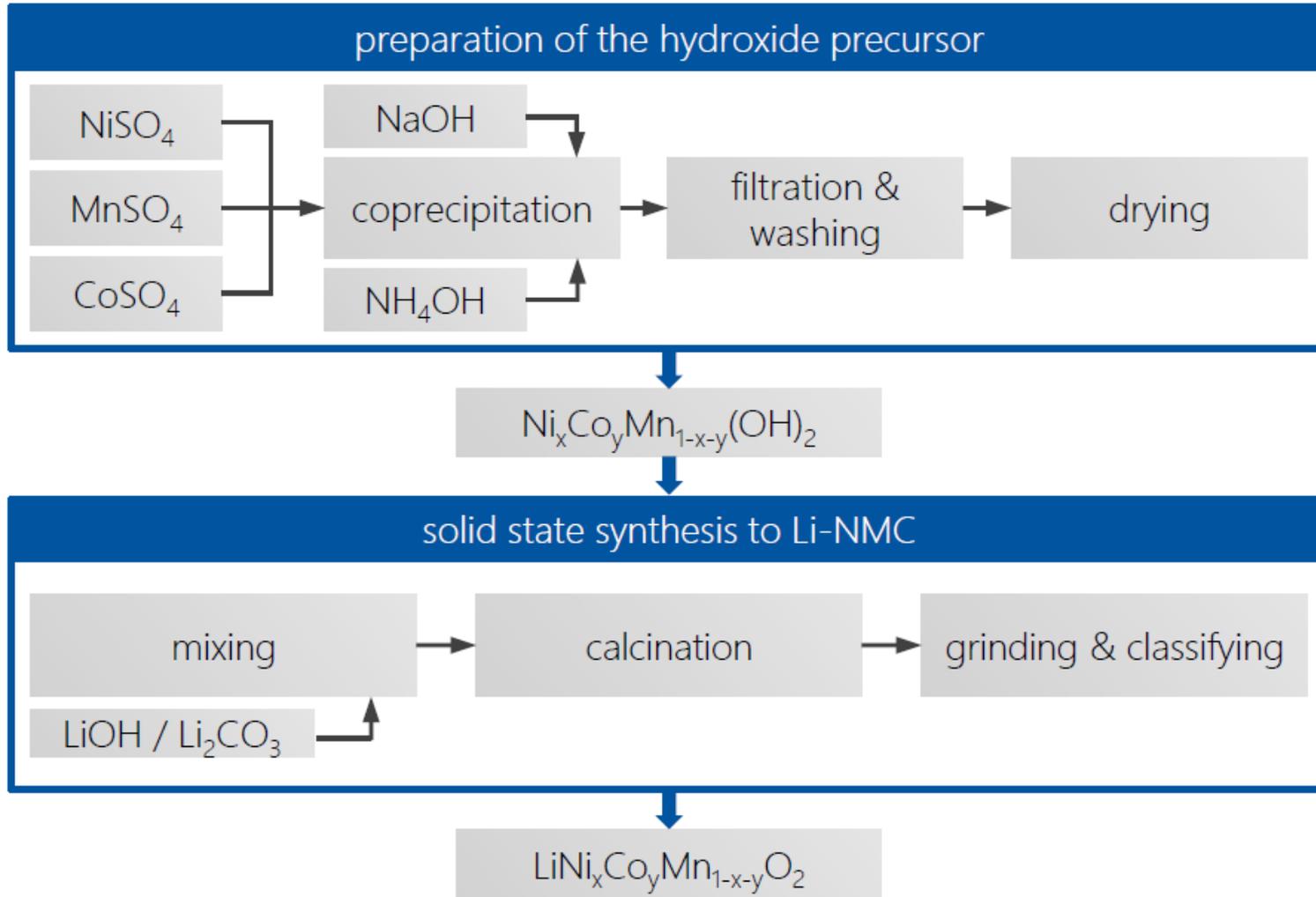


Synthesis of layered oxides

Inhomogeneous TM distribution

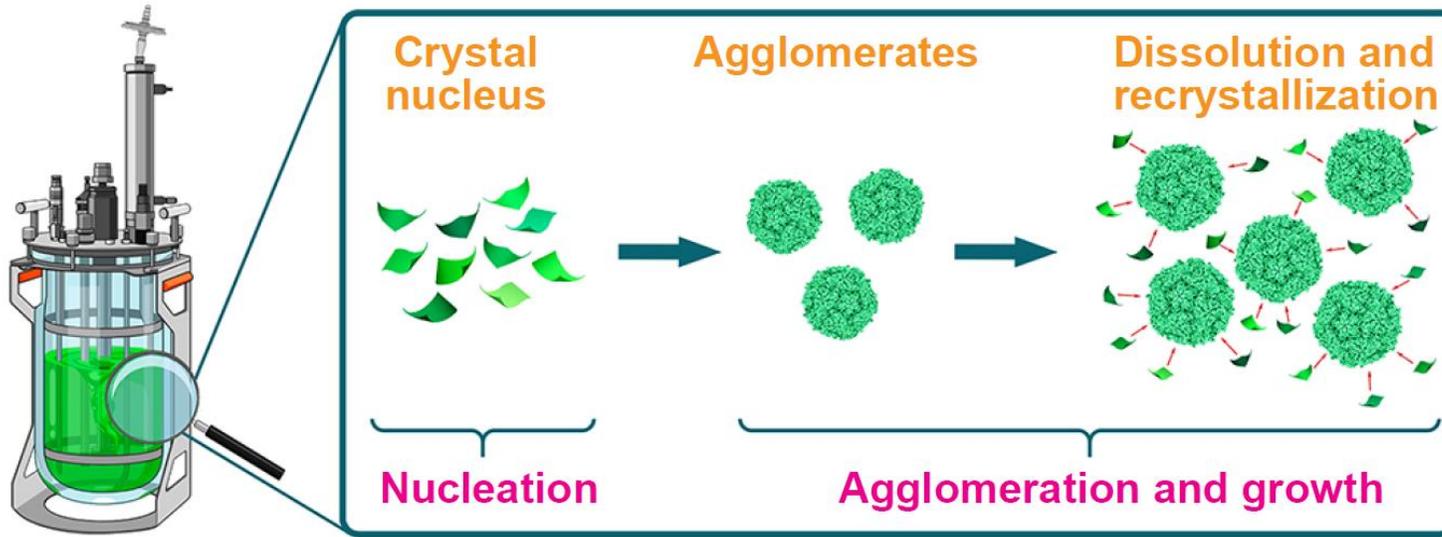


Synthesis of layered oxides

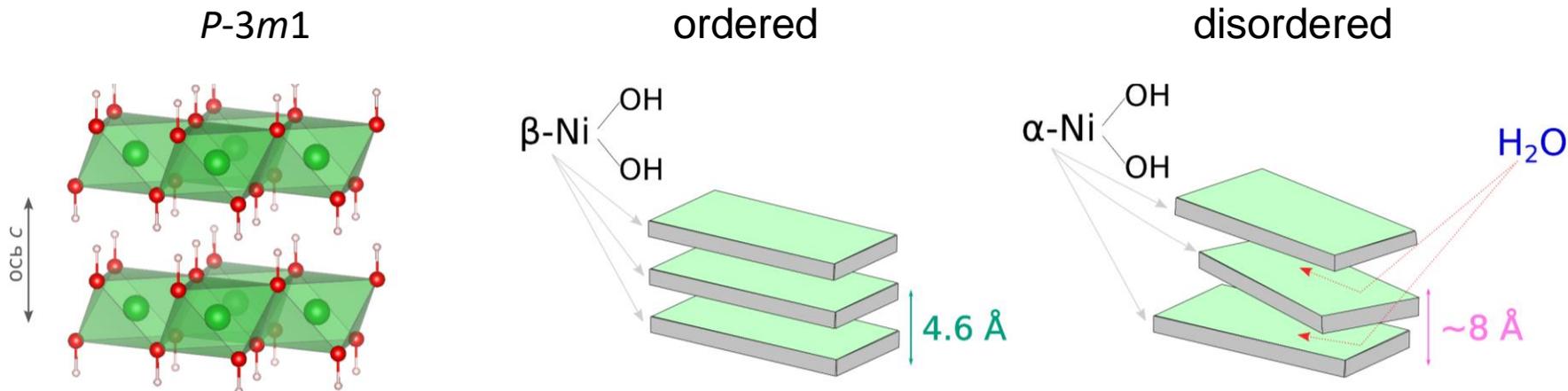
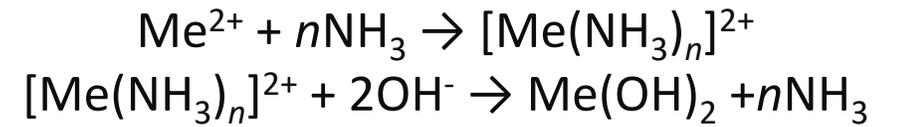


SEM image of NMC cathode

Co-precipitation

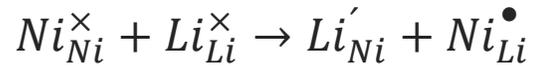


The scheme of co-precipitation of the hydroxide precursor $\text{TM}(\text{OH})_2$



Defects in layered oxides

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



2. Excess Ni in Li positions (low $p(\text{O}_2)$):



3. Excess Li in Ni positions (high $p(\text{O}_2)$):



LiCoO₂

NMC111

NMC532

NMC622

NMC811

NMC952525

LiNiO₂



air



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);

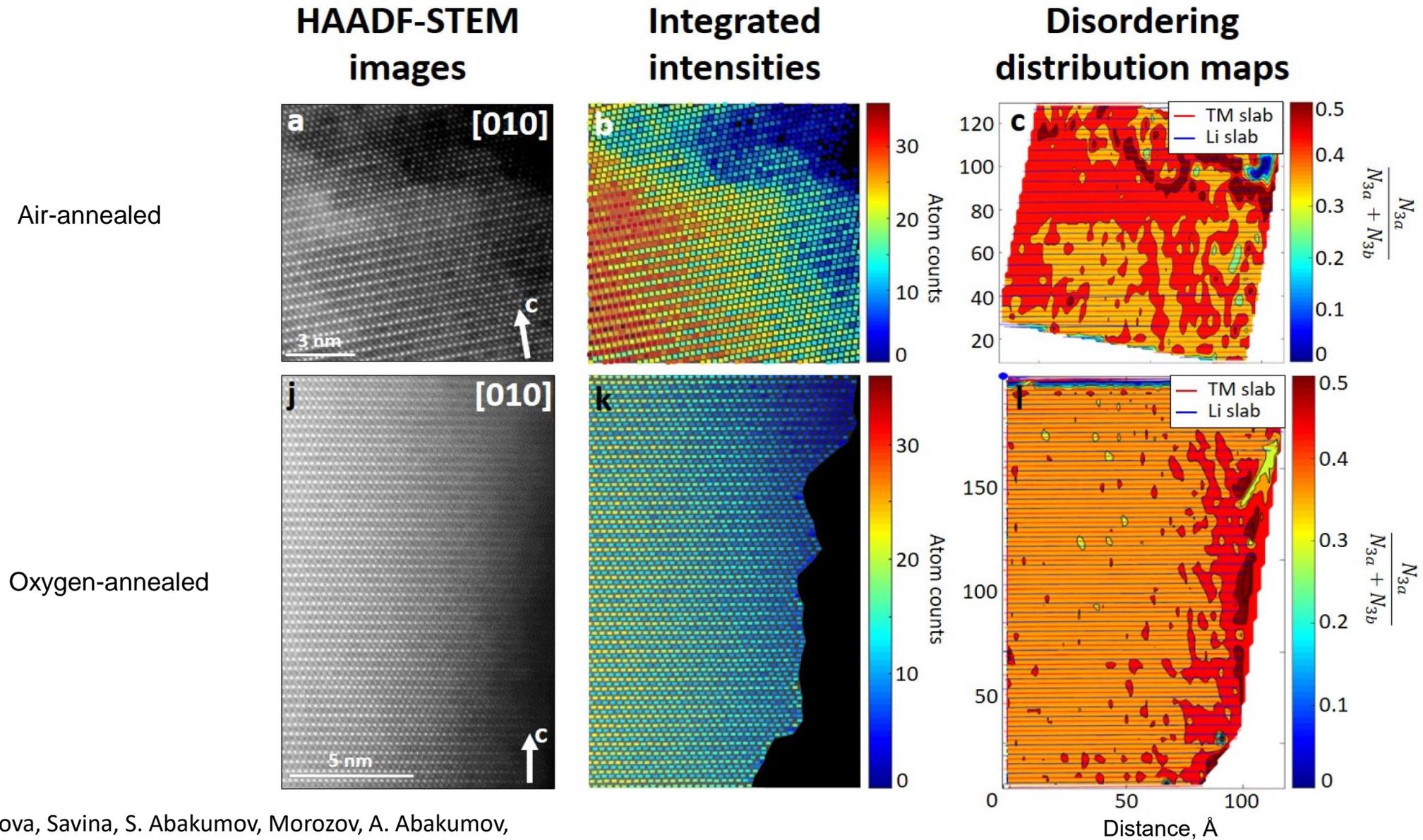
Z – charge relative to the normal ion charge on the site

' negative relative charge

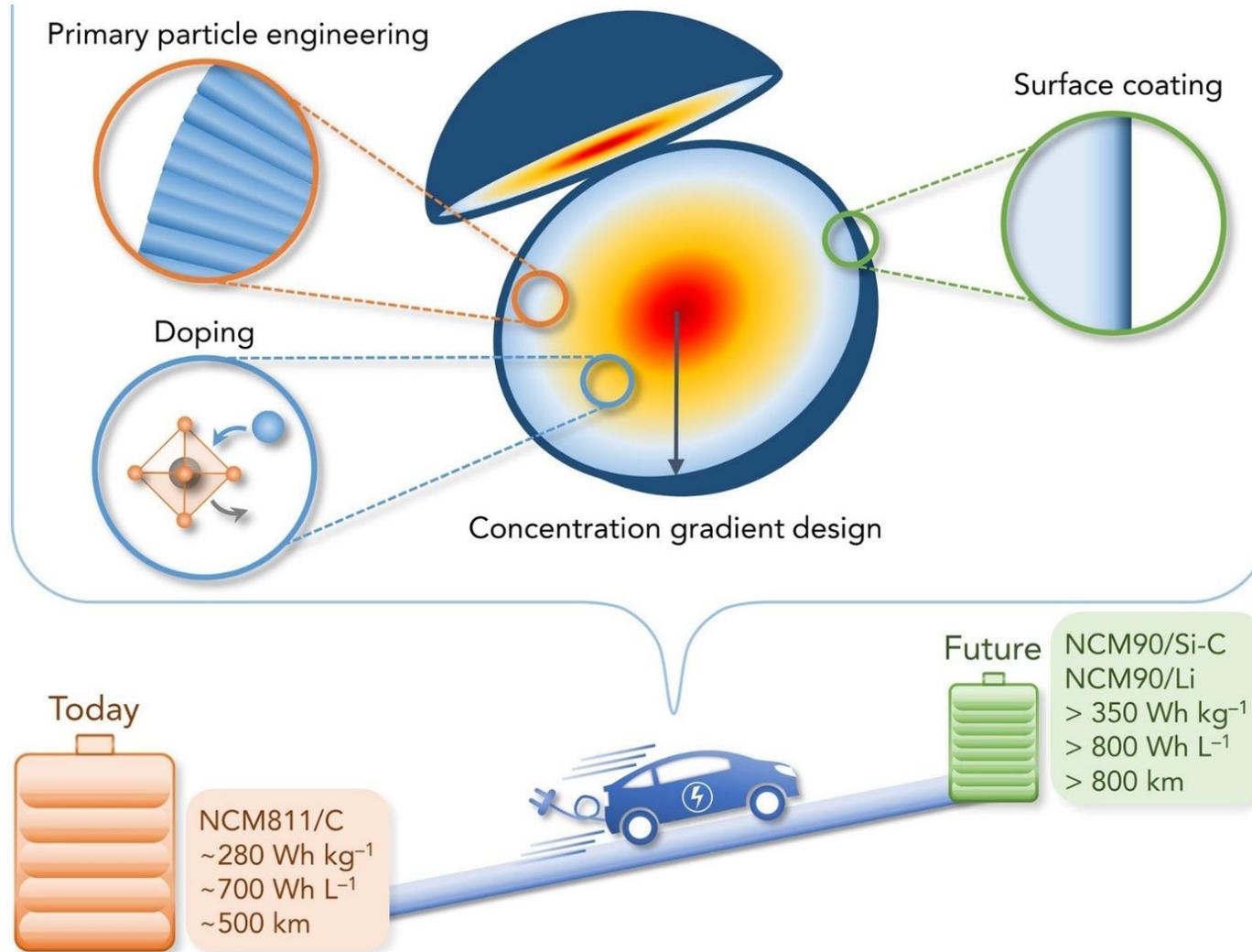
• positive relative charge

x zero relative charge (x is often omitted)

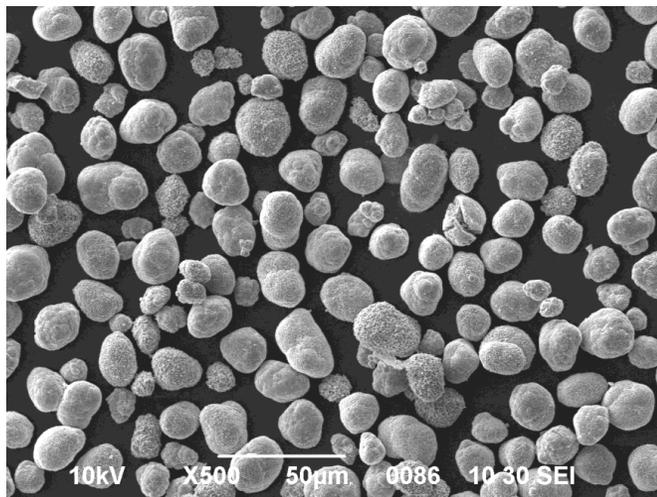
Defects in layered oxides



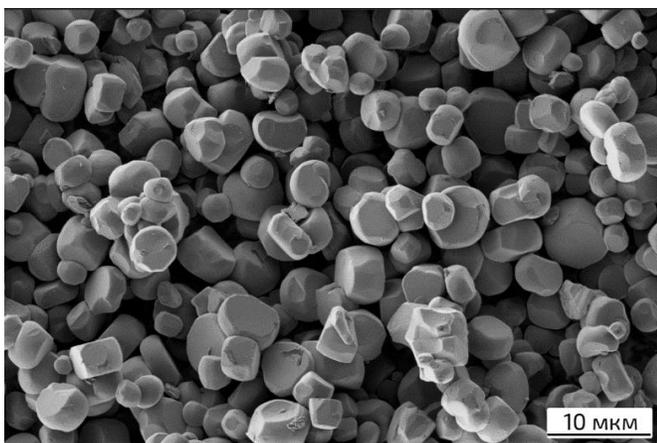
Modification strategies



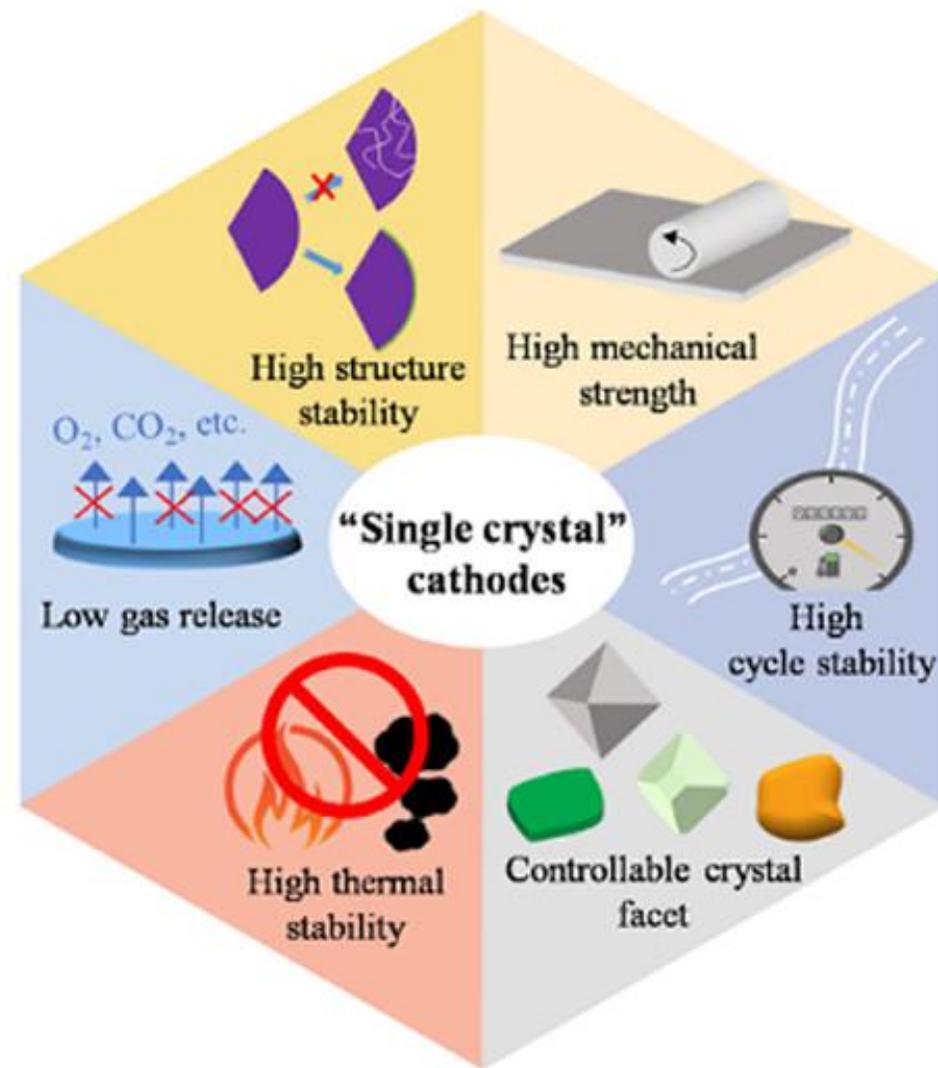
Single crystal layered oxides



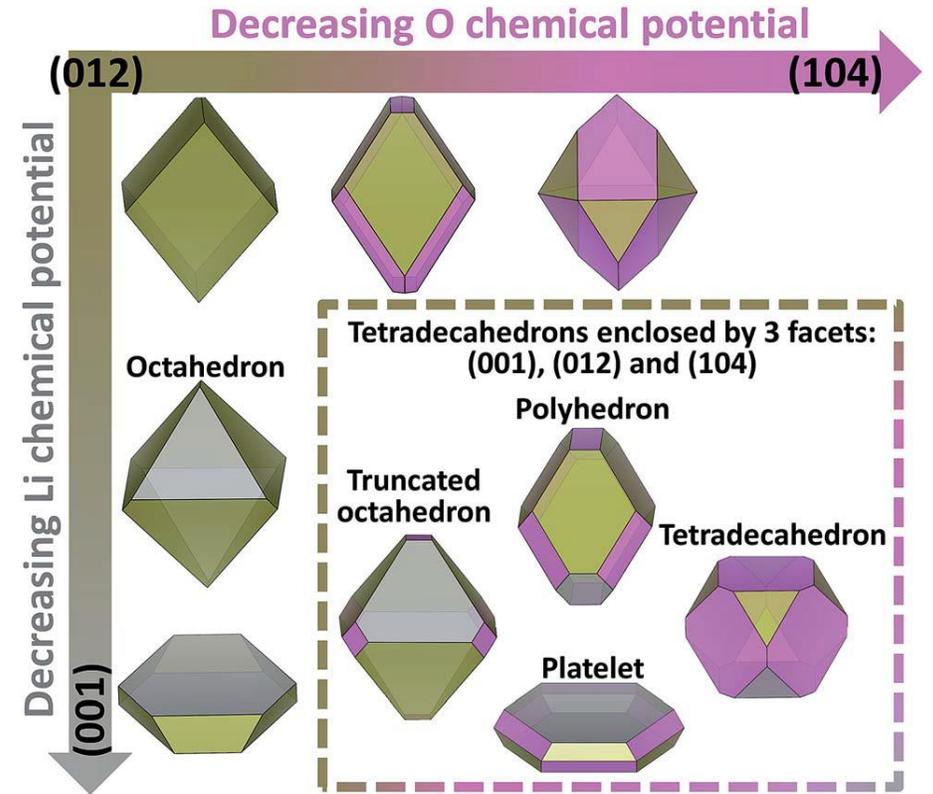
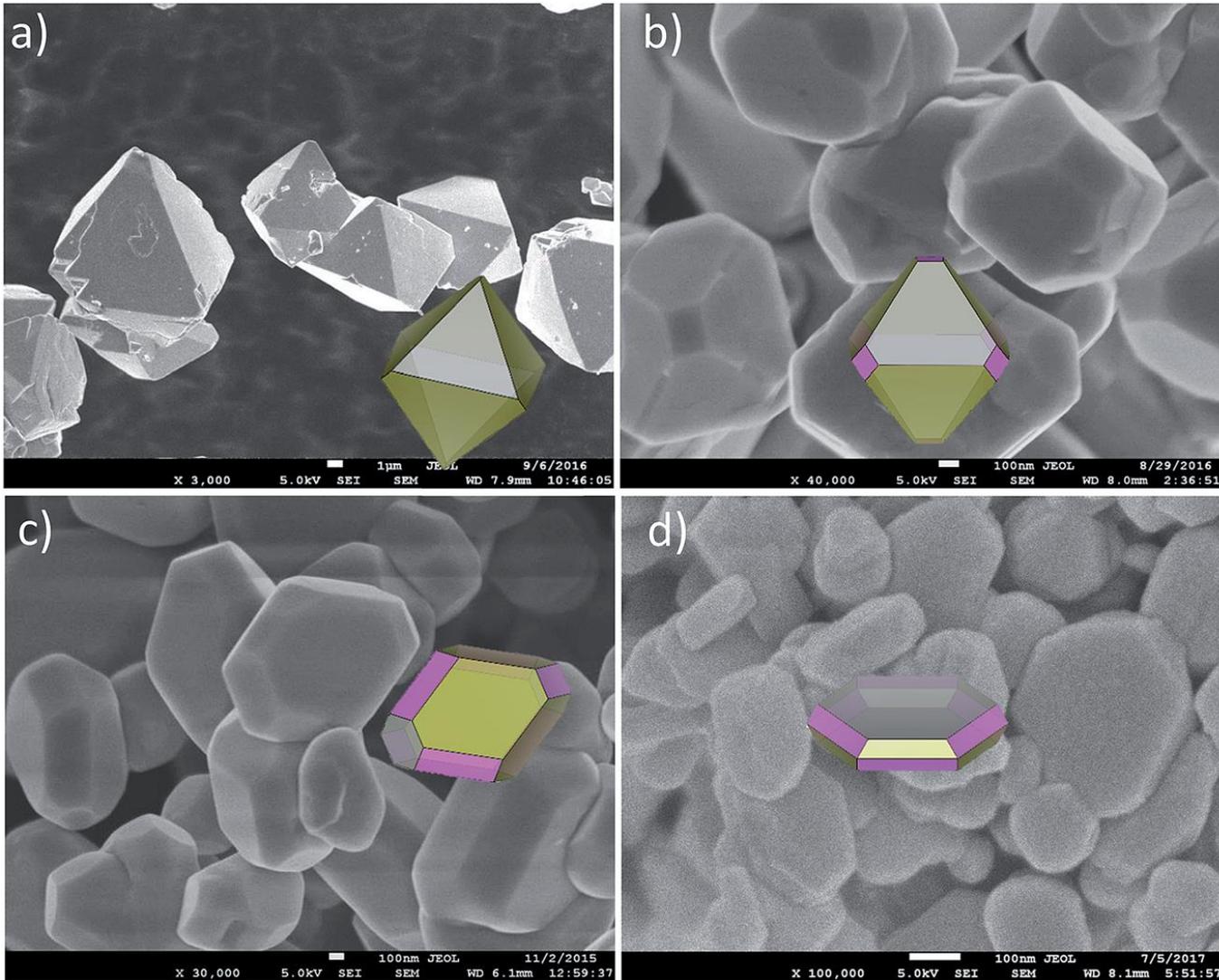
Spherical-like agglomerates



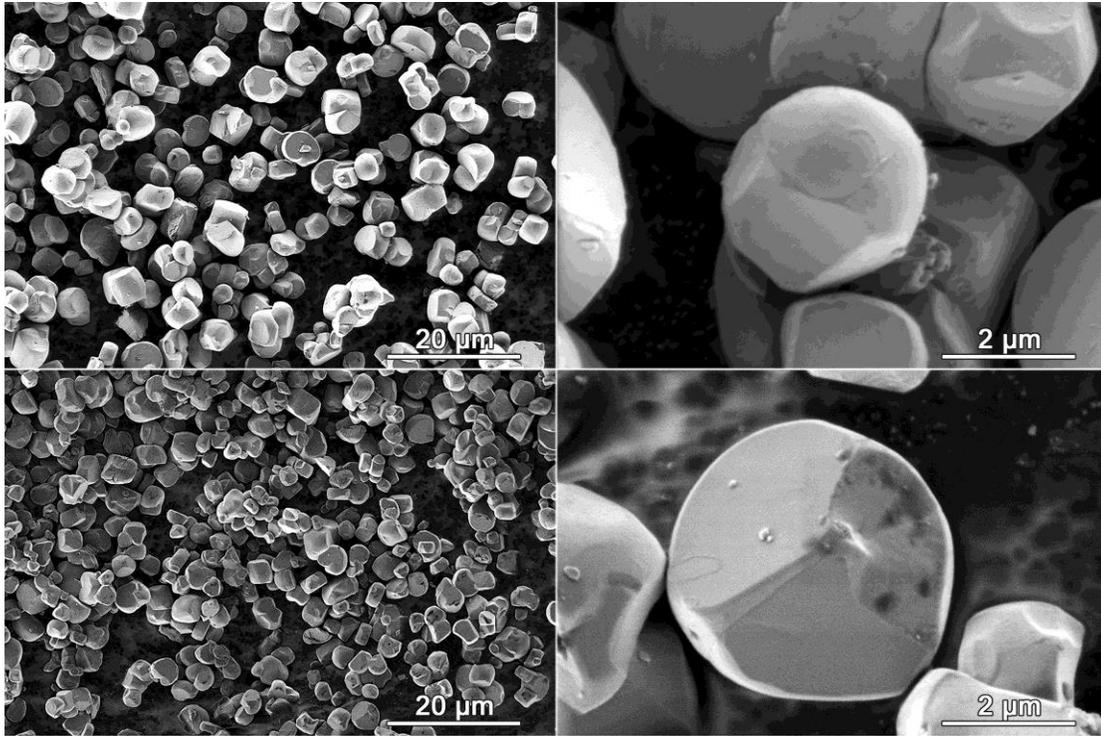
Single crystal



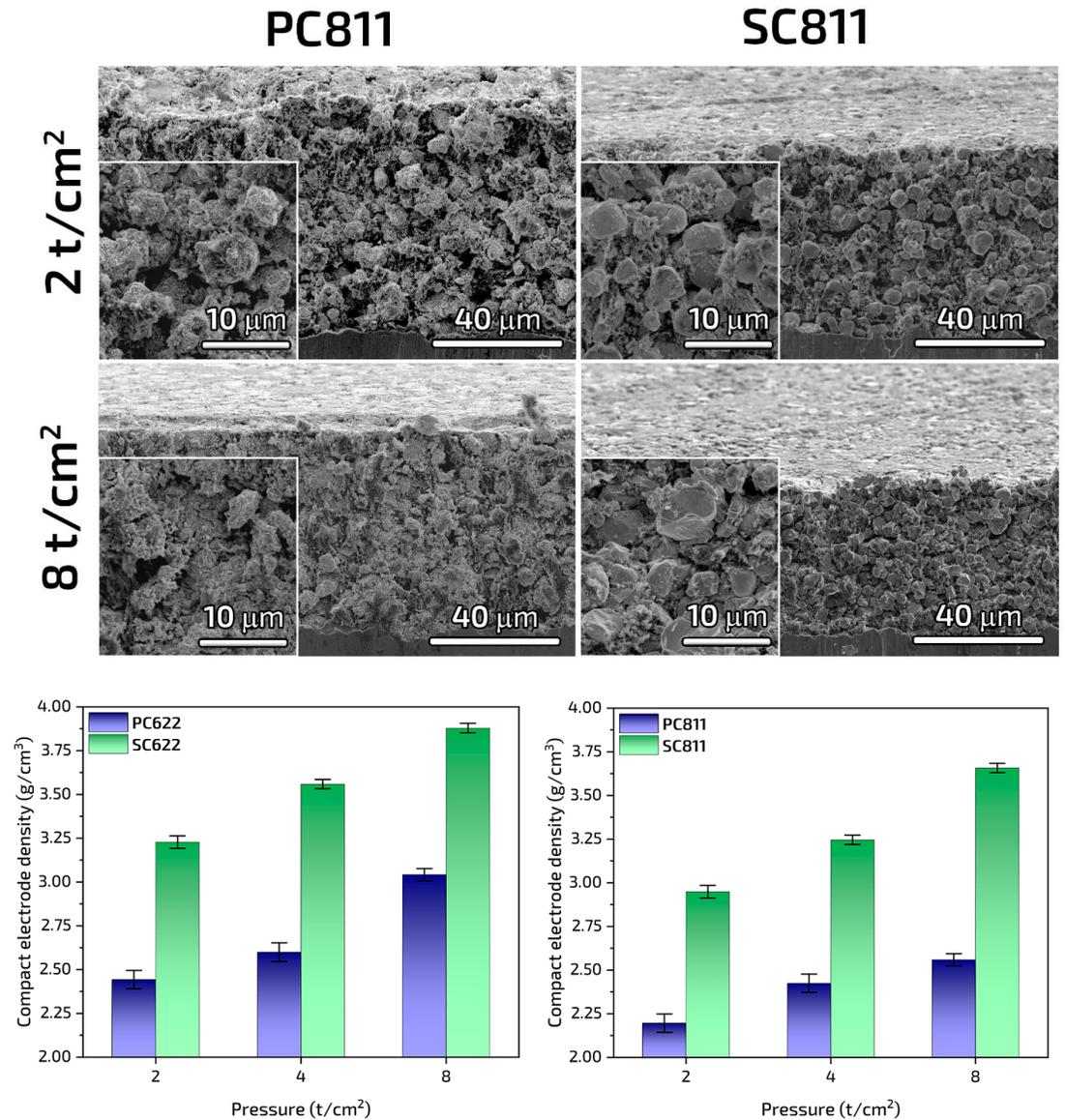
Single crystal layered oxides



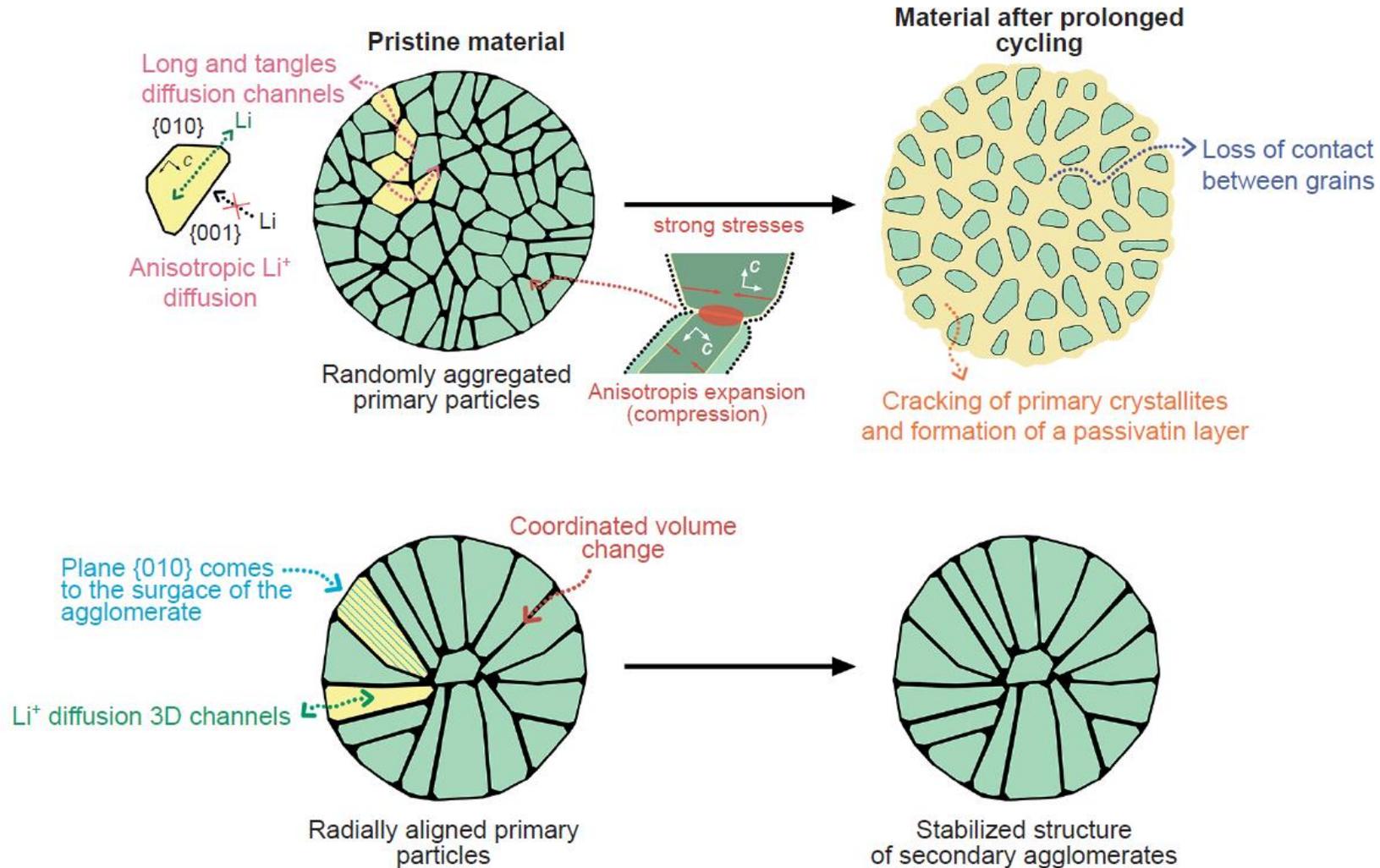
Single crystal layered oxides



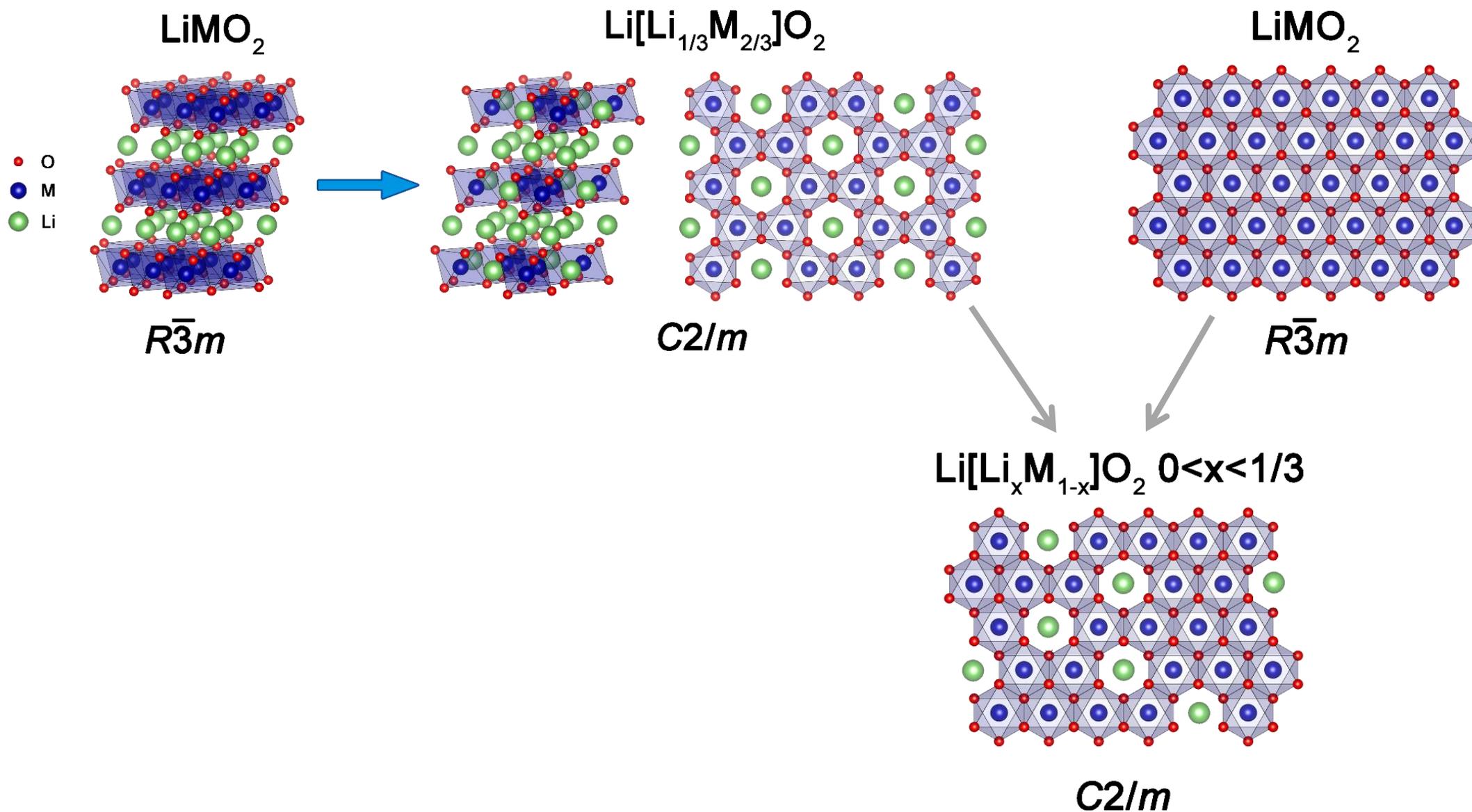
Moiseev, Savina, Pavlova, Abakumova, Pazhetnov, Abakumov,
 Energy Adv., 1, 677–681 (2022), patent RU 2 776 156, 14.07.2022



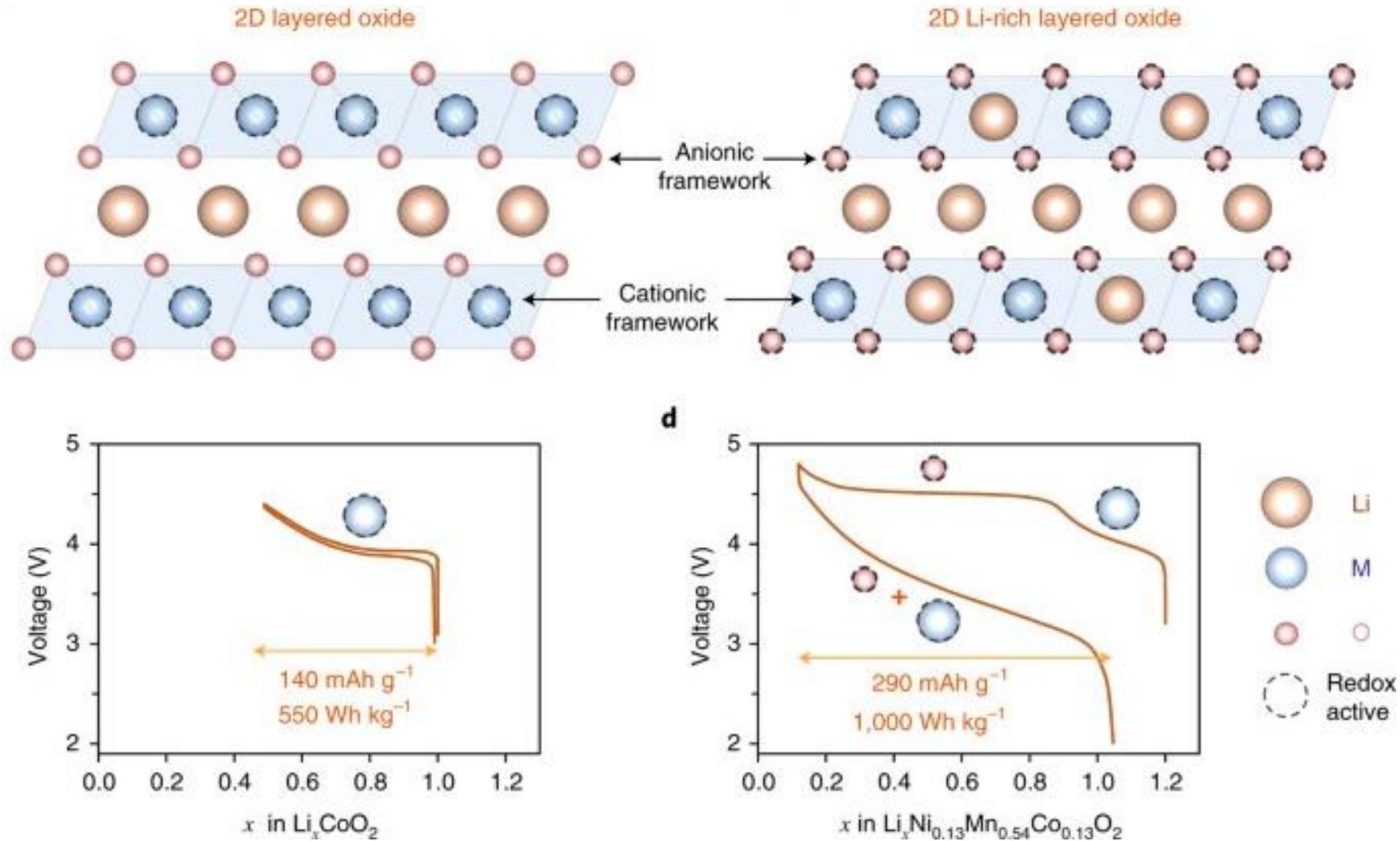
Microstructure organization of layered oxides



Crystal structure of Li-rich layered oxides



Electrochemical performance of Li-rich layered oxides

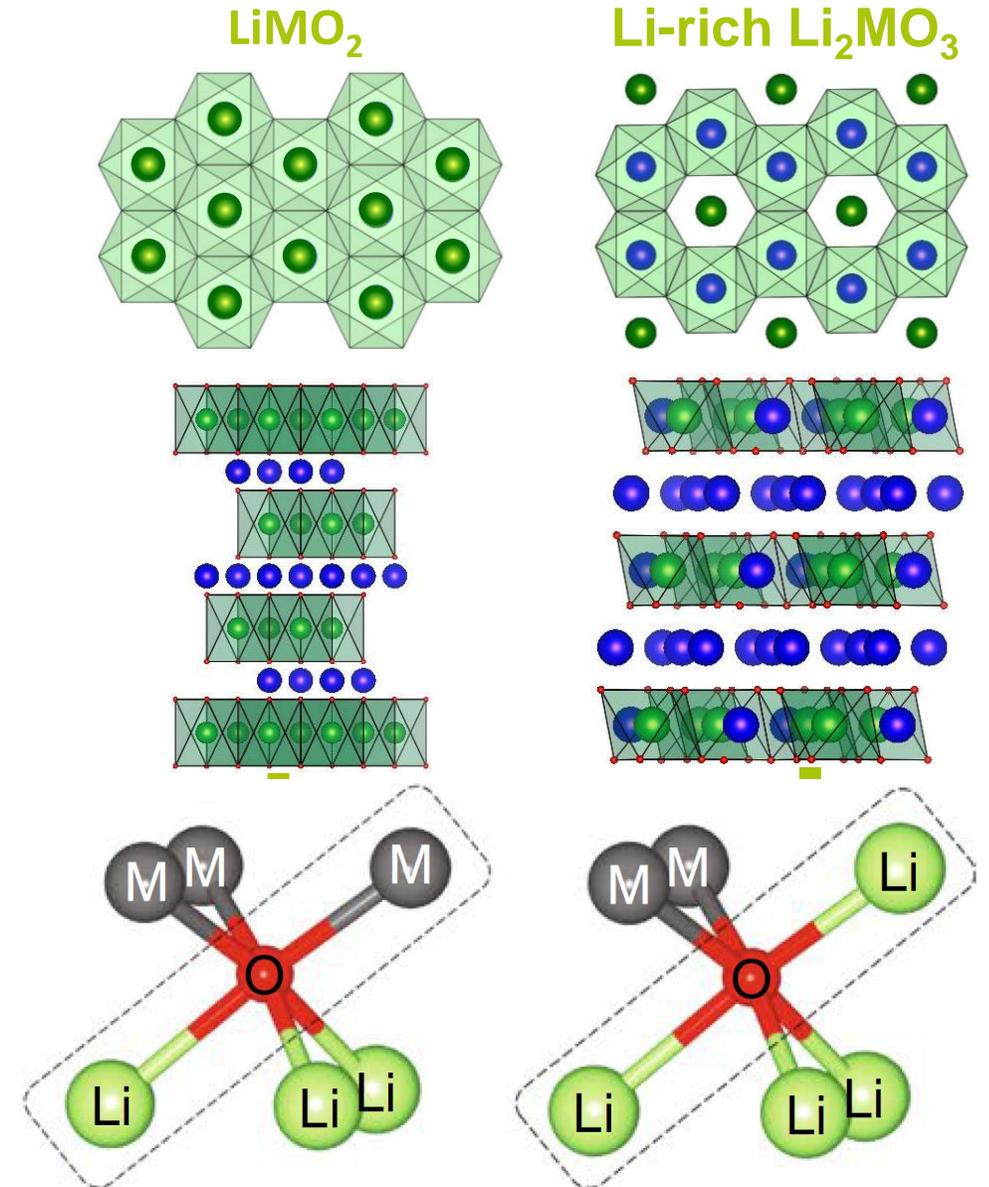
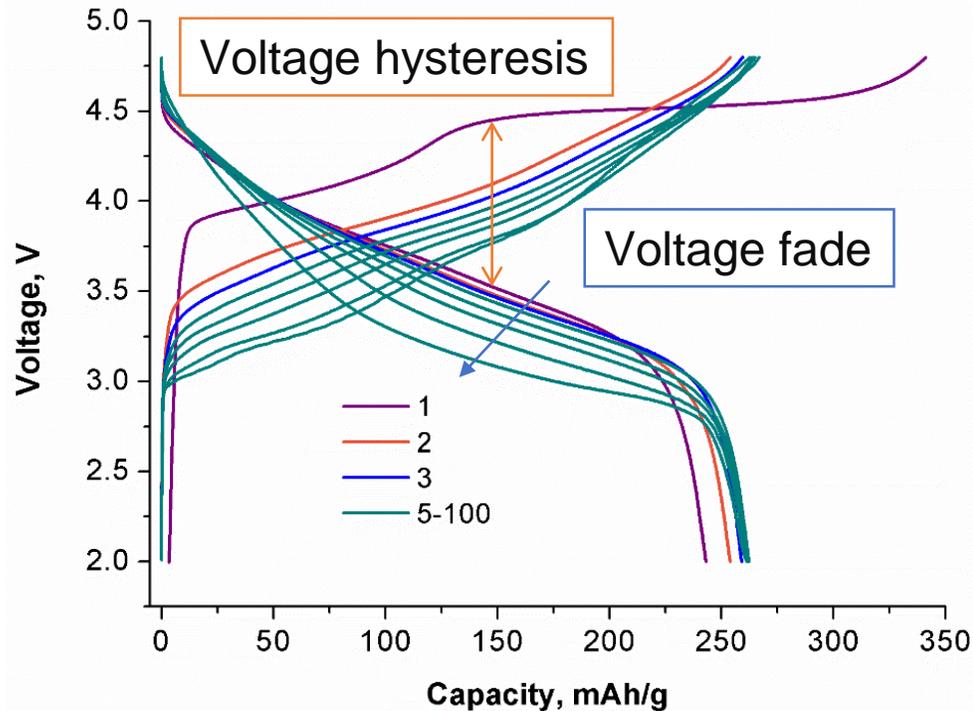


Negative side of Li-rich NMC

Drawbacks:

1. Slow kinetics
2. Voltage hysteresis
3. Voltage fade
4. Irreversible oxygen oxidation (gaseous O₂ evolution)

Li-rich NMC ($\text{Li}_{4/3-x}\text{Ni}_x\text{Mn}_{2/3-x}\text{Co}_x\text{O}_2$)



Thx

