X International School-Conference of Young Scientists “Electrode Materials: Bridging Theory and Experiment”

Lecture: Voltage in metal-ion batteries

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Some basic things

Capacity

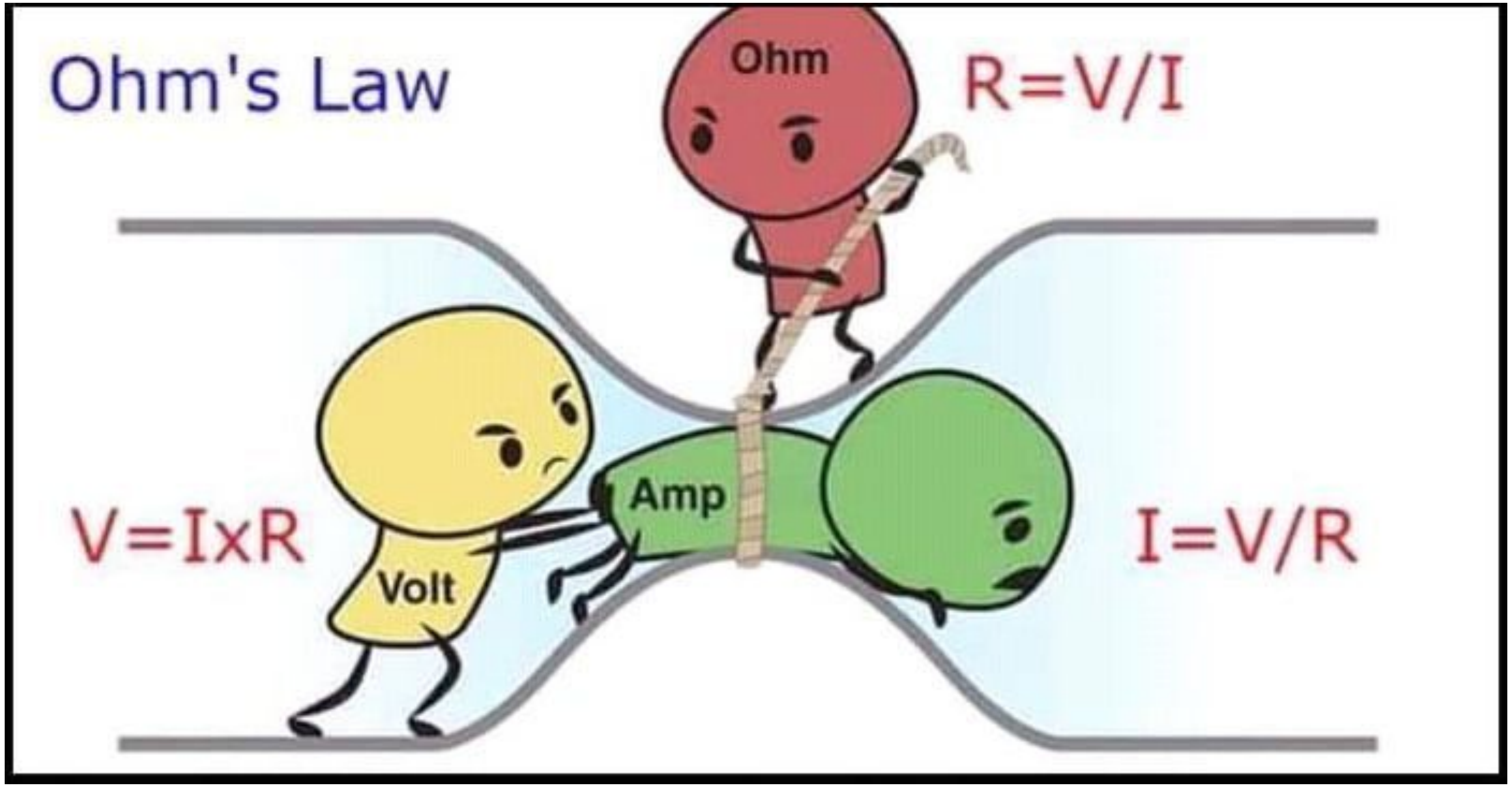
Capacity is the total amount of electric charge a battery can store and deliver over a specific period.

The theoretical capacity of a lithium-ion battery is calculated using the formula

$$\text{Capacity} = \left(\frac{nF}{3600 \times M} \right)$$

Electrode material	Mass of electrode [kg/mol]	Mass of electrode [atoms/kg]	Theoretical electric charge [Ah/kg]
LCO ($LiCoO_2$)	0.09788	$6.15*10^{24}$	274
NMC ($LiNi_{1/3}Mn_{1/3}Co_{1/3}O_2$)	0.09640	$6.25*10^{24}$	278
NMC ($LiNi_{0.8}Mn_{0.1}Co_{0.1}O_2$)	0.09728	$6.19*10^{24}$	275
LFP ($LiFePO_4$)	0.15776	$3.82*10^{24}$	170
Graphite-Anode (C_6)	0.07206	$8.35*10^{24}$	371
Lithium-Anode (Li)	0.00693	$8.69*10^{25}$	3867

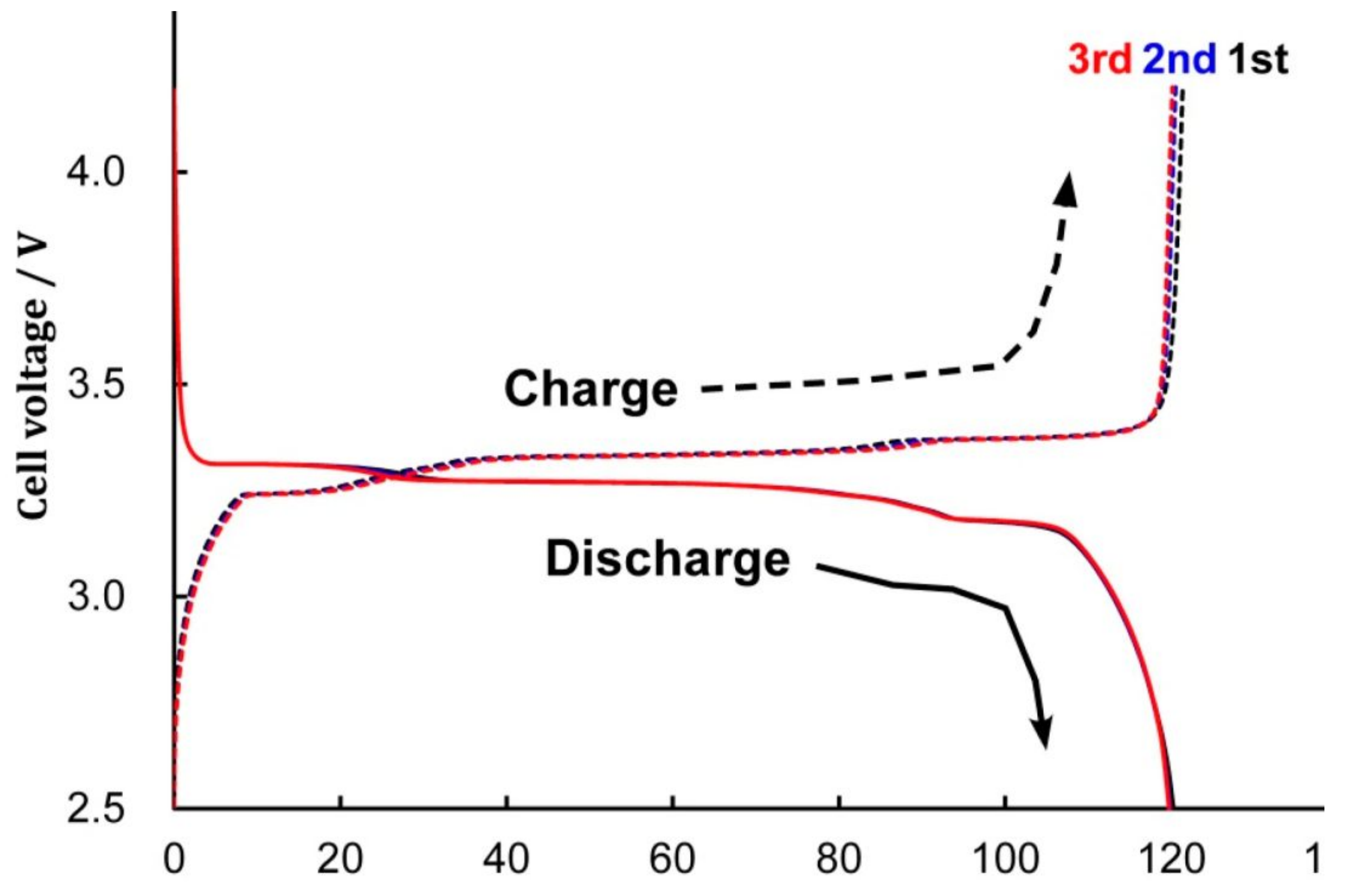
Voltage



Voltage is potential energy per unit of charge that drives electrons through a circuit.

What is voltage in metal-ion battery?

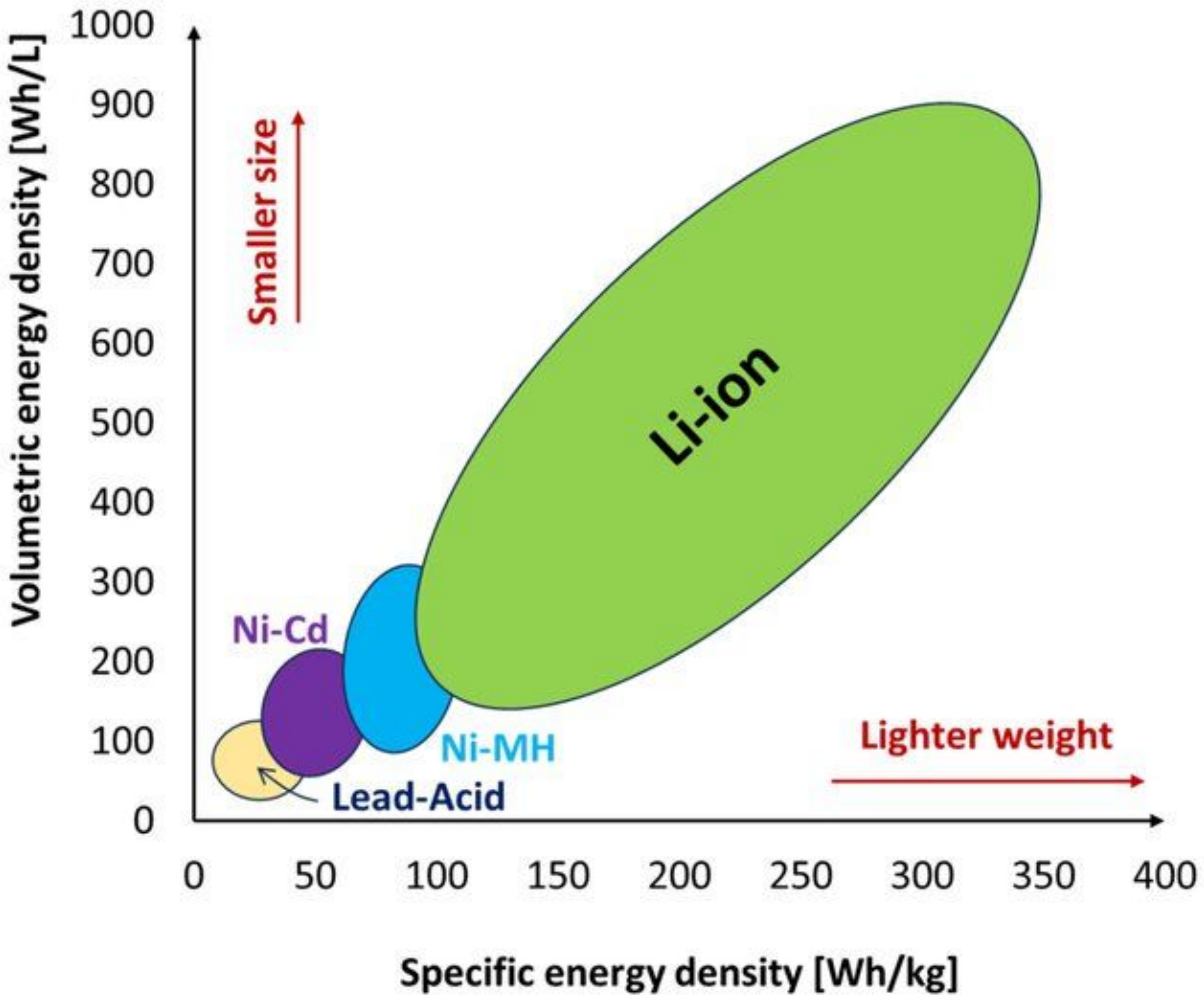
- **Nominal voltage:** The average or "named" voltage, typically **3.6 V or 3.7 V**. This is the figure most commonly used for marketing and general specification.
- **Maximum charge voltage:** The voltage when the cell is at 100% capacity, typically **4.2 V**. Charging beyond this level can cause damage and is prevented by the battery management system (BMS).
- **Discharge cutoff voltage:** The minimum safe voltage, typically around **2.5 V to 3.0 V**. The BMS will stop the battery from discharging below this point to prevent irreversible damage and a shortened lifespan.
- **Operating voltage range:** The usable voltage range that a lithium-ion cell operates within, running from its fully charged voltage down to its cutoff voltage.



The main property of a battery: energy density

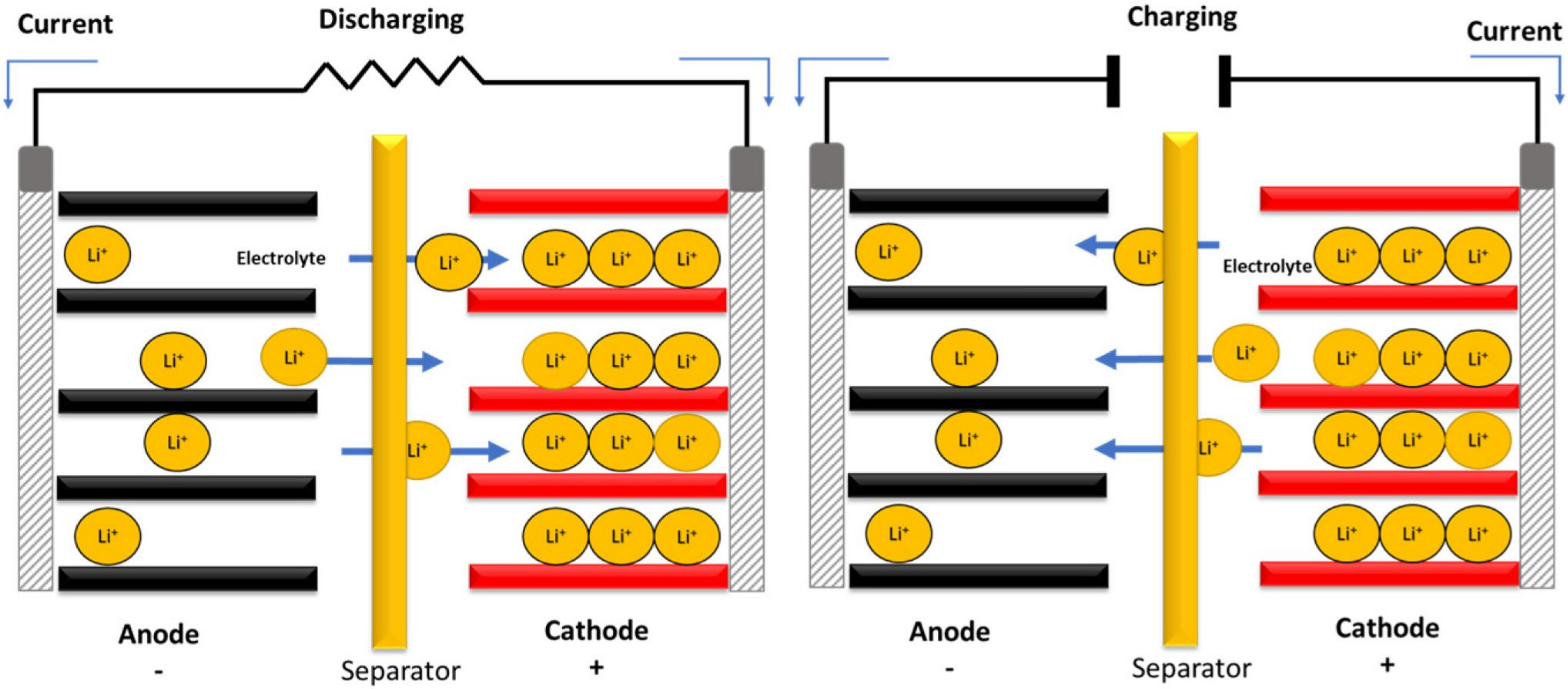
Energy Density (Wh) = **Voltage (V)** x Capacity (Ah), with different formulas for gravimetric (weight-based) and volumetric (volume-based) density.

For gravimetric energy density, divide the total energy by the battery's mass (in kg) to get Wh/kg, which is common for weight-sensitive applications like electric vehicles.

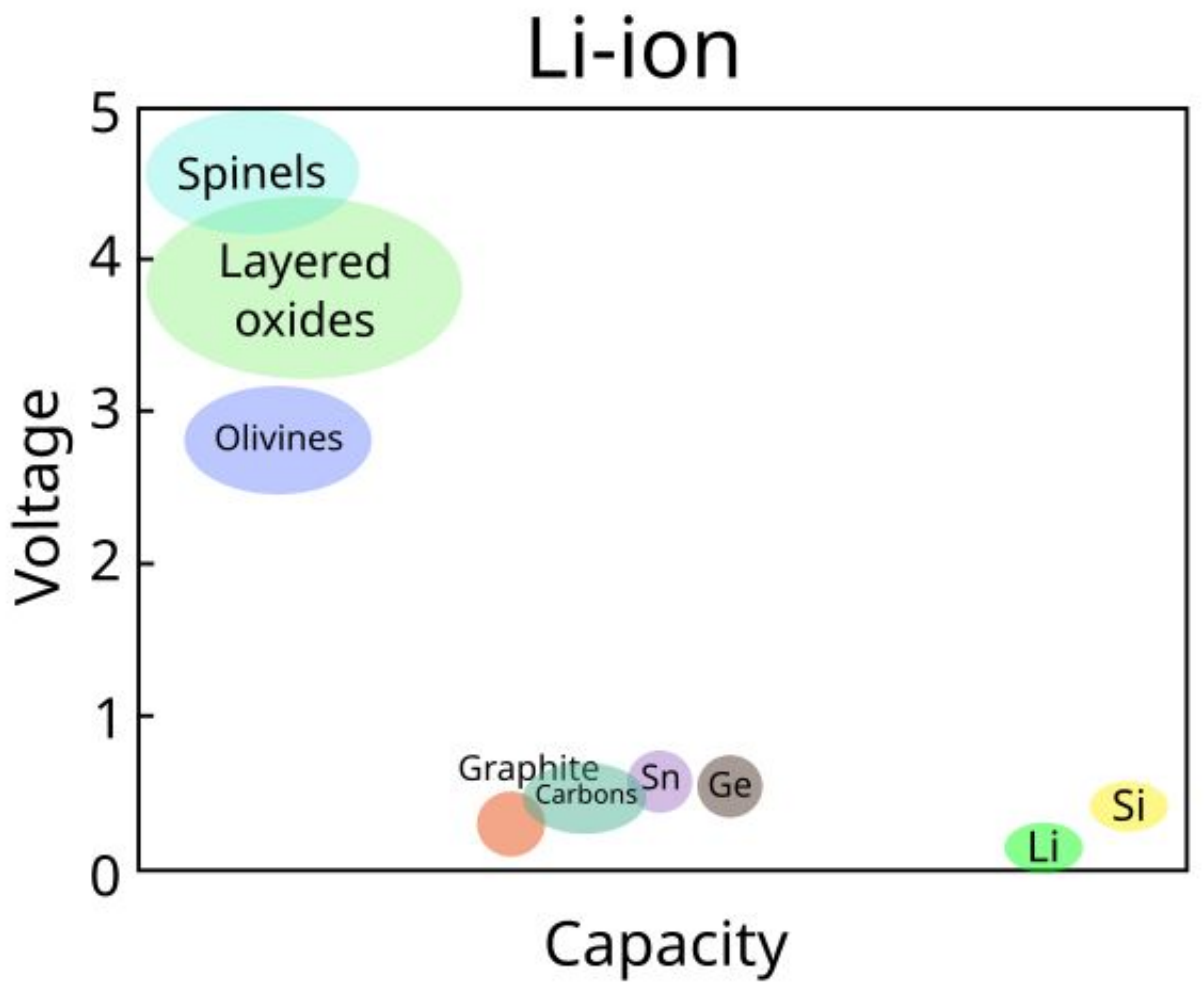


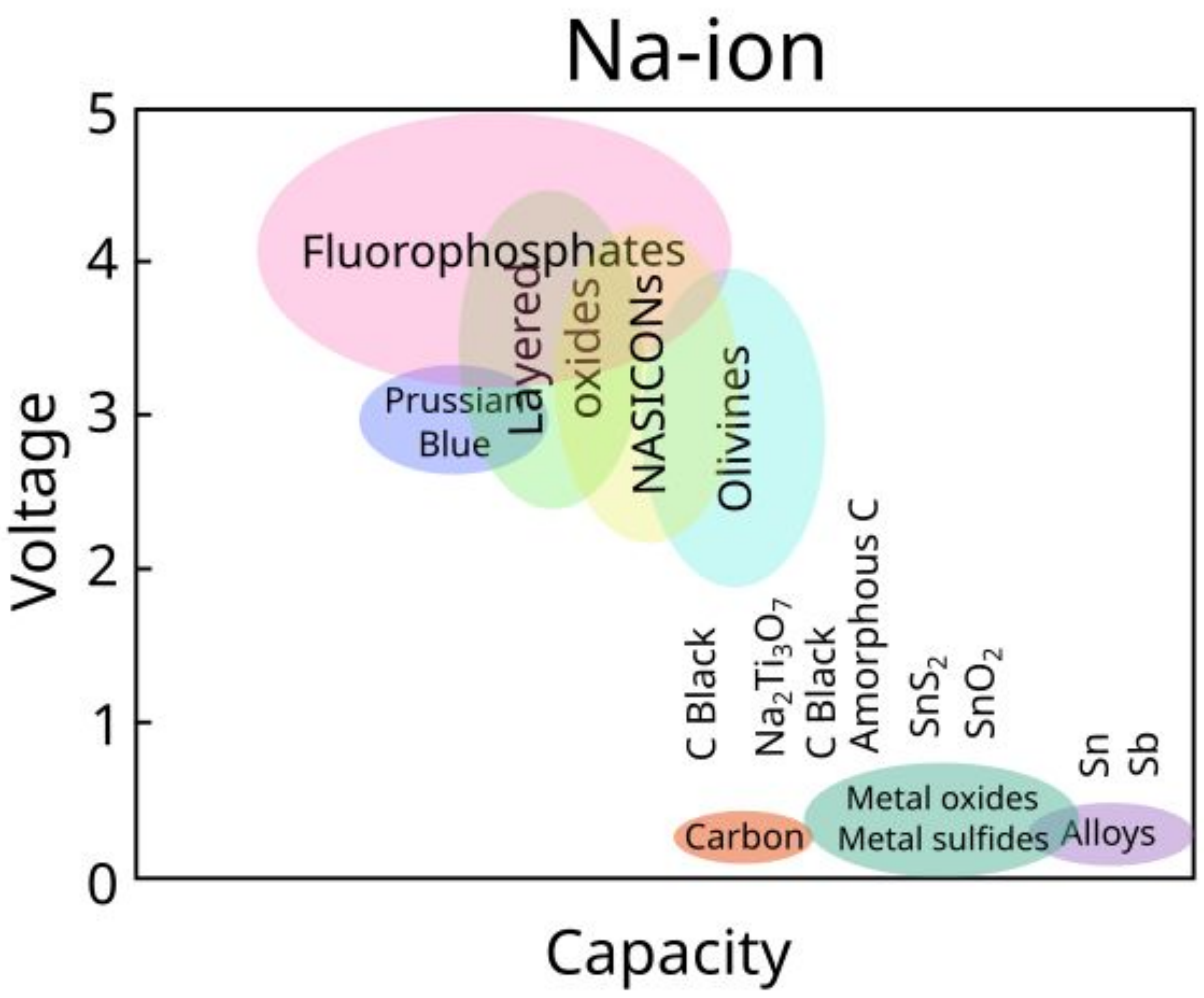
How metal-ion battery works?

Principal scheme of battery

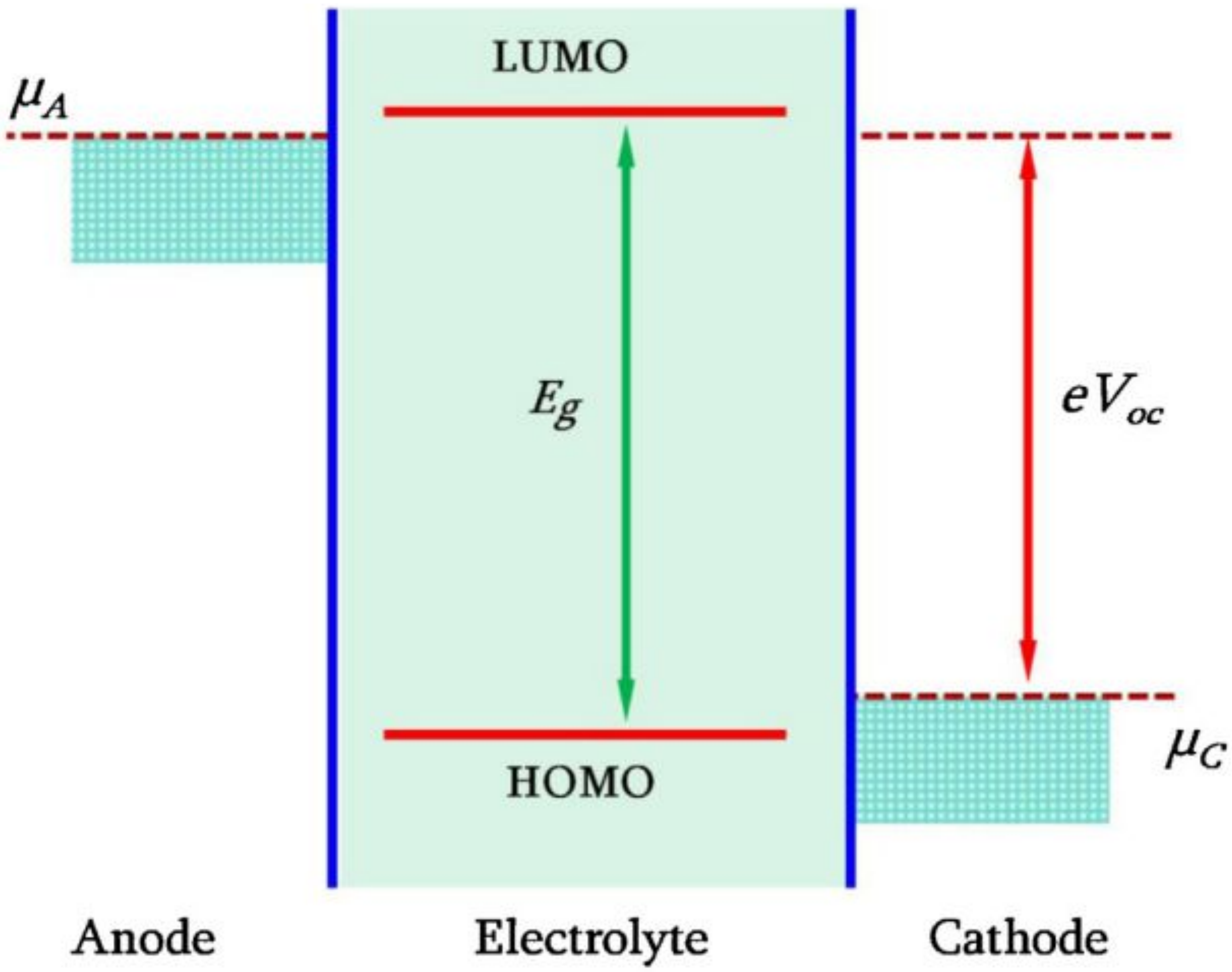


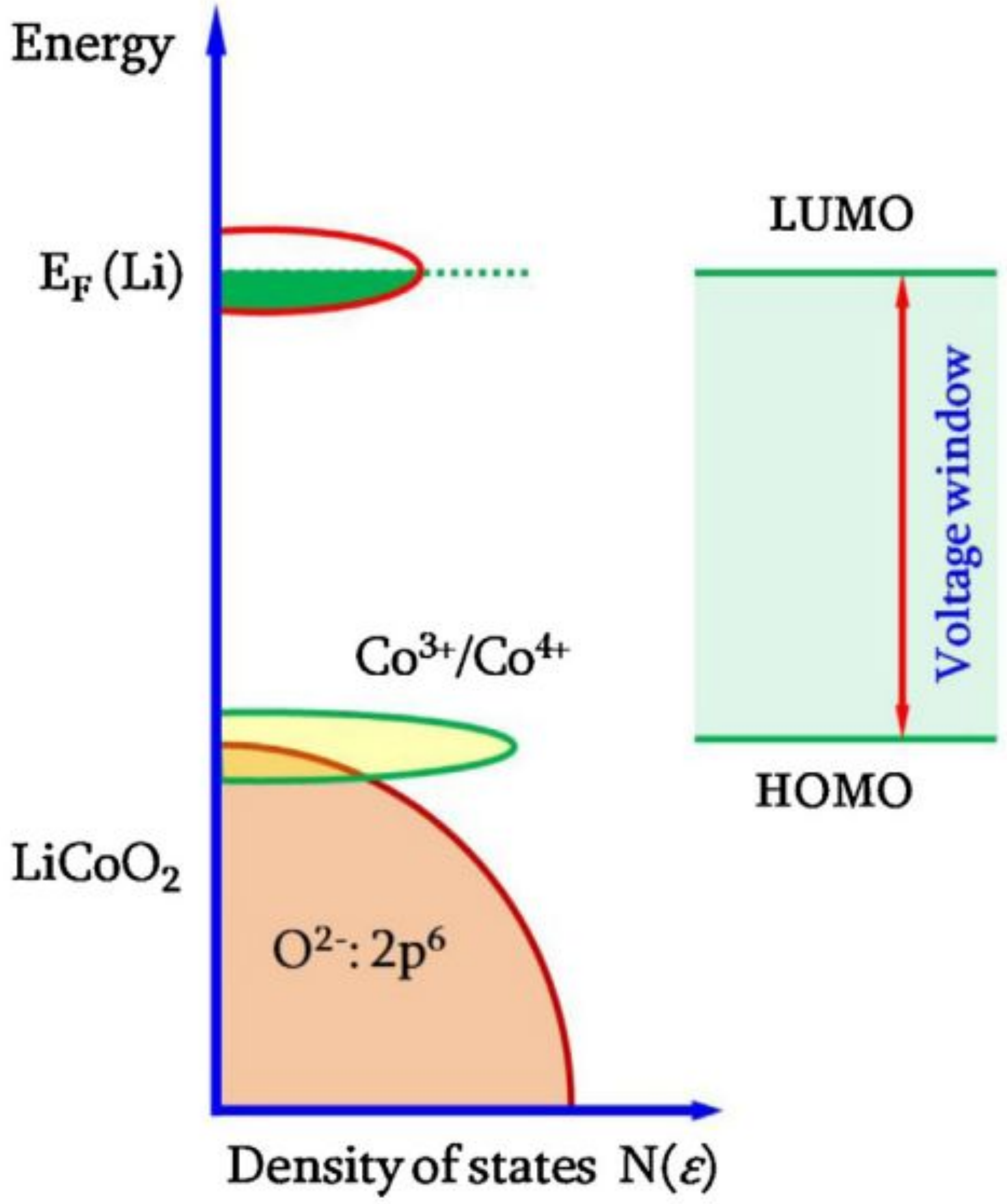
Anode vs Cathode





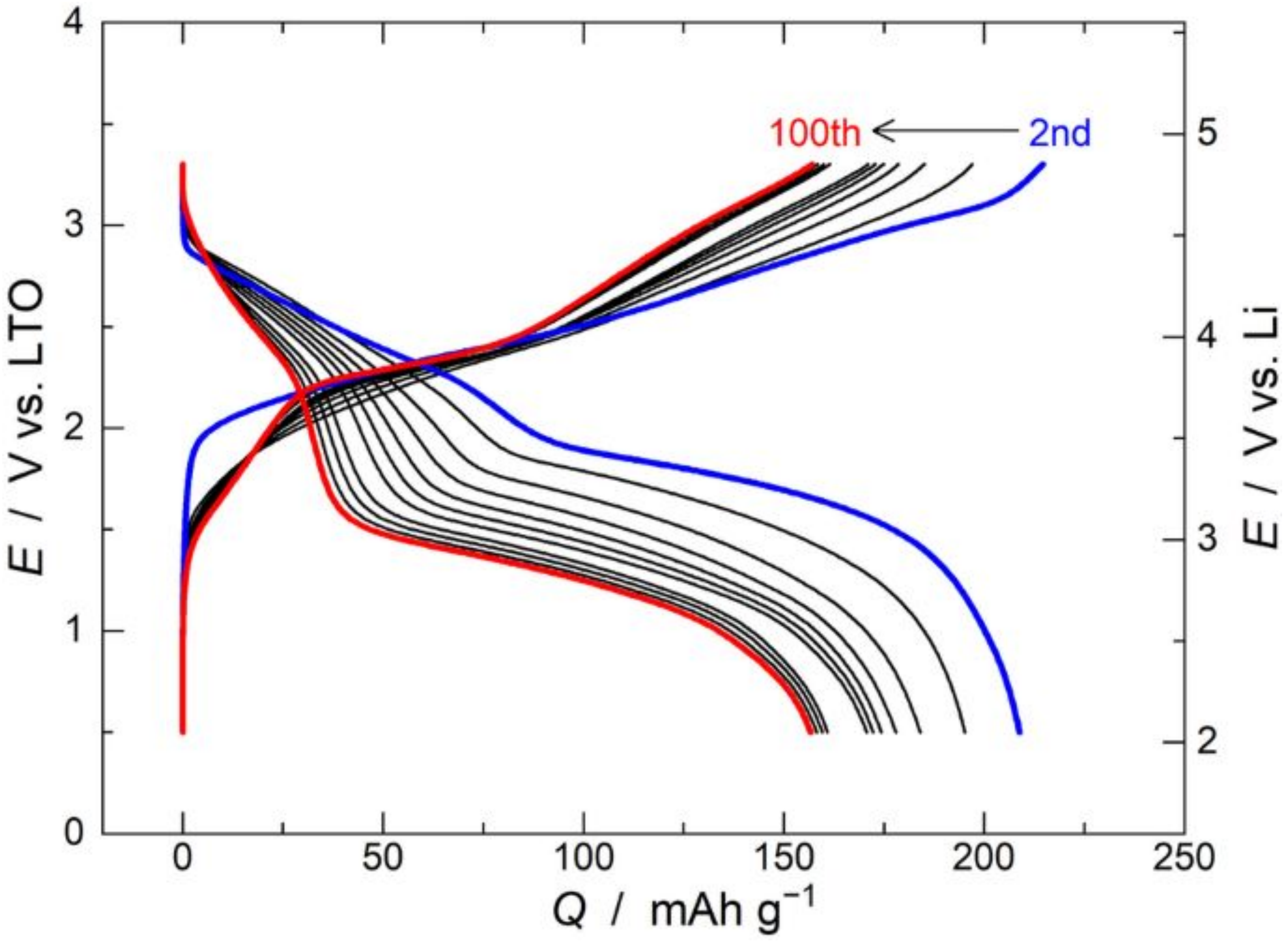
Where the energy comes from?



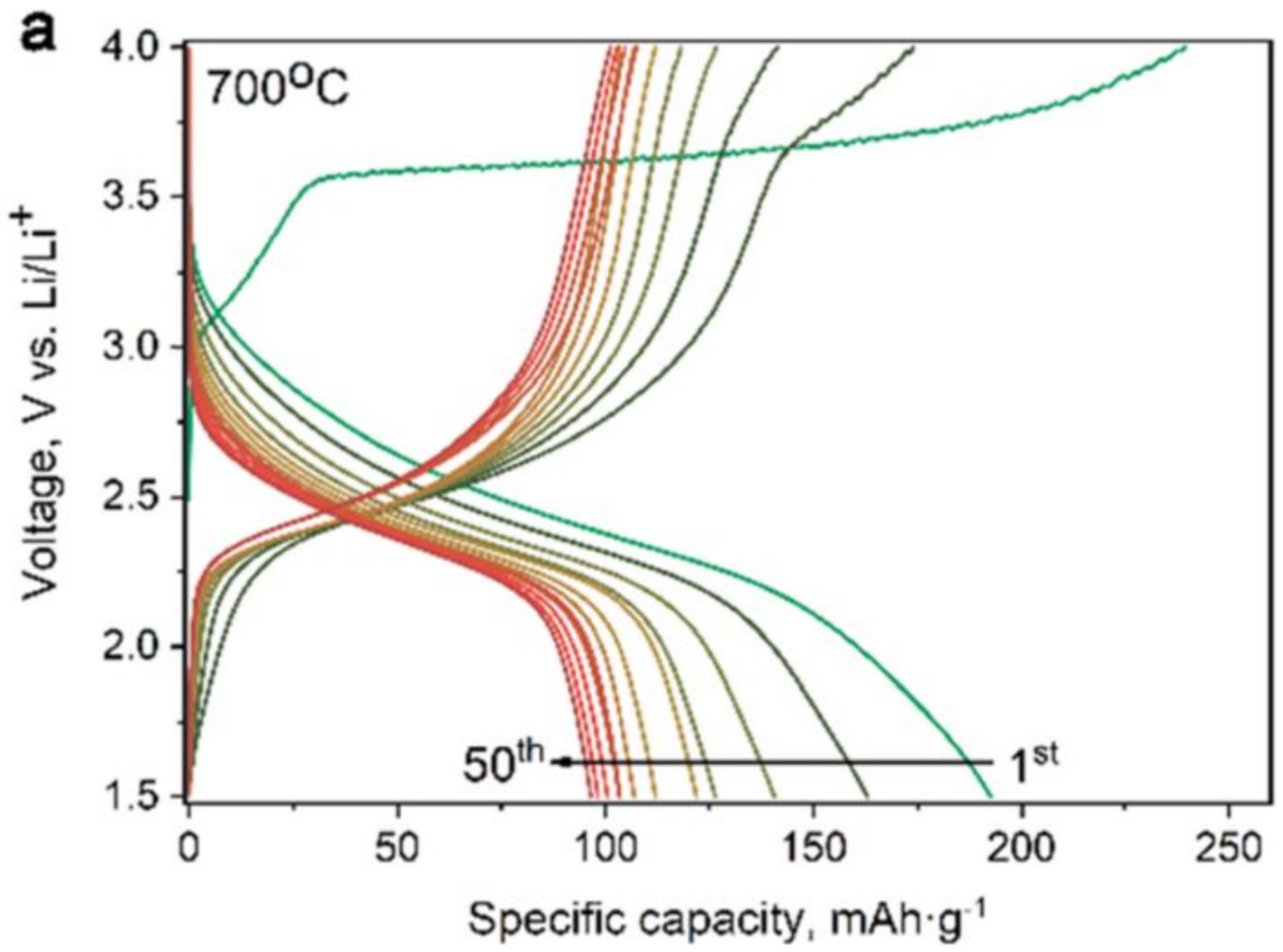


What influences electrochemical performance?

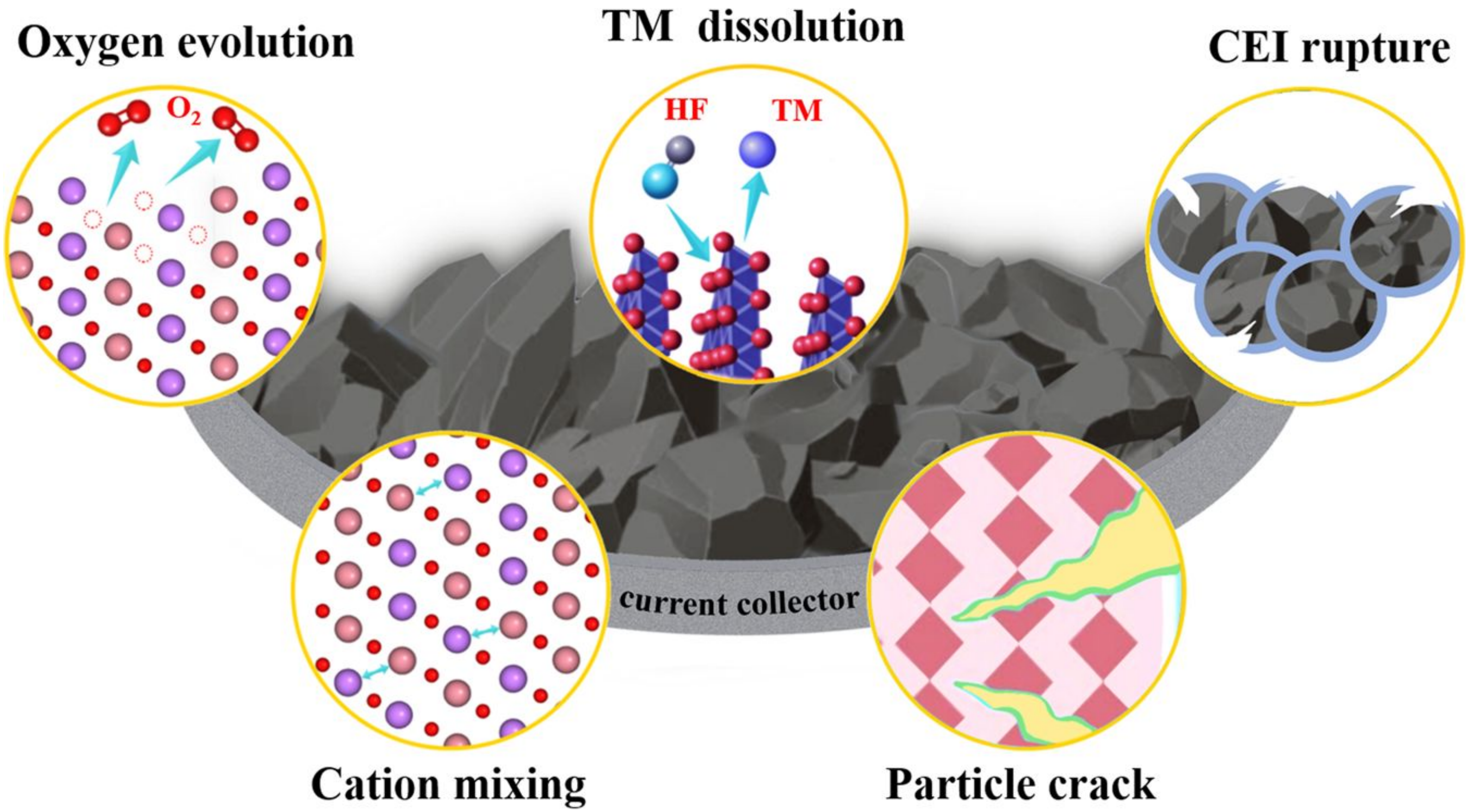
1. Cycling



100th
2nd
E / V vs. LTO
E / V vs. Li
Q / mAh g⁻¹

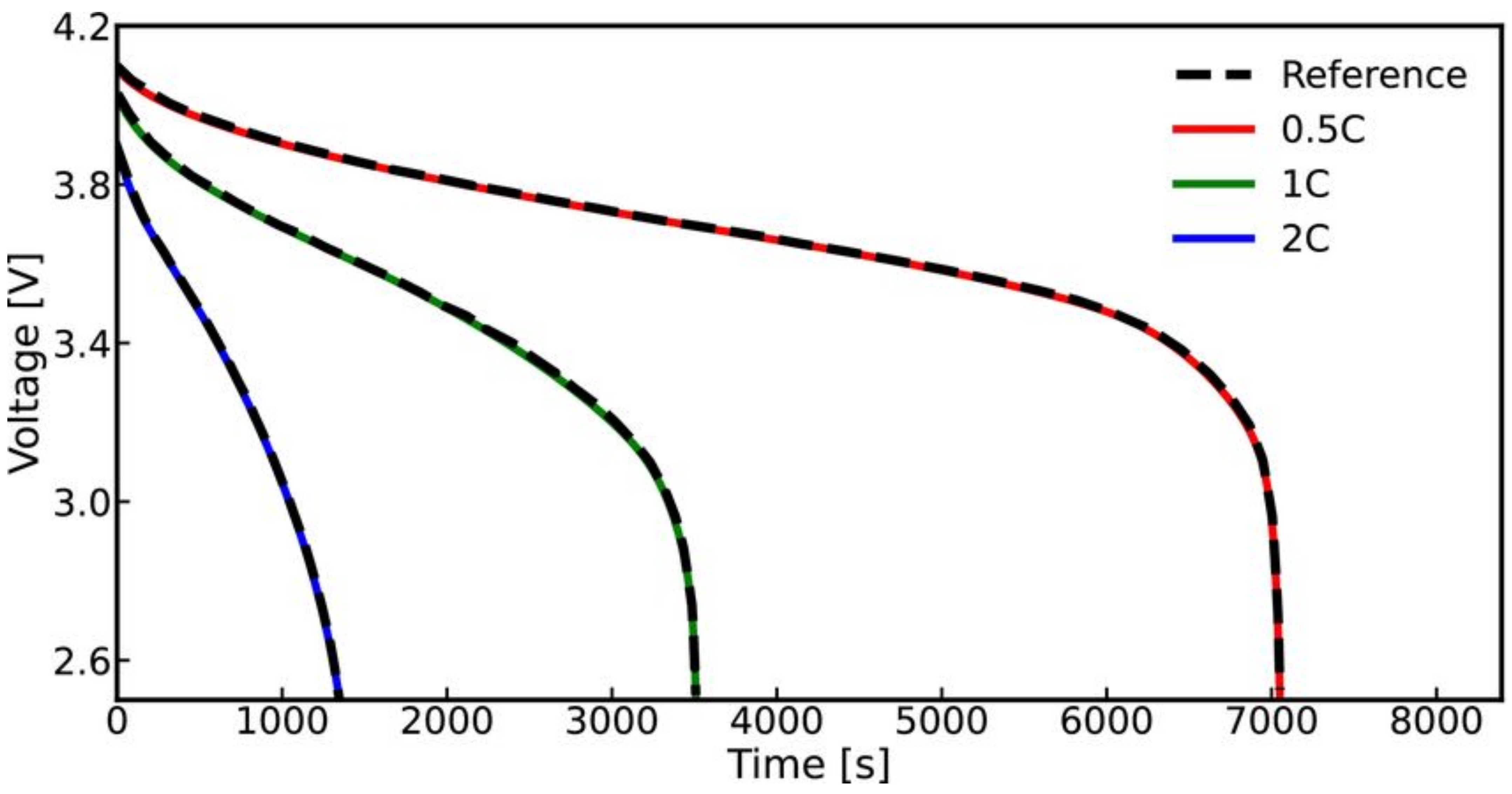


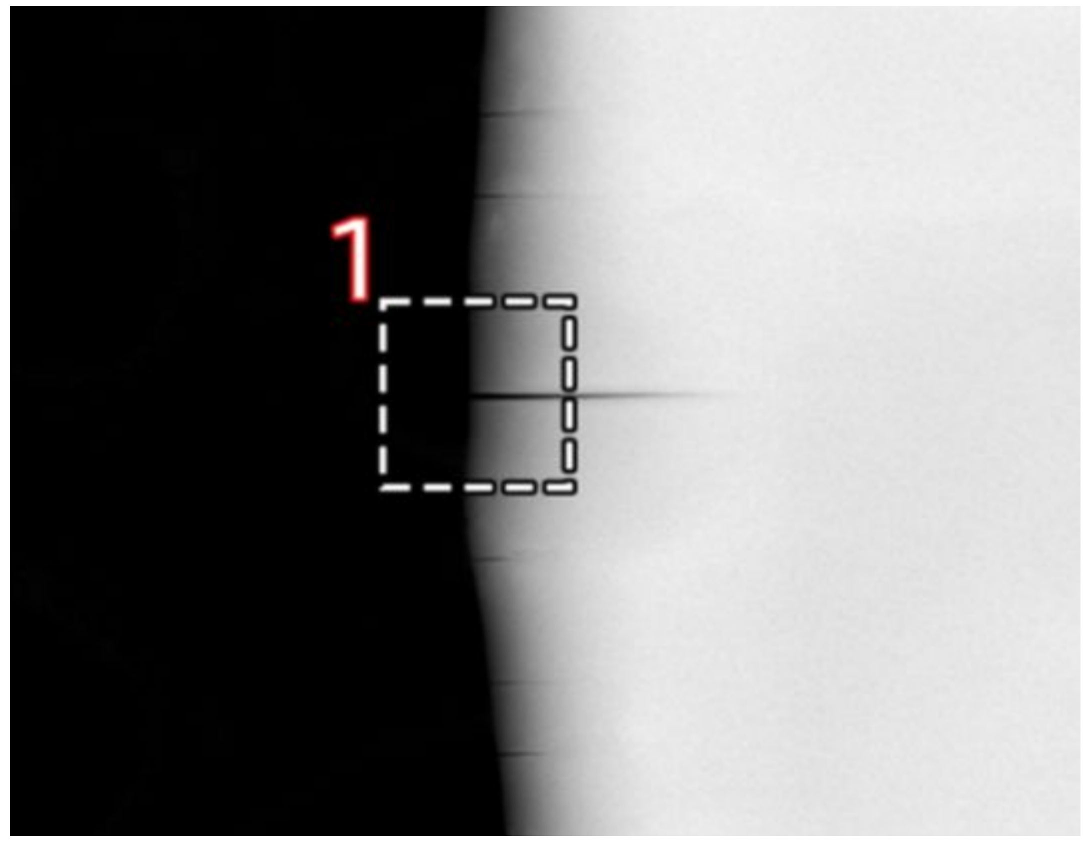
a
700°C
50th
1st
Voltage, V vs. Li/Li+
Specific capacity, mAh·g⁻¹

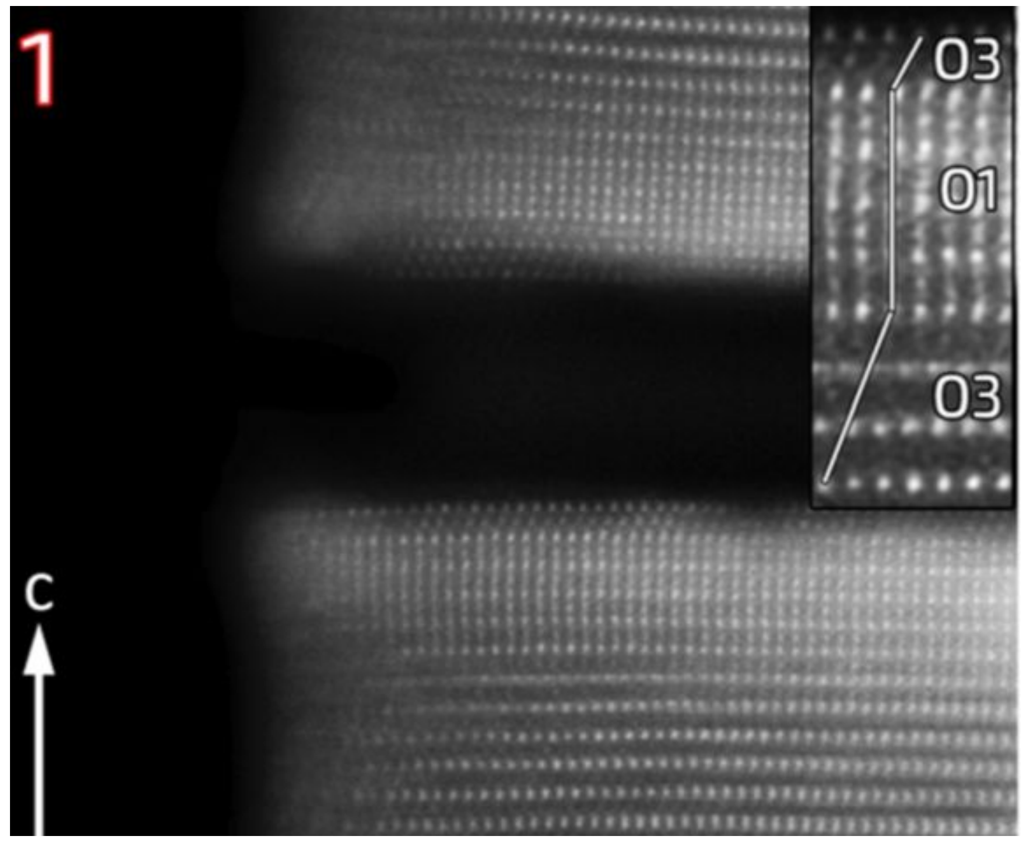


Oxygen evolution
O2
TM dissolution
HF
TM
CEI rupture
current collector
Cation mixing
Particle crack

2. C-rate





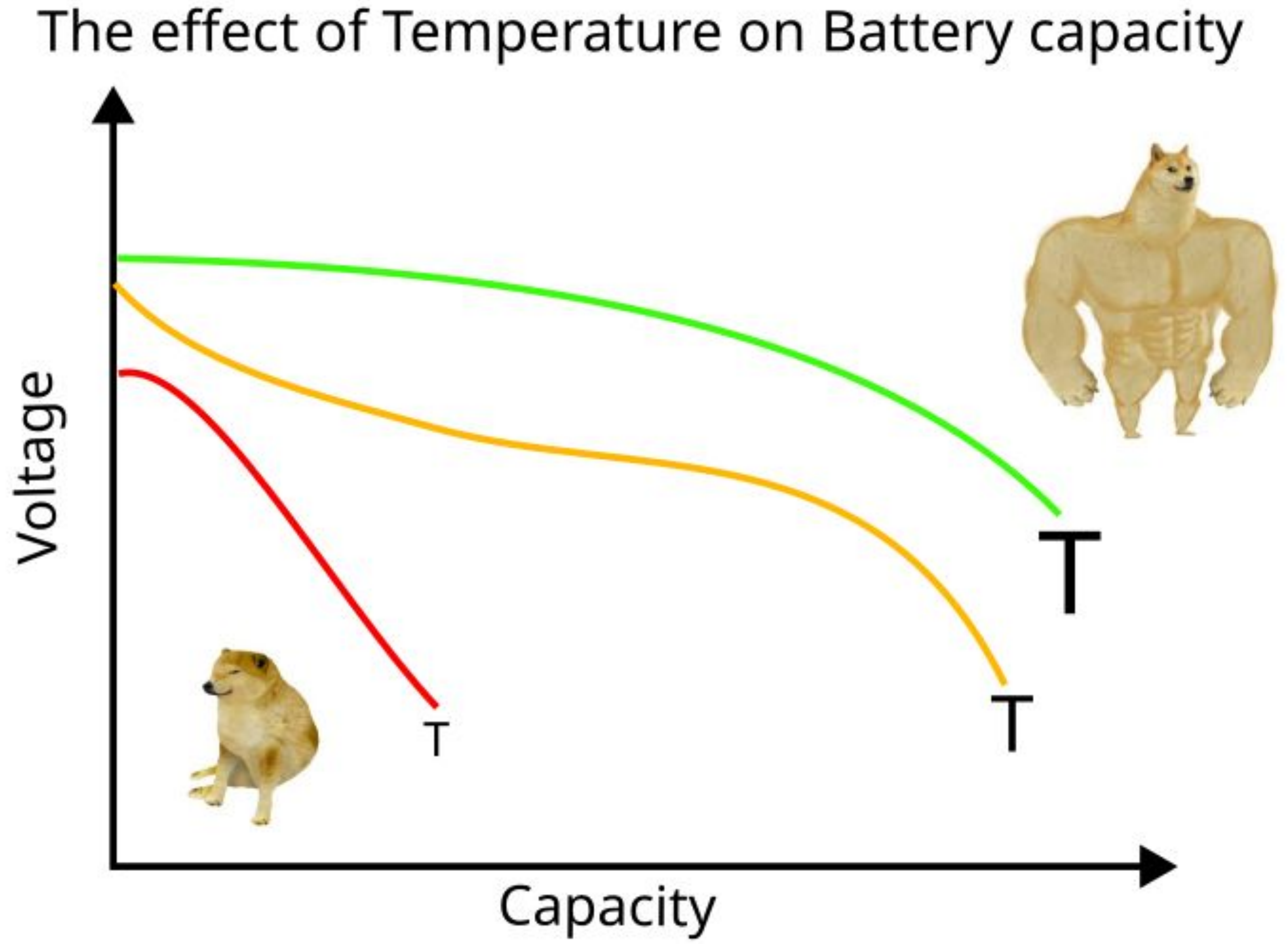


- **Increased heat generation** due to internal resistance accelerating chemical reactions and cause the battery to degrade faster.
- **Lithium plating** on the anode surface faster than ions can be smoothly intercalated into the graphite.
- **SEI layer growth**: High C-rates can accelerate the growth and breakdown of the solid-electrolyte interphase (SEI), leading to a thickening of this layer.
- **Mechanical stress:** Rapid intercalation and de-intercalation of lithium ions at high currents induce more mechanical stress and strain

3. Temperature

Low temperatures reduce battery capacity:

- Sluggish ion movement: The electrolyte becomes more viscous, and the diffusion rate of lithium ions through the cathode and electrolyte decreases significantly.
- Reduced activity: The activity of internal battery components decreases at low temperatures, making the de-intercalation of lithium ions from the cathode much slower.
- Anode plating (charging issue): A major risk of charging at very low temperatures is lithium plating on the anode, which can cause internal short circuits and lead to permanent capacity loss.

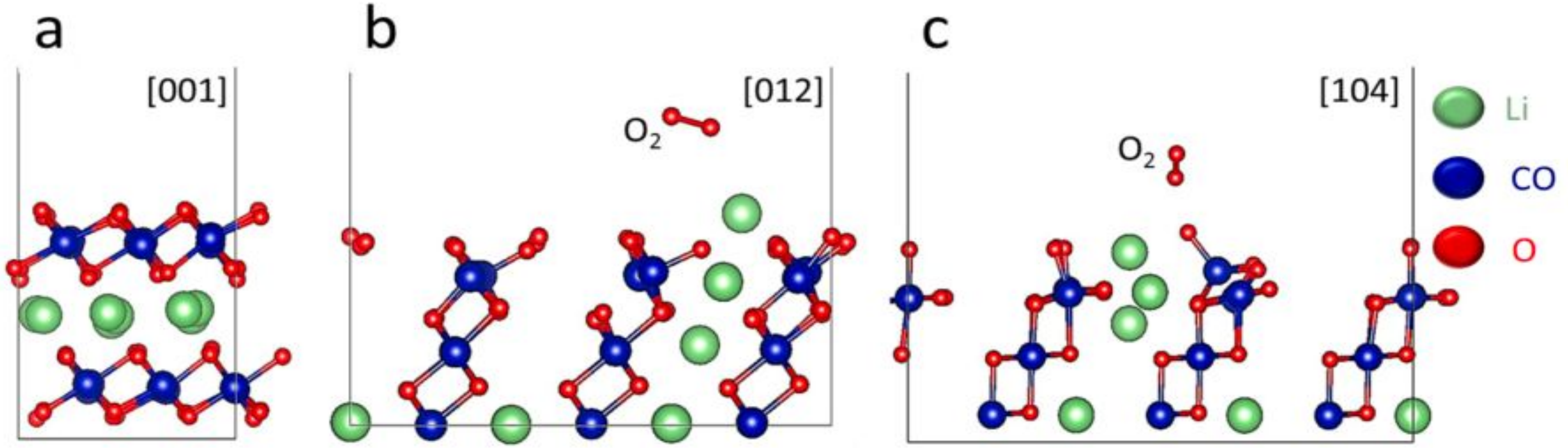


4. Practical limits ($LiCoO_2$)

Theoretical capacity 274 mAh g^{-1}

Voltage (vs Li/Li$^+$)	4.2 V	4.3 V	4.4 V	4.5 V	4.6 V
Capacity [mAh g^{-1}]	140	155	170	185	220
Average Voltage [V]	3.91	3.92	3.94	3.97	4.03
Specific energy [Wh kg^{-1}]	547.3	607.6	669.6	733.5	885.9
Specific energy [Wh L^{-1}]	2299	2552	2812	3081	3721
Increasing ratio[a]		11%	10%	9.5%	21%

Lyu, Y.et al. (2021). *Advanced Energy Materials*, *11*(2), 2000982.



Sharifi-Asl, et al. (2017). *Nano Letters, 17(4), 2165–2171.*

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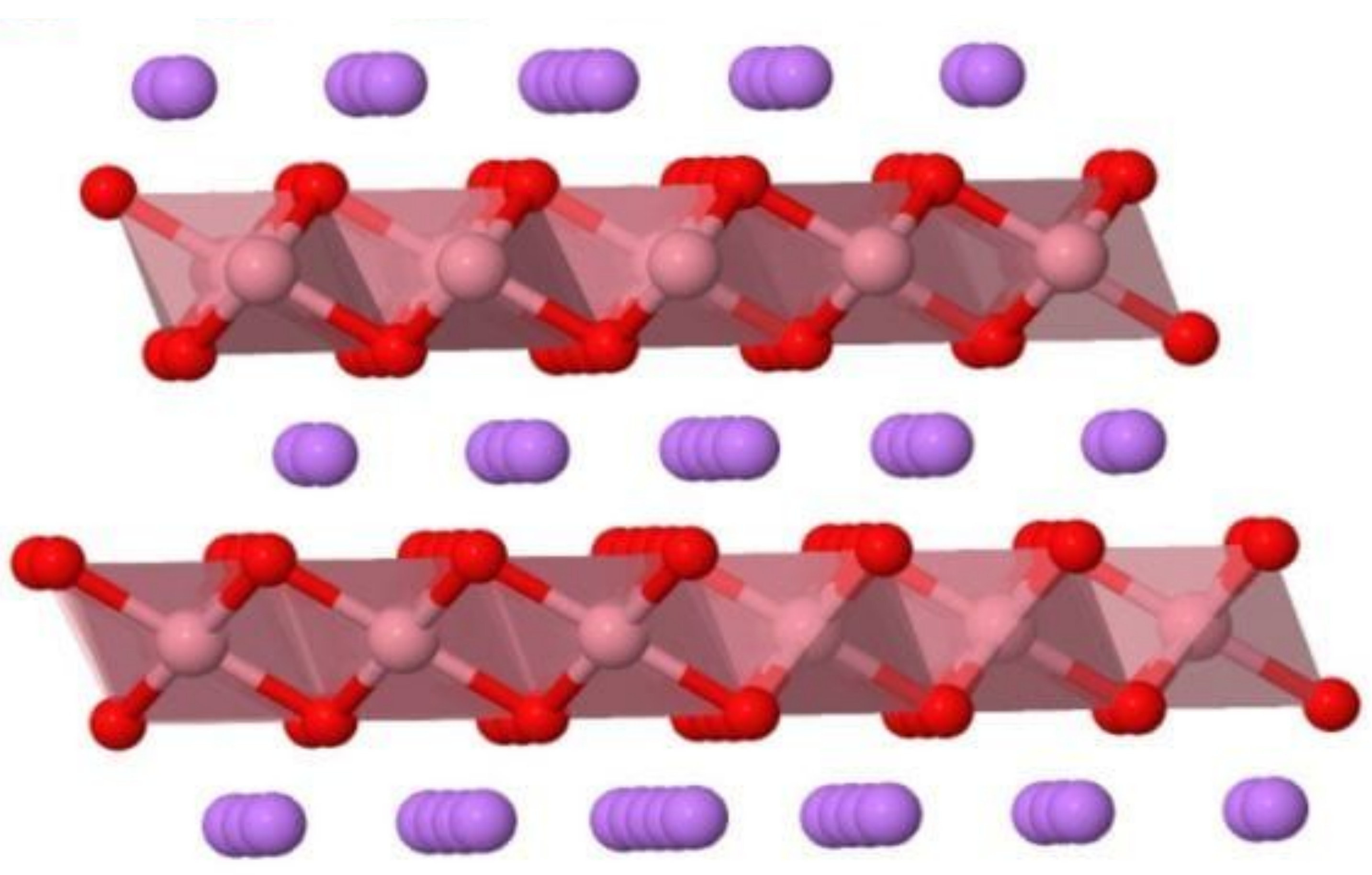

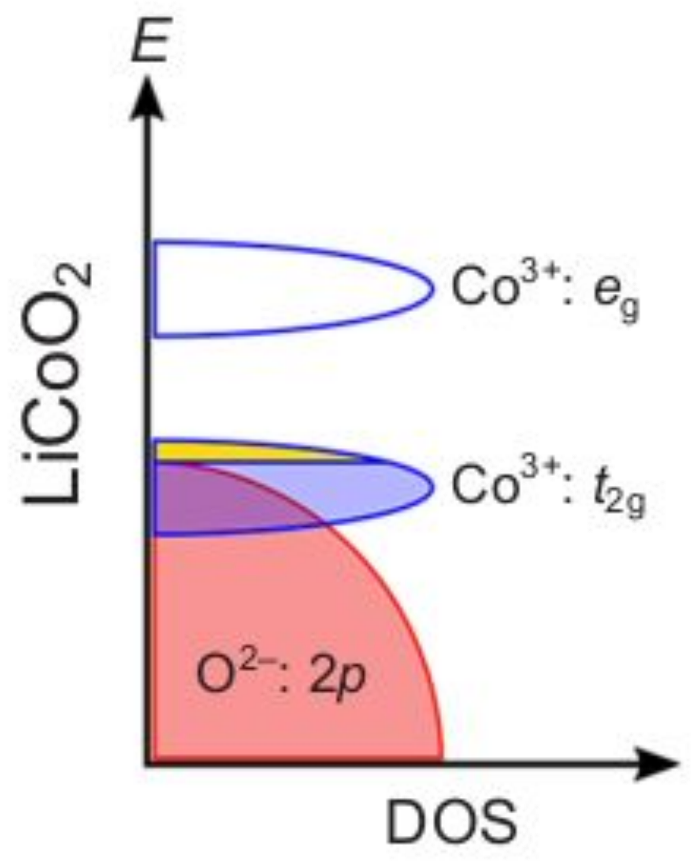

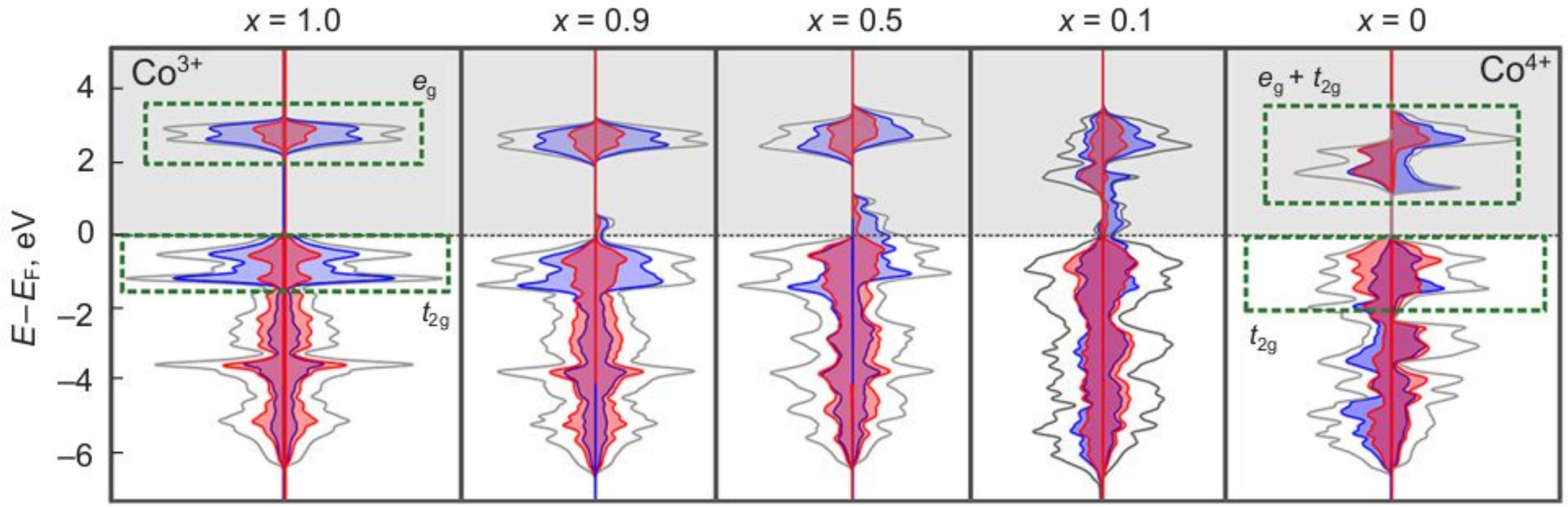

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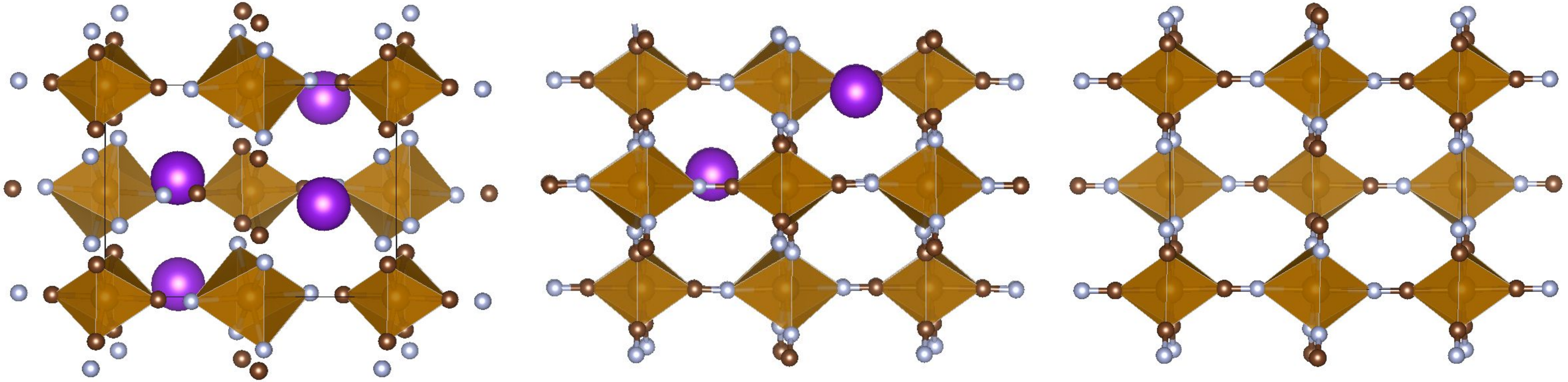
What is voltage from computational point of view?

How to calculate voltage from DFT?

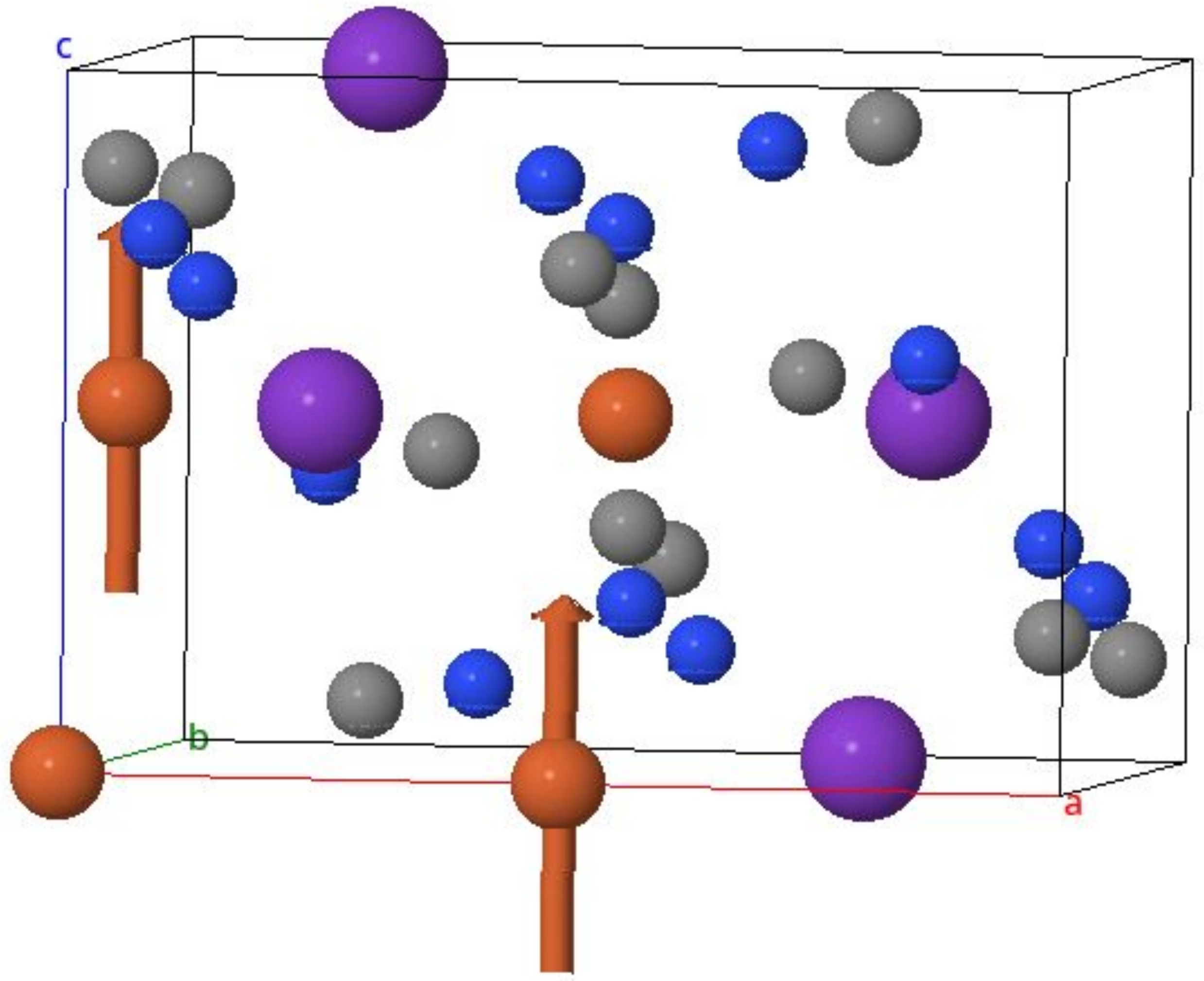
$K_2Fe[Fe(CN)_6]$ $K_1Fe[Fe(CN)_6]$ $Fe[Fe(CN)_6]$



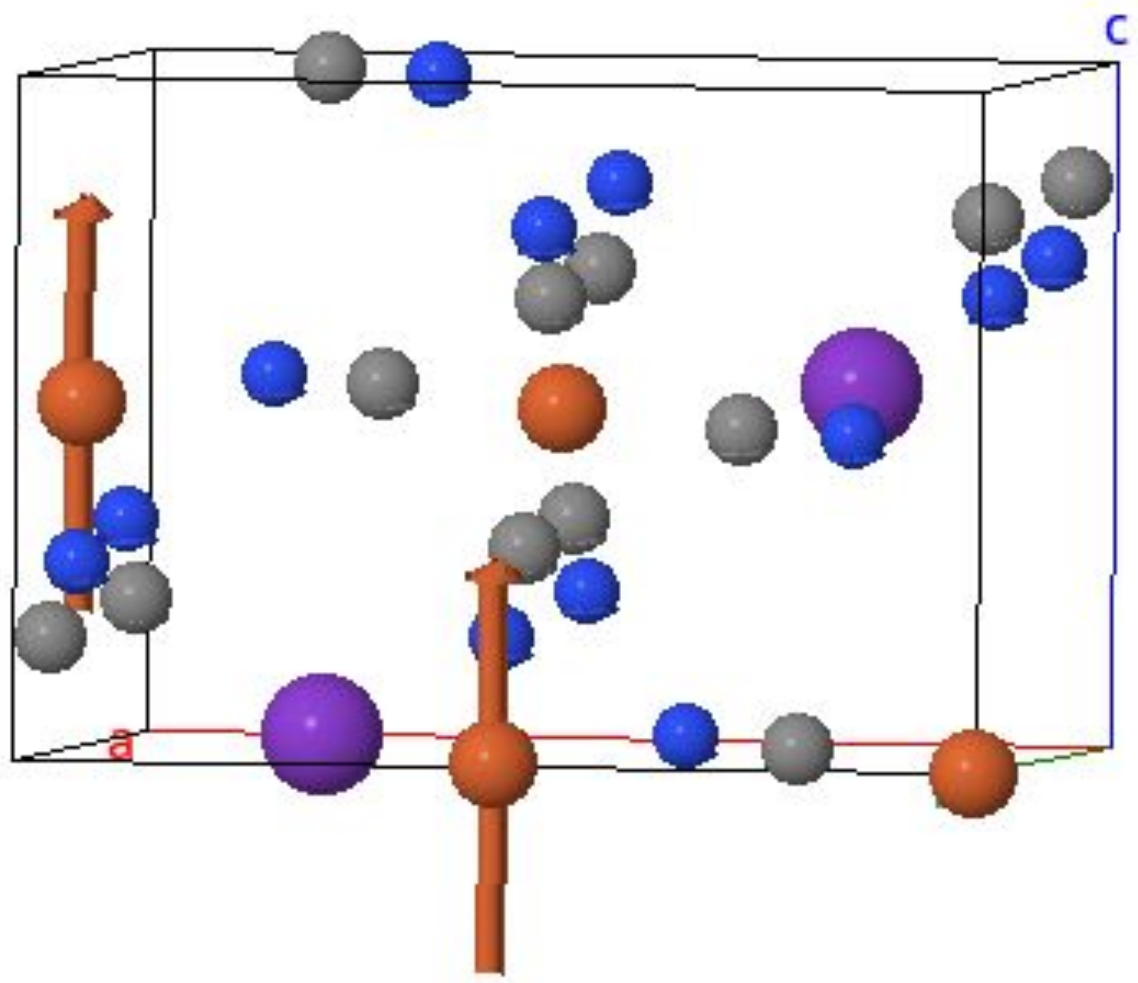
$$V = -\frac{E(K_{x1}Fe[Fe(CN)_6]) - E(K_{x2}Fe[Fe(CN)_6]) - (x_1-x_2)E(K)}{x1-x2}$$

How to check the states of 3d metals?

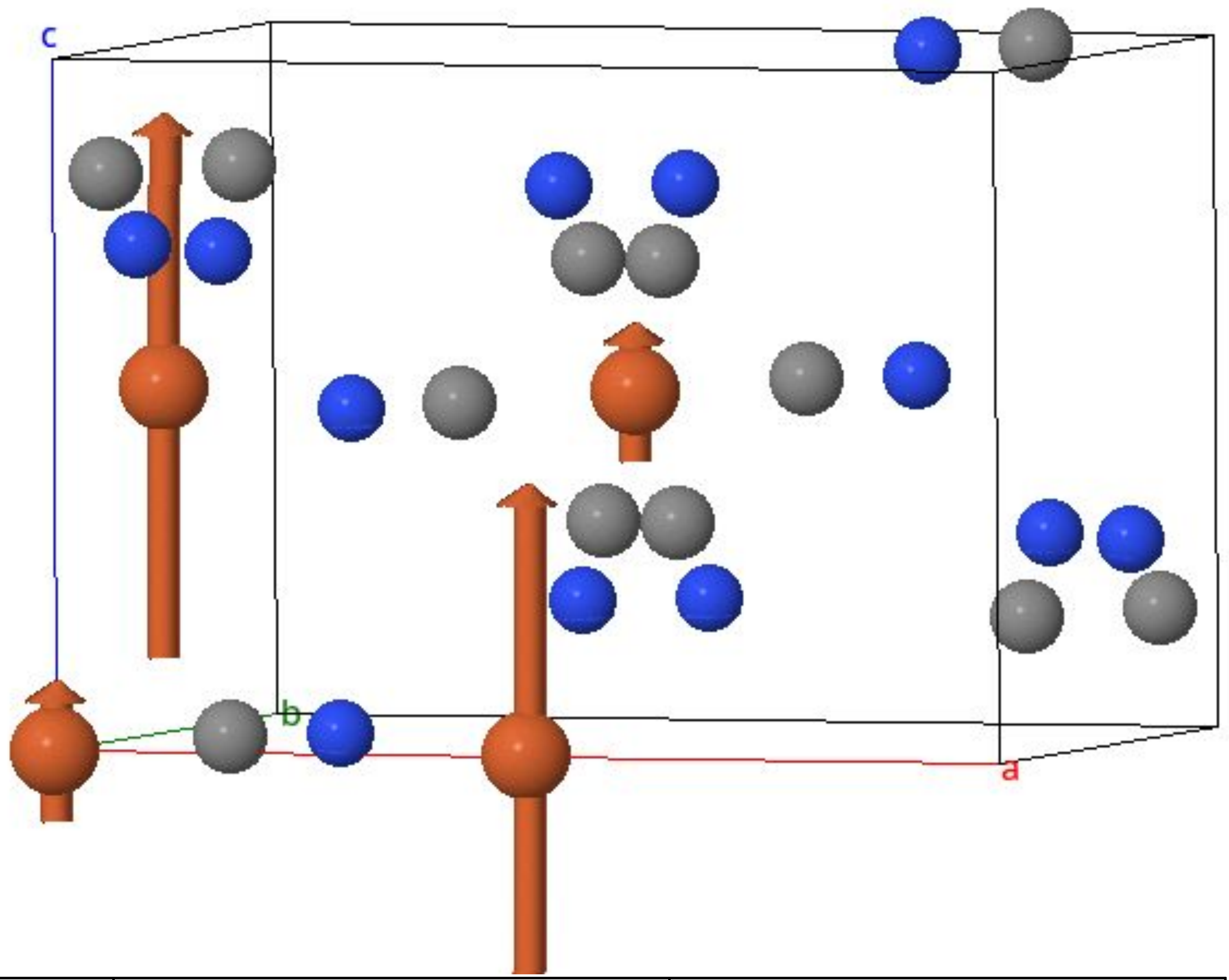
$K_2Fe[Fe(CN)_6]$



$K_1Fe[Fe(CN)_6]$



$Fe[Fe(CN)_6]$

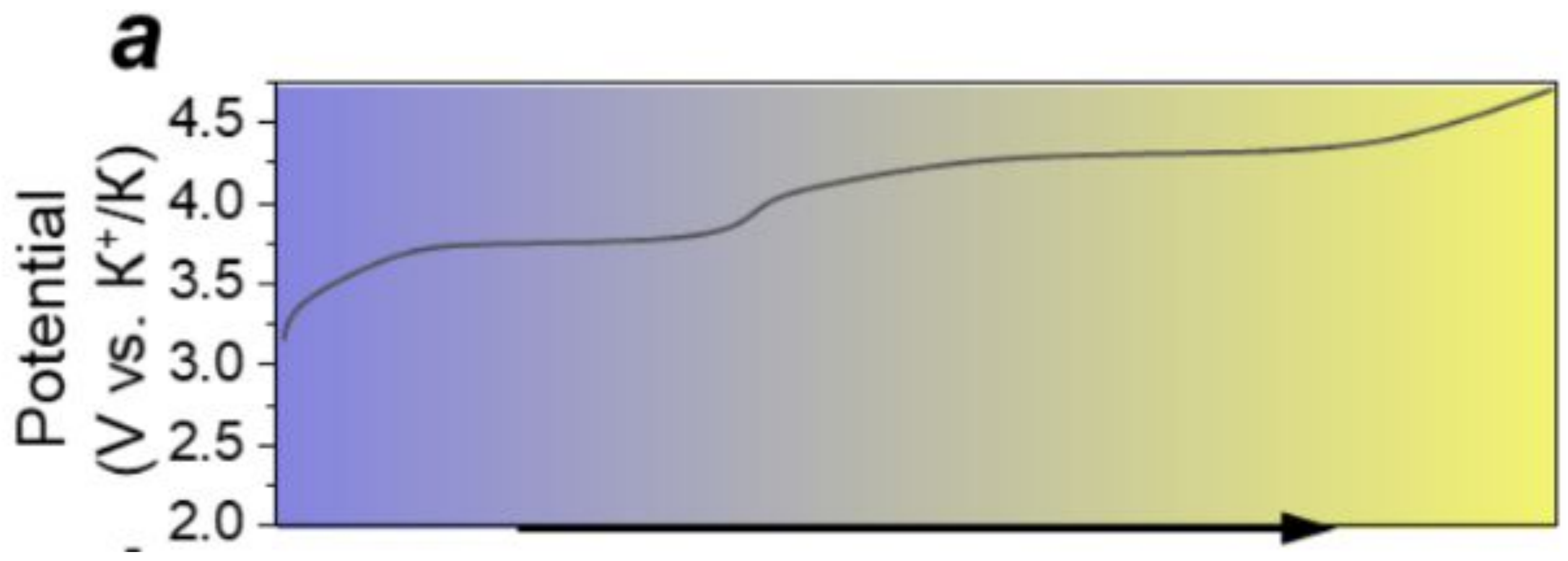


	K2		K1		K0	
Magmom Fe	0.04 3.75	0.04 3.75	0.19 **4.30**	0.19 **4.30**	**1.11** 4.33	**1.11** 4.33

	2+		3+	
State	LS	HS	LS	HS
Fe	0.0	3.7	1.1	4.2

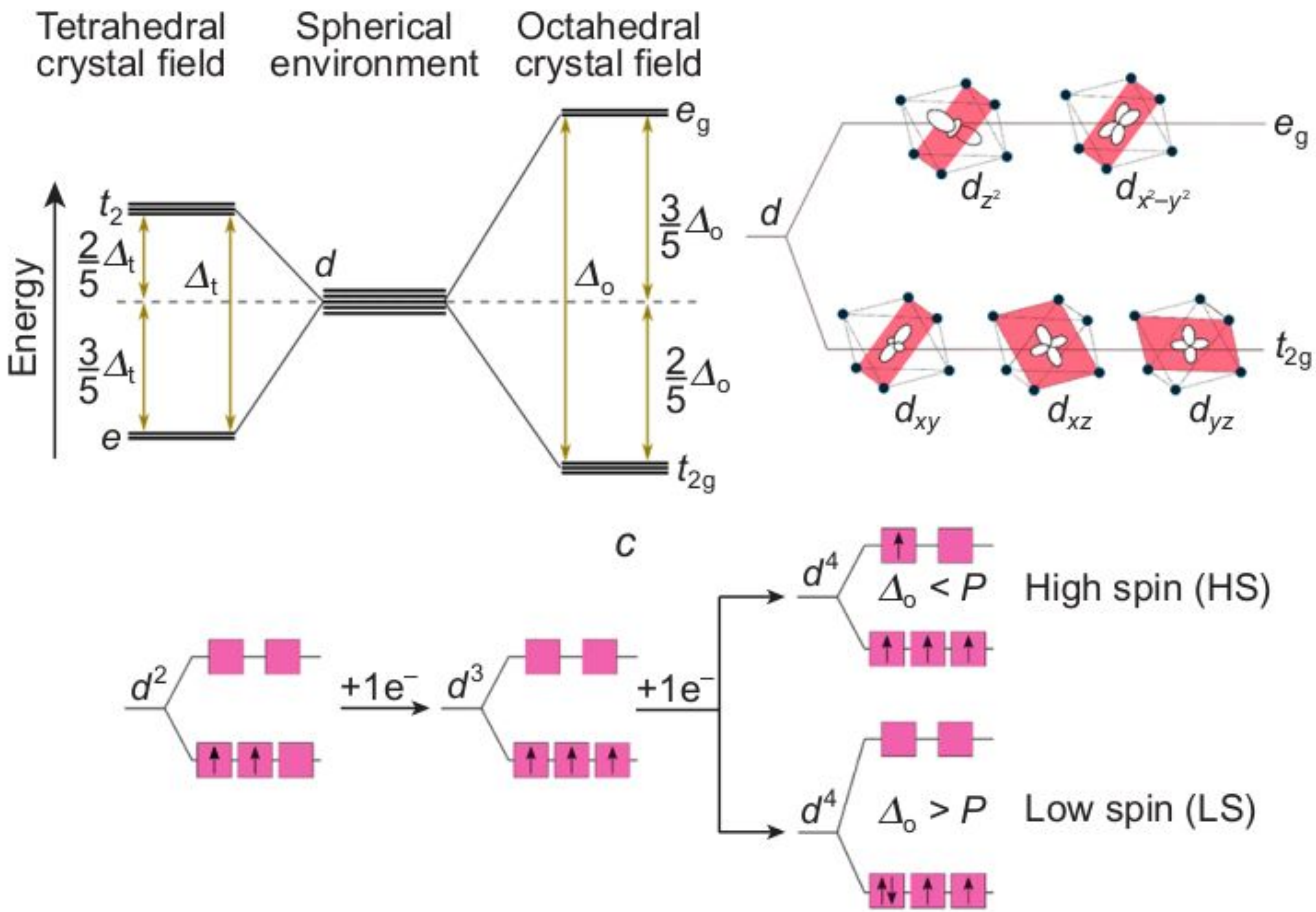
HS-Fe^{2+} -> HS-Fe^{3+}
3.20 V, dV = −0.9 %

LS-Fe^{2+}-> LS-Fe^{3+}
3.24 V , dV = -1.7 %



Basics of electronic structure

3d-orbitals of transition metals



Configuration of 3d-orbitals of transition metals in tetrahedral (MO_4) and octahedral (MO_6) complexes

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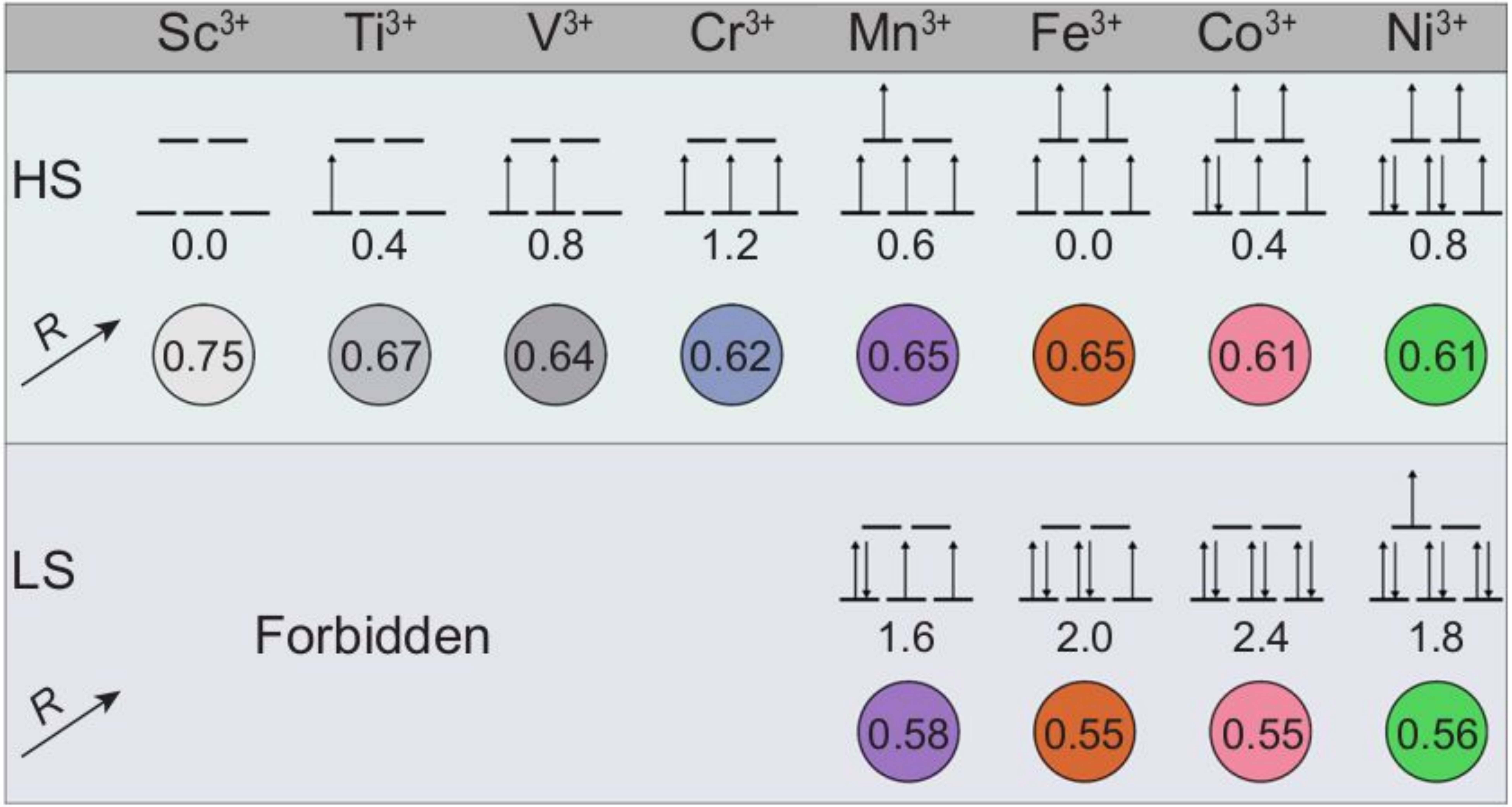
Electronic structure of 3d-orbitals



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How to track the obtained state for transition metals

		2+		3+		4+	
	U, eV	R_{ion}, Å	μ_B	R_{ion}, Å	μ_B	R_{ion}, Å	μ_B
Mg	–	0.72	0	–	–	–	–
Al	–	–	–	0.54	0	–	–
Ti	0.0	0.86	*	0.67	0.26	0.61	0.00
V	3.1	0.79	2.09	0.64	0.00/1.98	0.58	1.03
Cr	3.5	0.73 / 0.80	*	0.62	2.96	0.55	*
Mn	3.9	0.67 / 0.83	1.31 / 4.55	0.58 / 0.65	2.00 / 3.82	0.53	3.11
Fe	4.0	0.61 / 0.78	* / 3.72	0.55 / 0.65	1.09 / 4.24	0.59	*
Co	3.2	0.65 / 0.75	0.98 / 2.68	0.55 / 0.61	0.00 / 3.05	0.53	1.02
Ni	6.2	0.69	1.77	0.56 / 0.60	1.29 / *	0.48	0.00

Ionic radii and magnetic moments of considered metallic components.

Hubbard corrections used for GGA+U calculations are also provided.

Co^{3+} in LCO has magnetic moment of 0 μ_B

Co^{2+} in LCO has magnetic moment of 2.7 μ_B

Boev A. O. et al. //Physical Review Materials. – 2024. – T. 8. – №. 5. – C. 055403.

Fundamental things affecting voltage

Type of cation

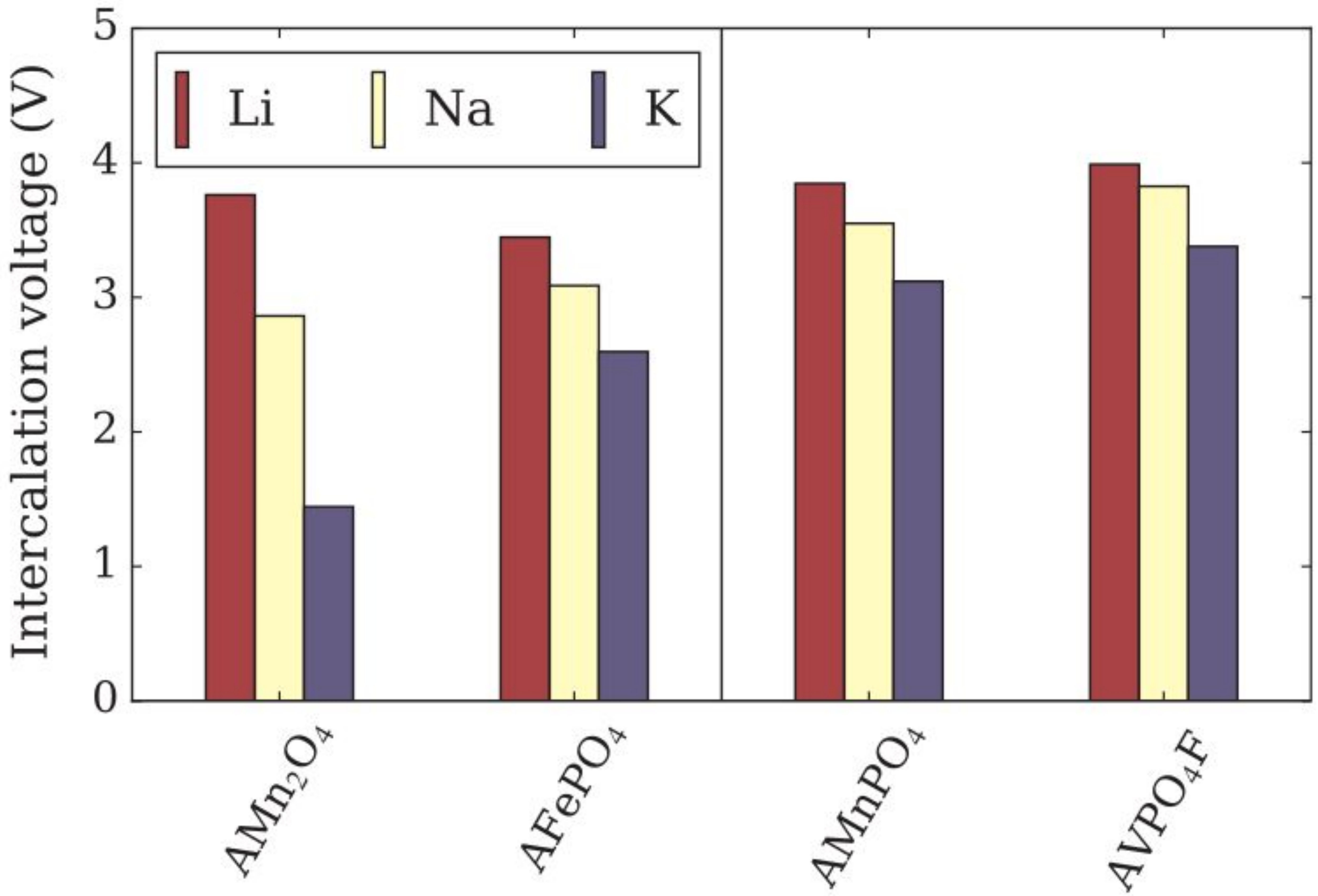
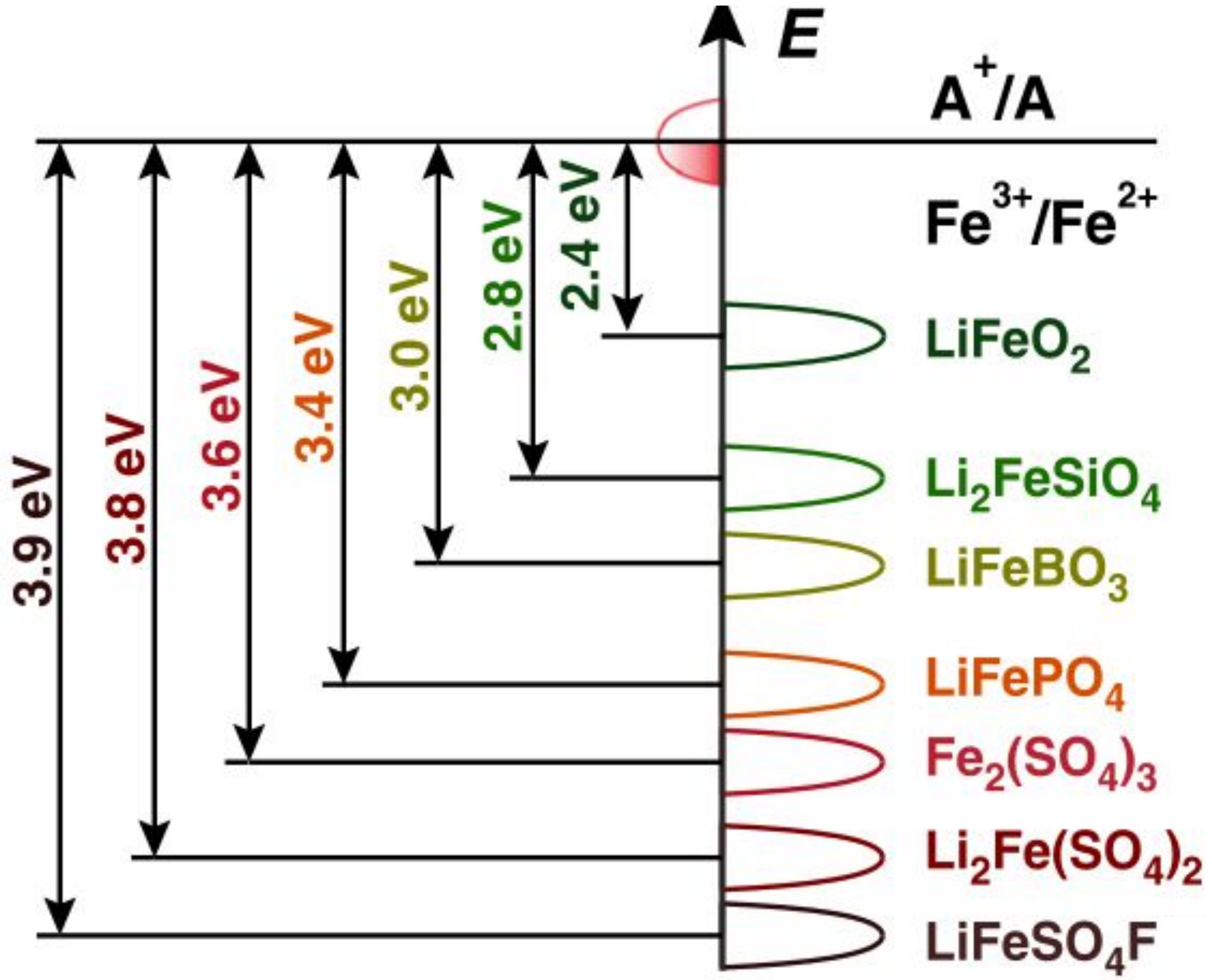
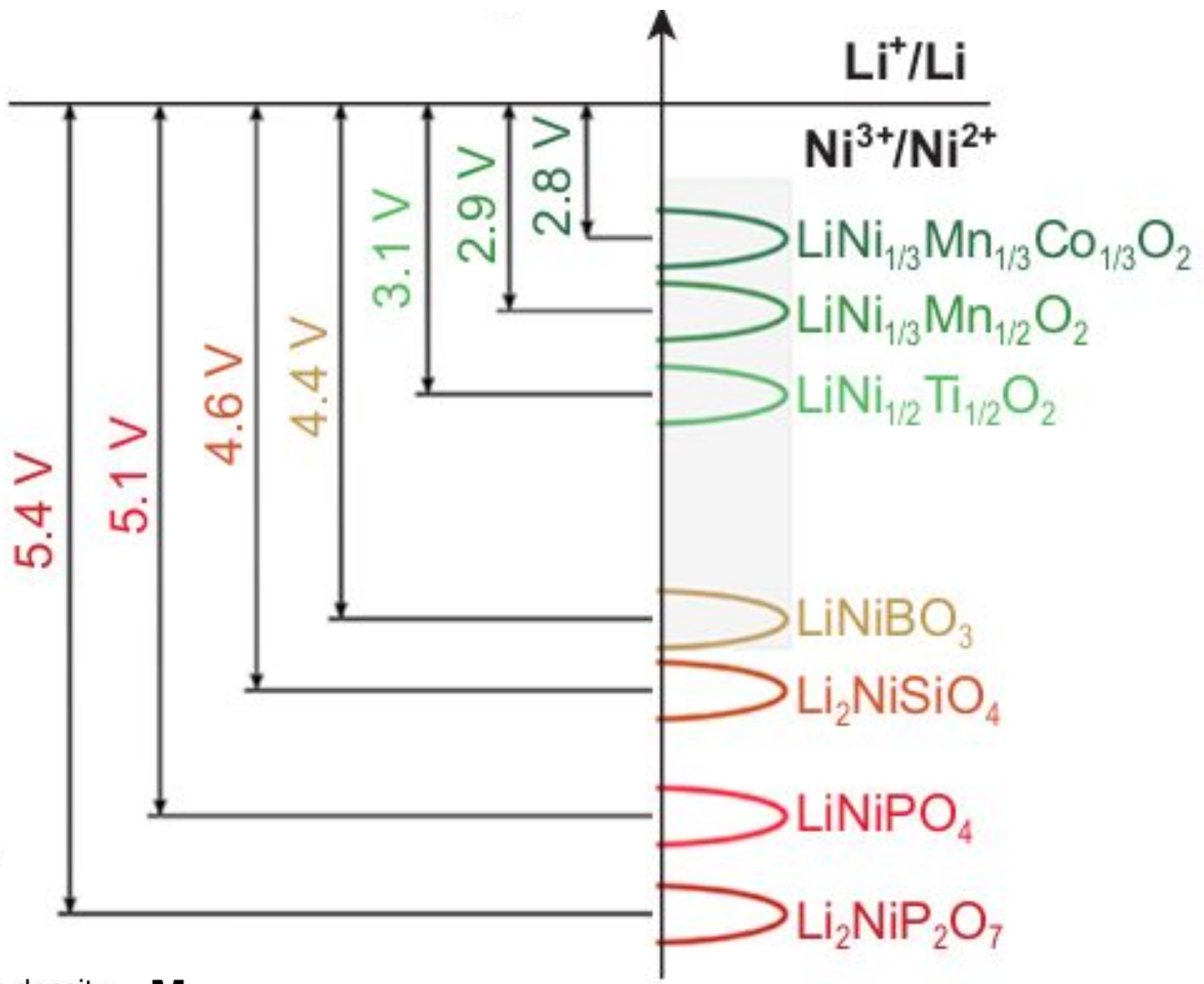


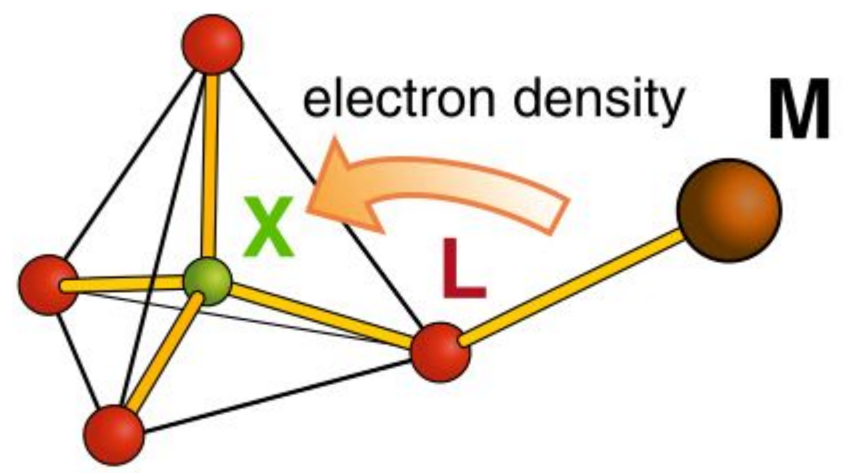
Fig. 3. Intercalation voltages for Li, Na and K based cathode compounds calculated with Eq. (2) using DFT + U results.

Aksyonov D. A. et al. //Computational Materials Science. – 2018. – T. 154. – C. 449-458.

Type of anion (inductive effect)







A. Abakumov Nat Comm (2020)11:4976 / A.A.Savina, **A.O.Boev** et al. Russ. Chem. Rev., 2023, 92 (7) RCR5086

Type of transition metal

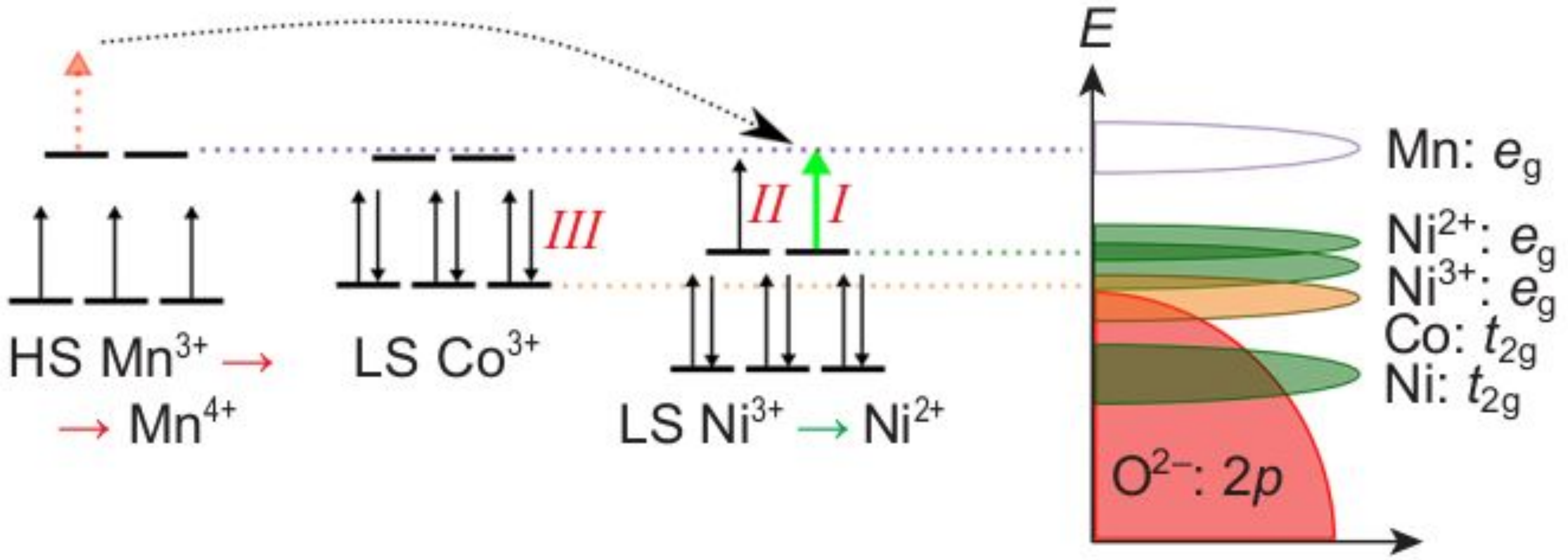
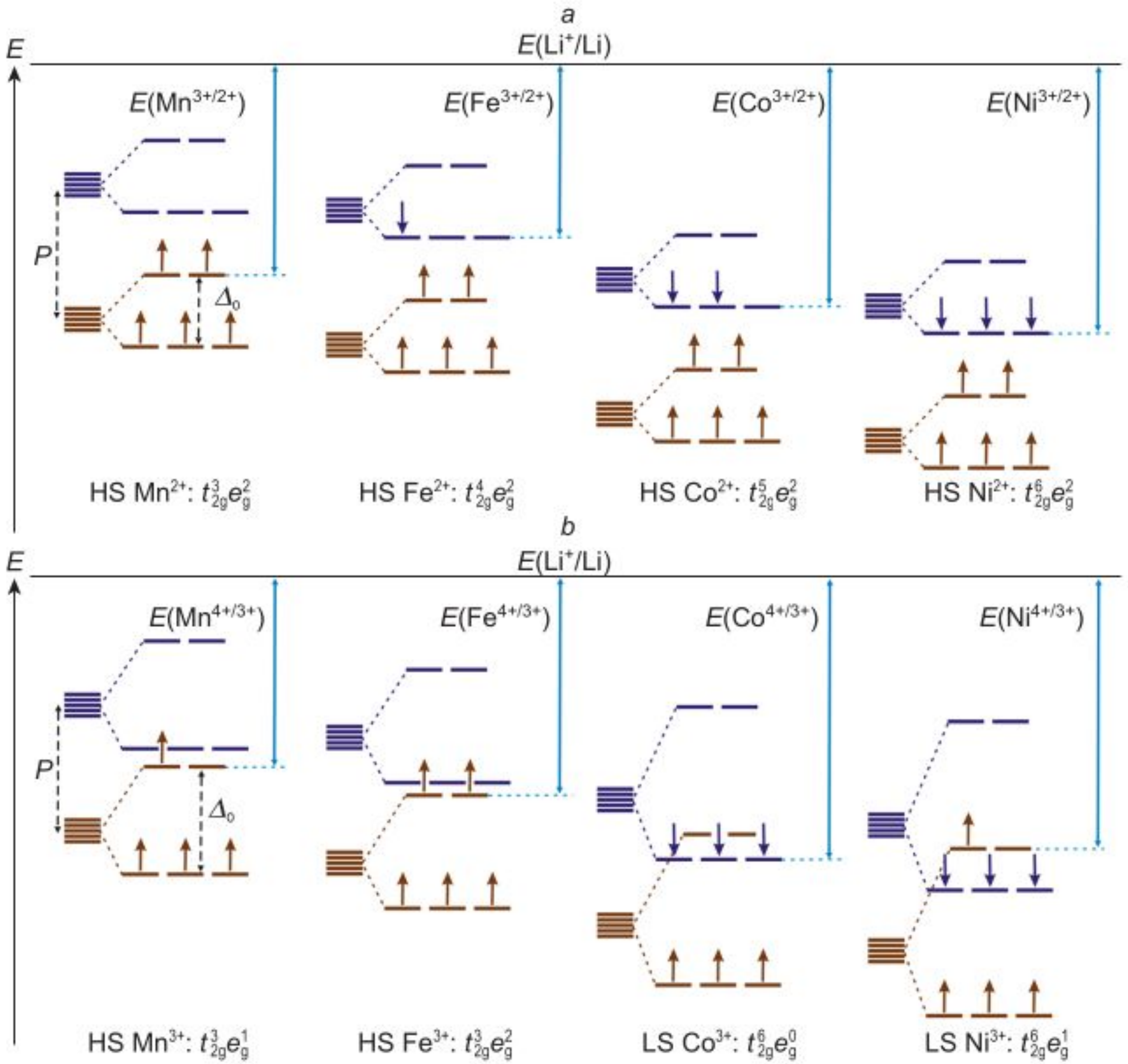


Figure 29. Schematic alignments of energy 3*d*-orbitals in layered NMC oxides. The dotted arrow shows the electron transfer corresponding to the reaction $Mn^{3+} + Ni^{3+} \rightarrow Mn^{4+} + Ni^{2+}$. The order of electron extraction is reflected by Roman numerals I–III. The figure was created by the authors of the review based on the data of the Refs 151, 152.



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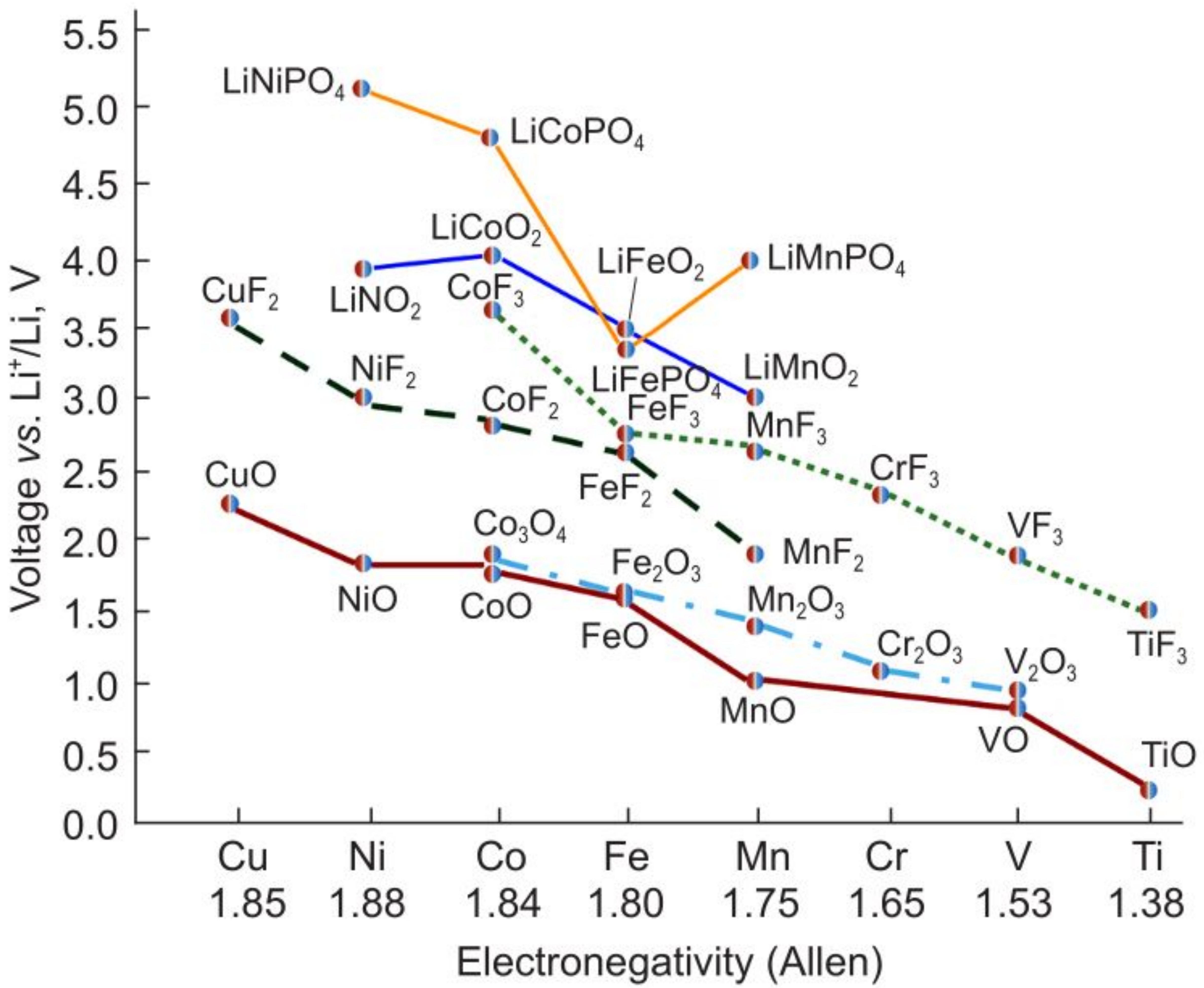

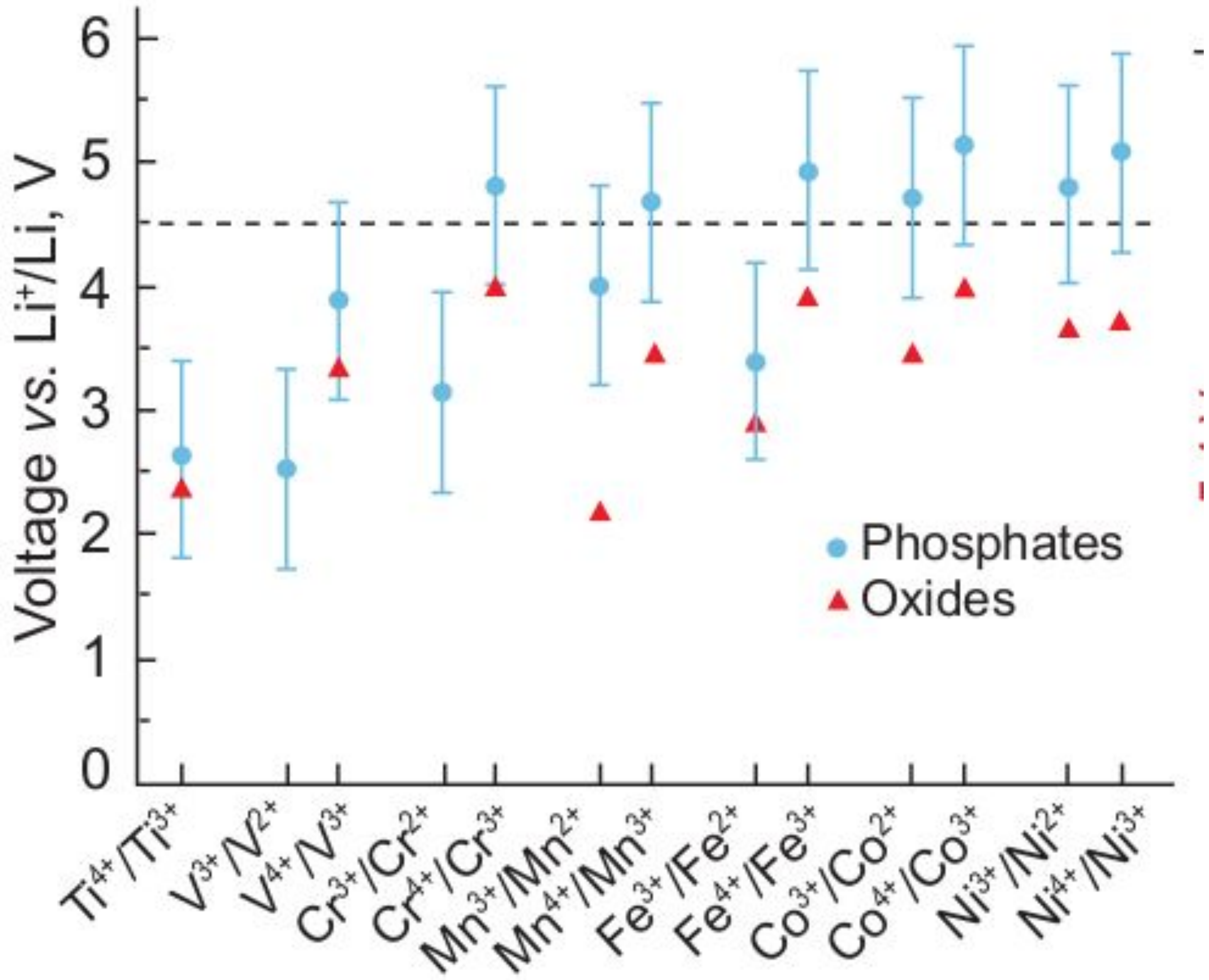

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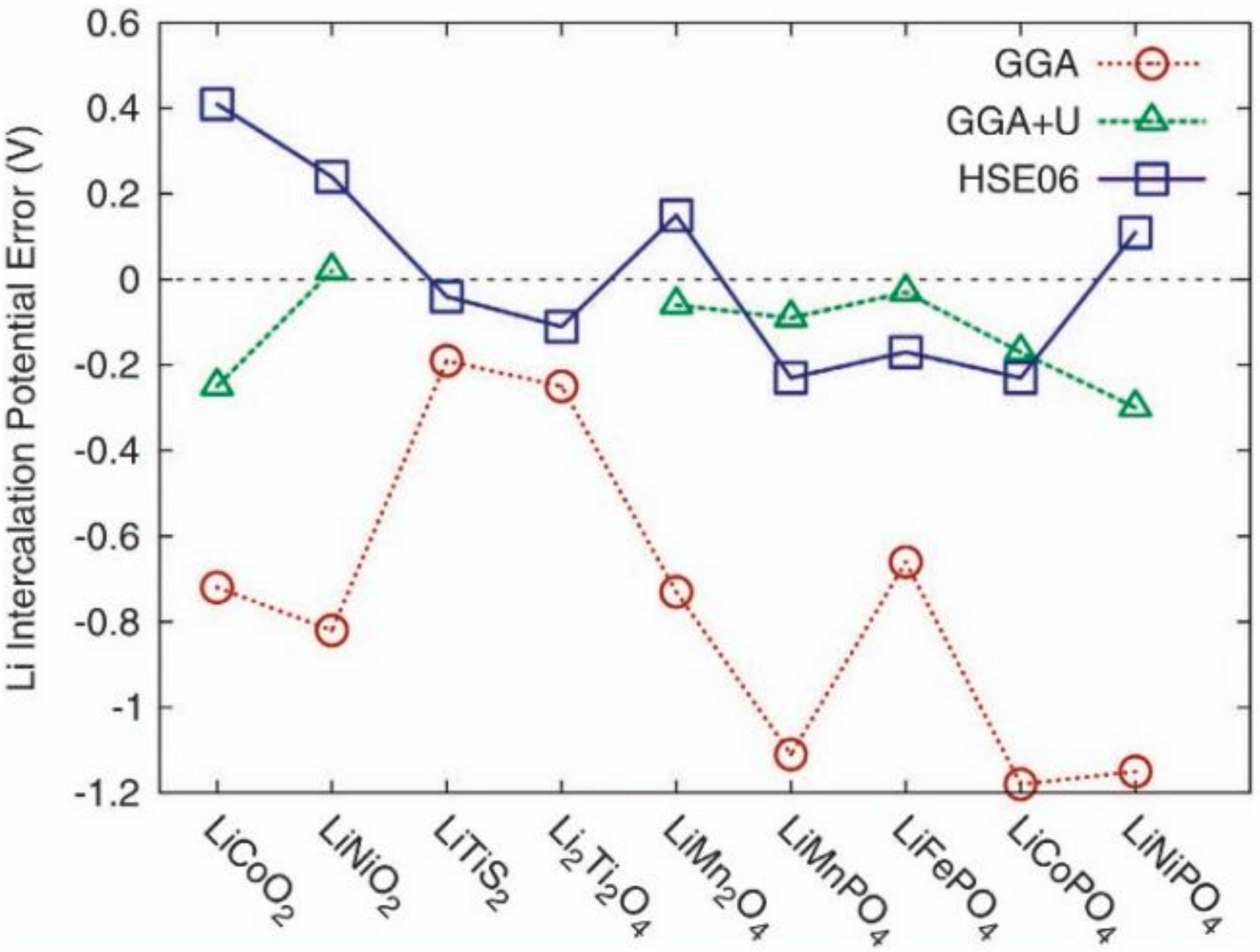
Type of exchange-correlation functional



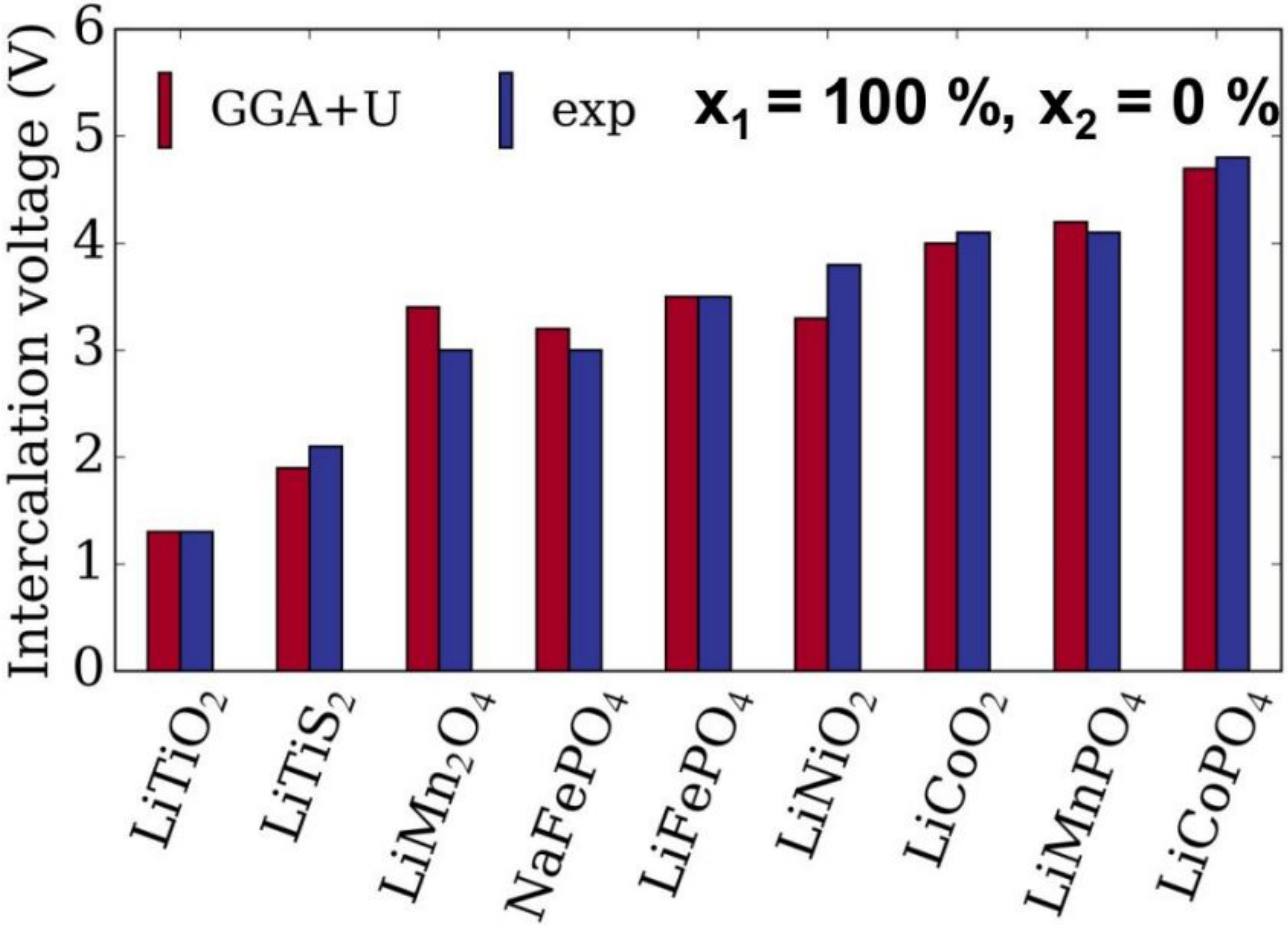
Comparison of the errors in intercalation voltages calculated with GGA, GGA+U and HSE hybrid functional.

U (Ti) = 0, so GGA+U = GGA for Ti-containing materials

Urban, A., Seo, DH. & Ceder, G. *npj Comput Mater* 2, 16002 (2016).

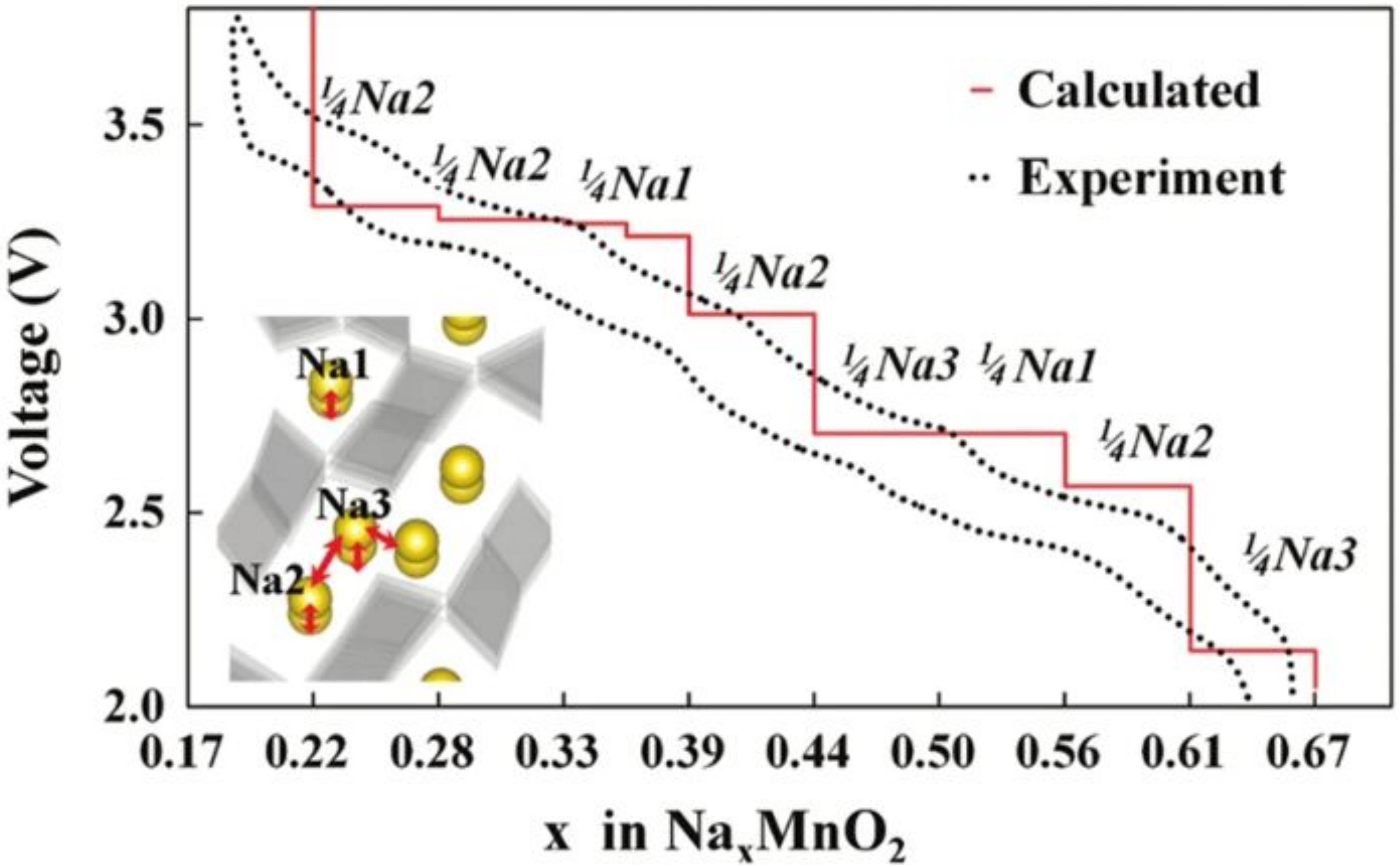
Benchmarks

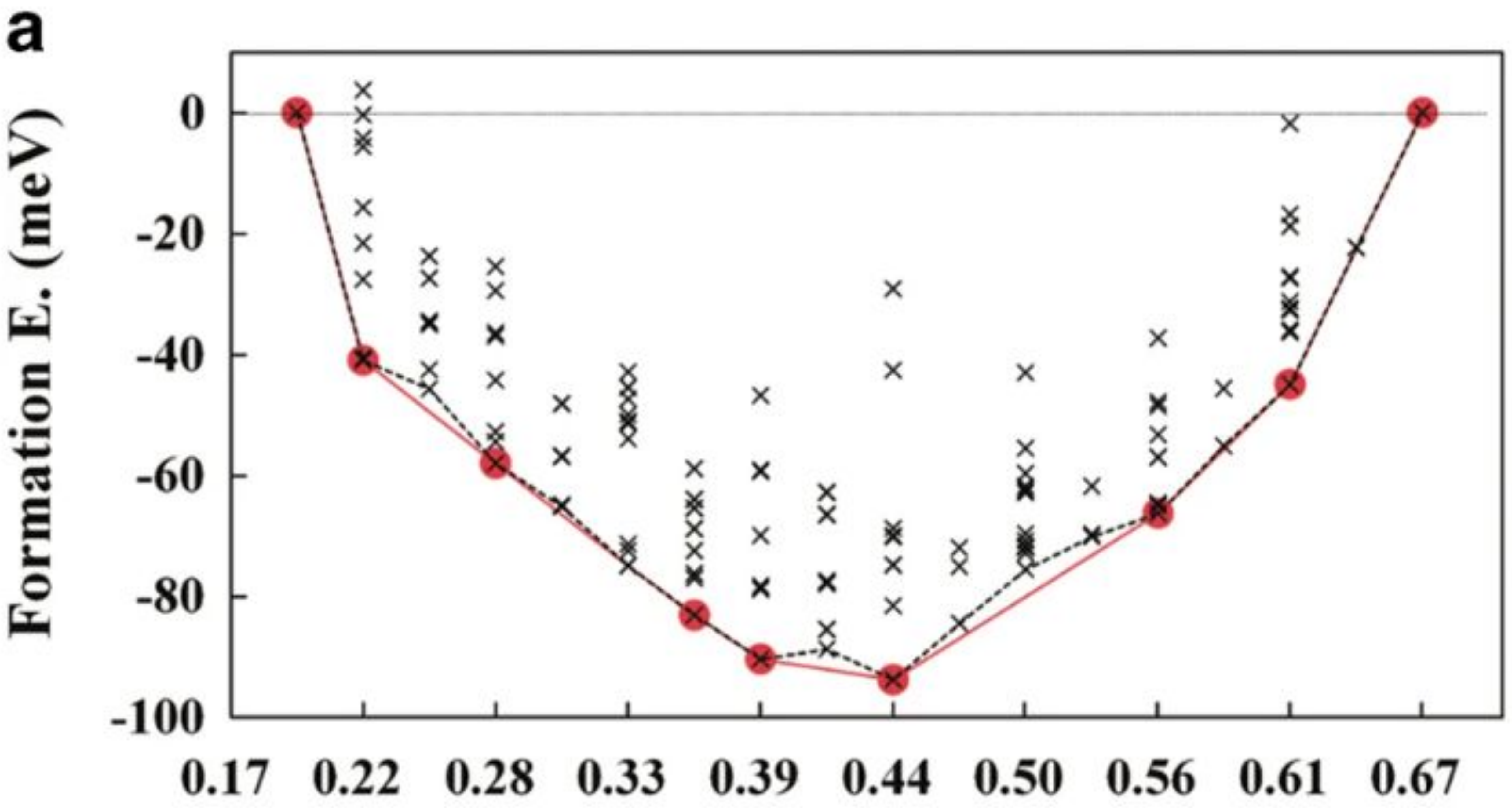
Benchmarks



Intercalation voltage (V)
0
1
2
3
4
5
6
GGA+U
exp
x_1 = 100 %, x_2 = 0 %
$LiTiO_2$
$LiTiS_2$
$LiMn_2O_4$
$NaFePO_4$
$LiFePO_4$
$LiNiO_2$
$LiCoO_2$
$LiMnPO_4$
$LiCoPO_4$

Benchmarks





Urban, A., Seo, DH. & Ceder, G. *npj Comput Mater* 2, 16002 (2016).

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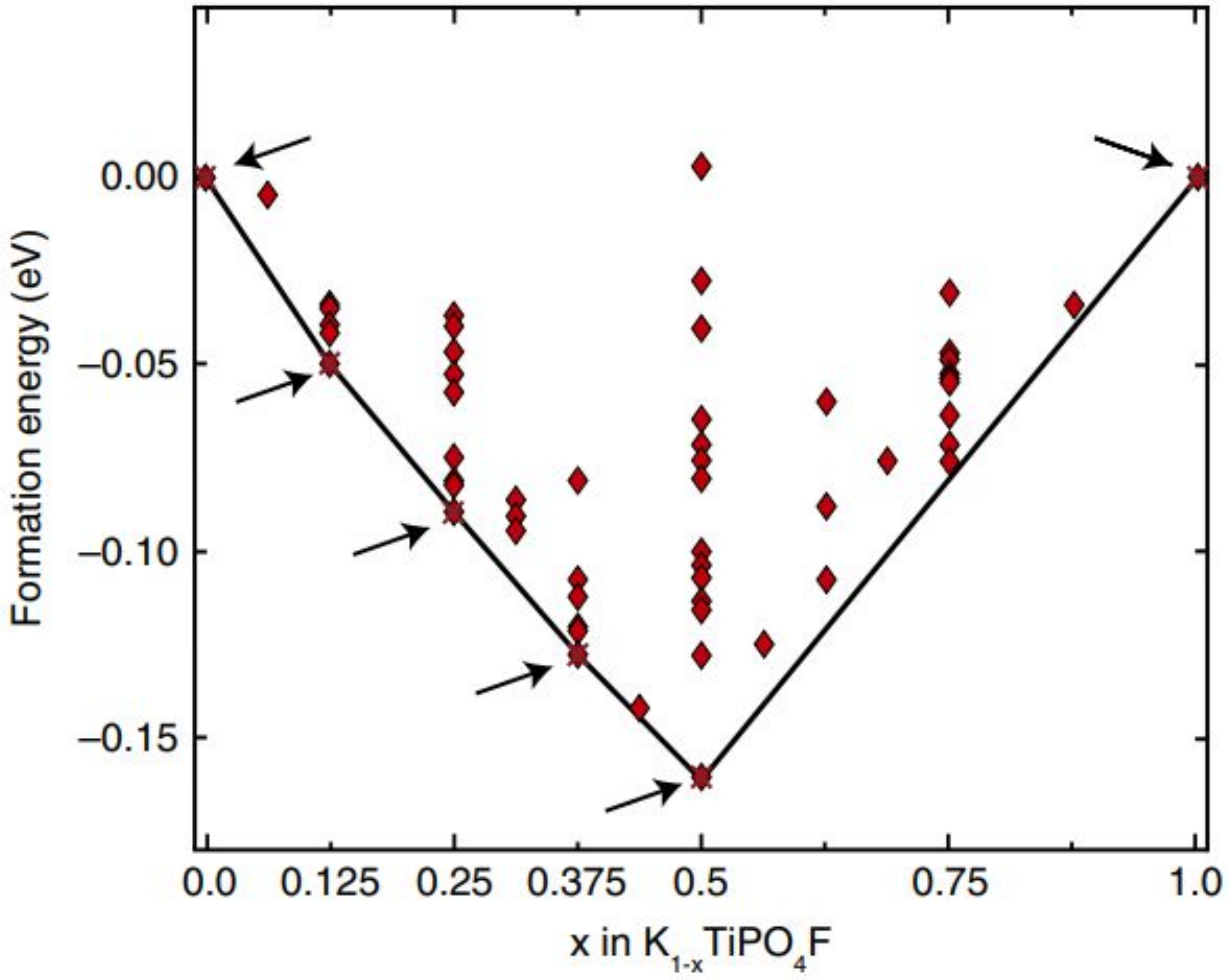
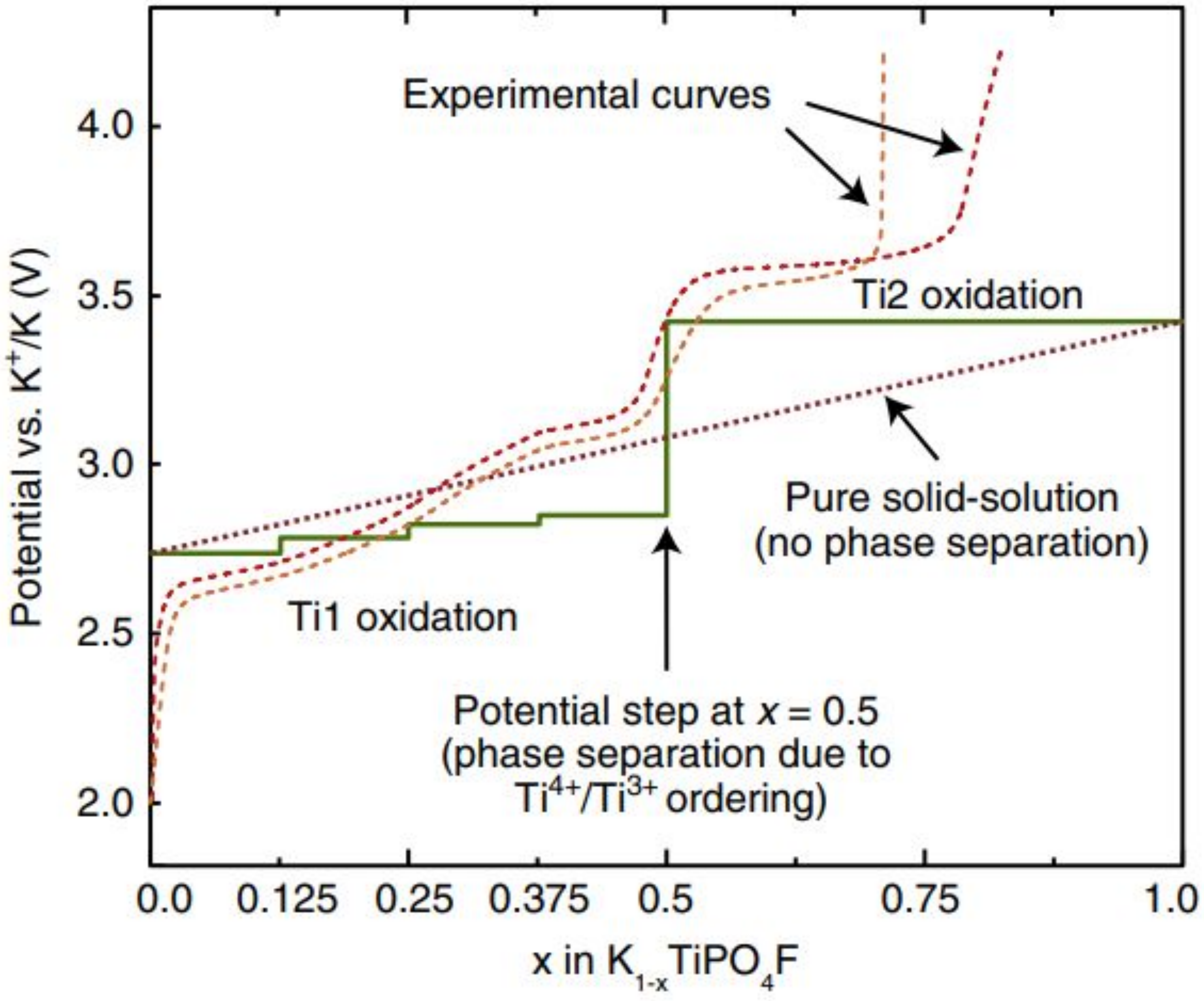
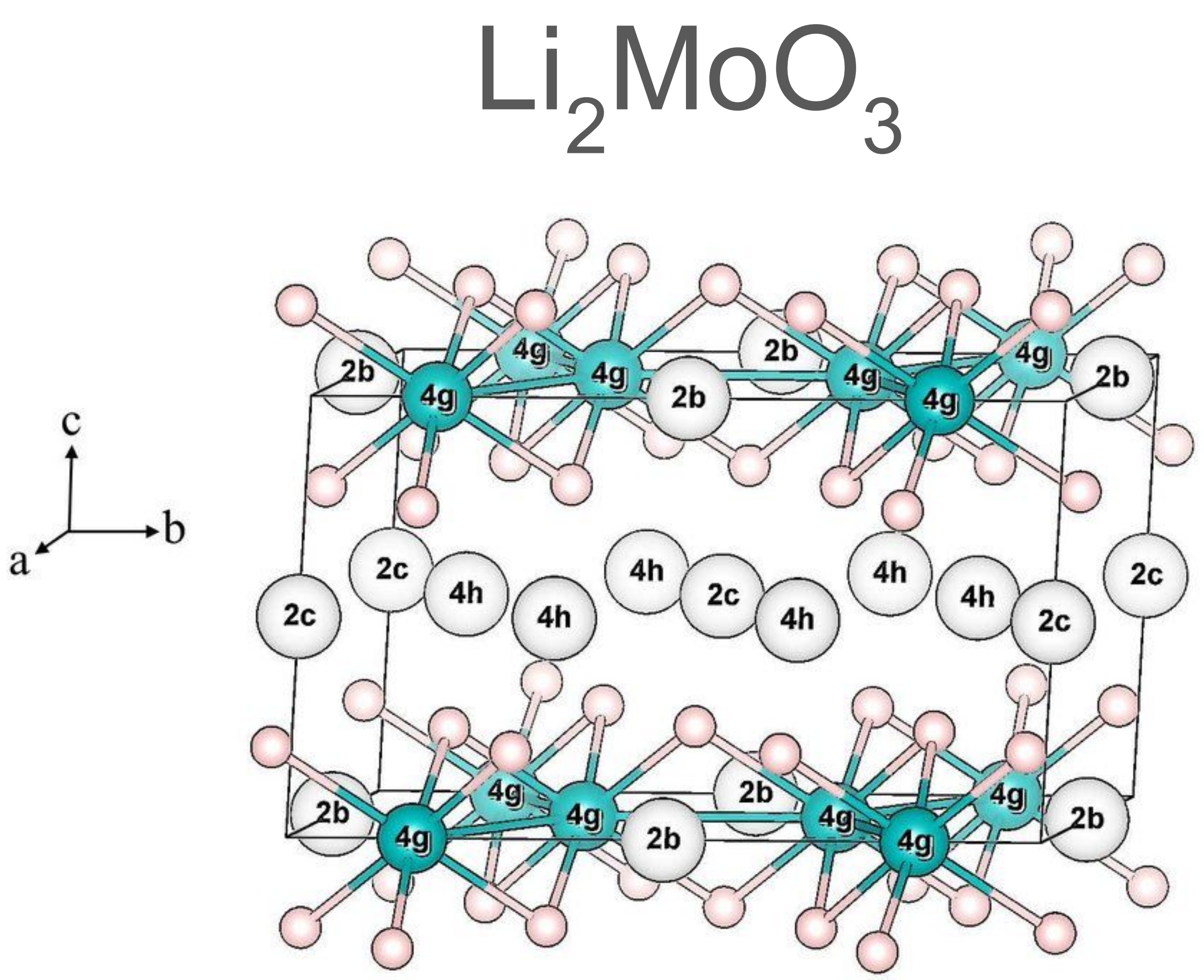


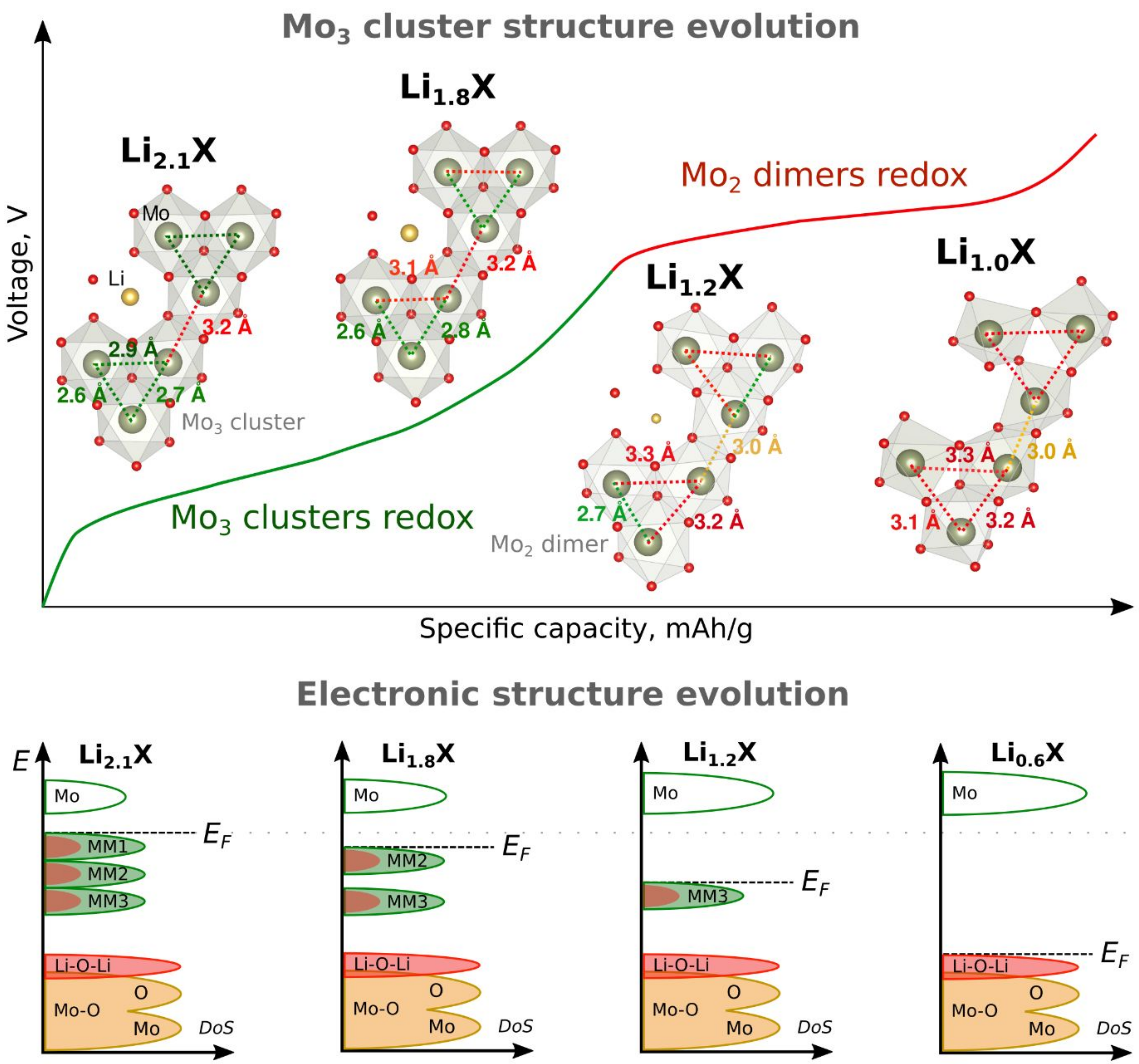


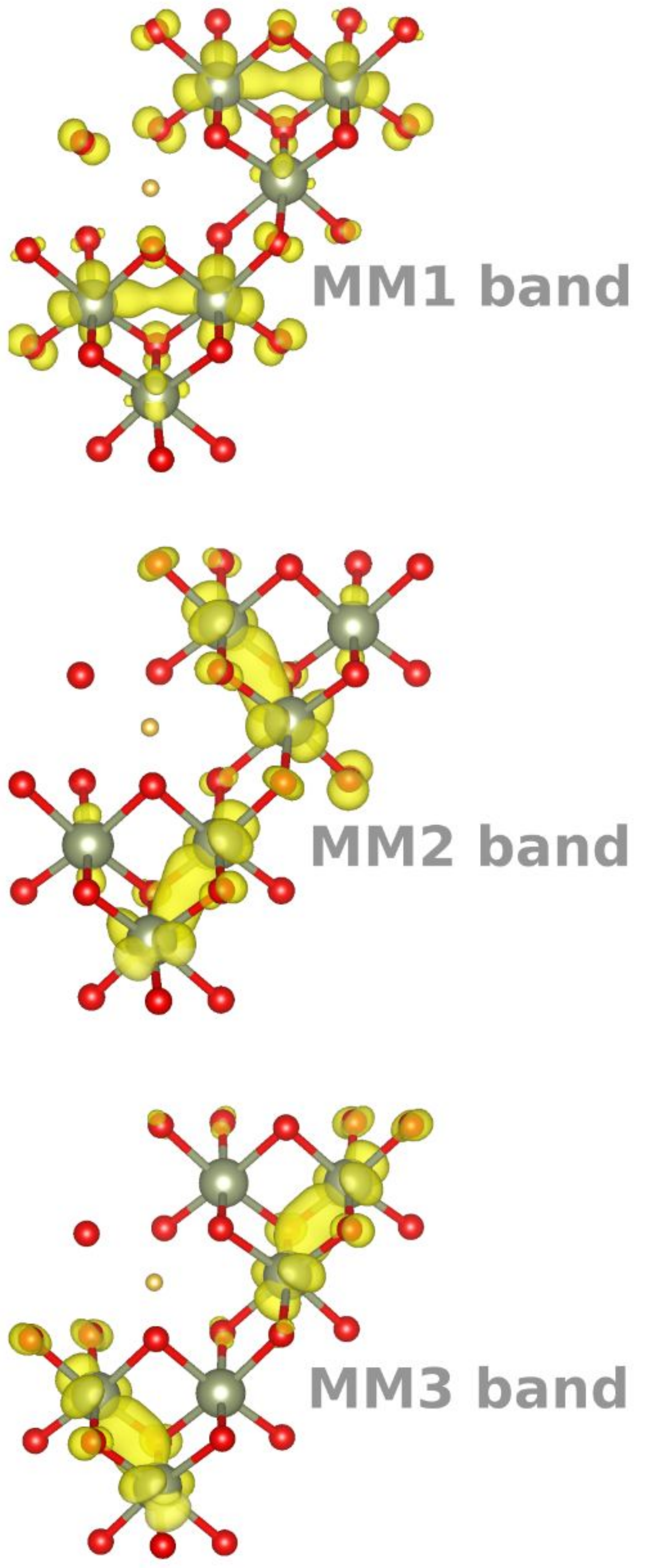
Fedotov, S.S., Luchinin, N.D., Aksyonov, D.A. et al. Nat Commun 11, 1484 (2020).

True stories

Story 1: we have no idea what is happening inside cathode

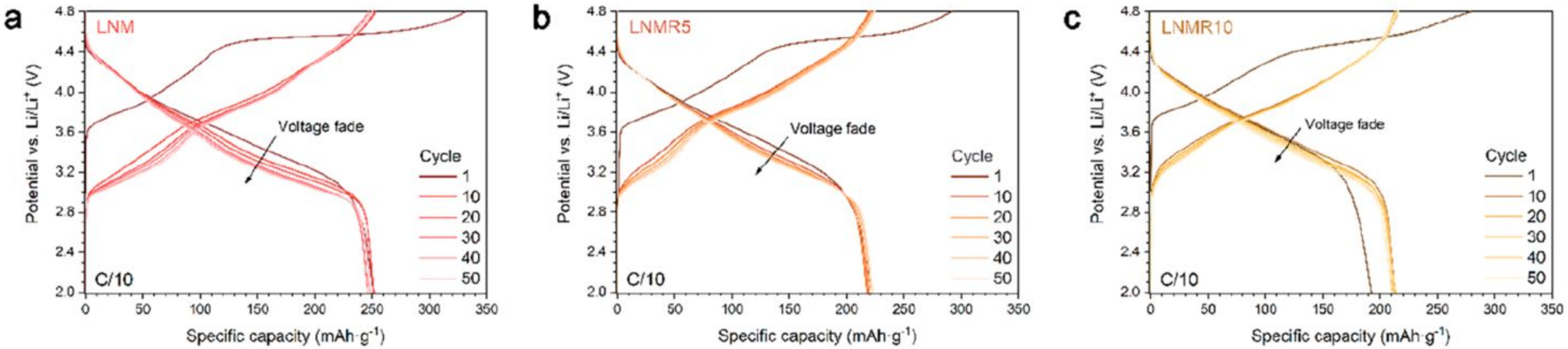




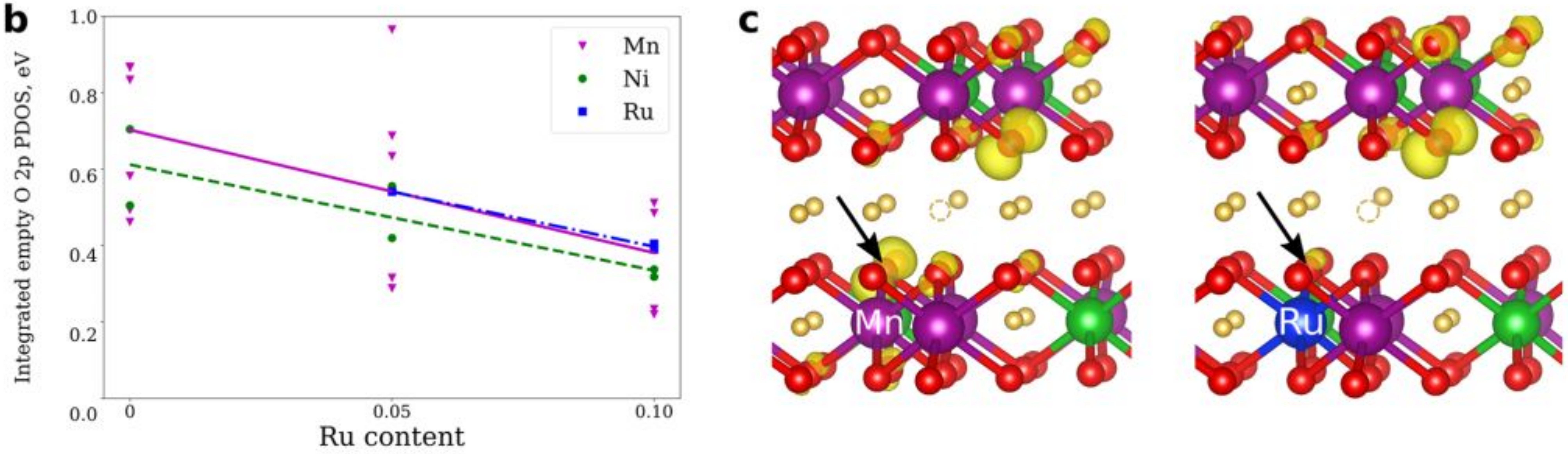


Savina A,.. Boev A.. Inorg. Chem. 2022, 61, 14, 5637–5652

Story 2: why Ru doping decreases voltage fade



Ru decreases oxygen redox



Individual tasks

Lithium group

Normal mode
Task 1. Voltage calculation for layered NMC oxide cathode
Task 2. Voltage calculation for graphite anode

Advanced mode
Task 3. Voltage calculation for LTO anode

Sodium group

Task 1. Voltage calculation for layered $NaCrO_2$ cathode

Task 2. Voltage calculation for Bi anode

Thx!

Acknowledgement

Skoltech
Energy

Center for
Energy Science
and Technology

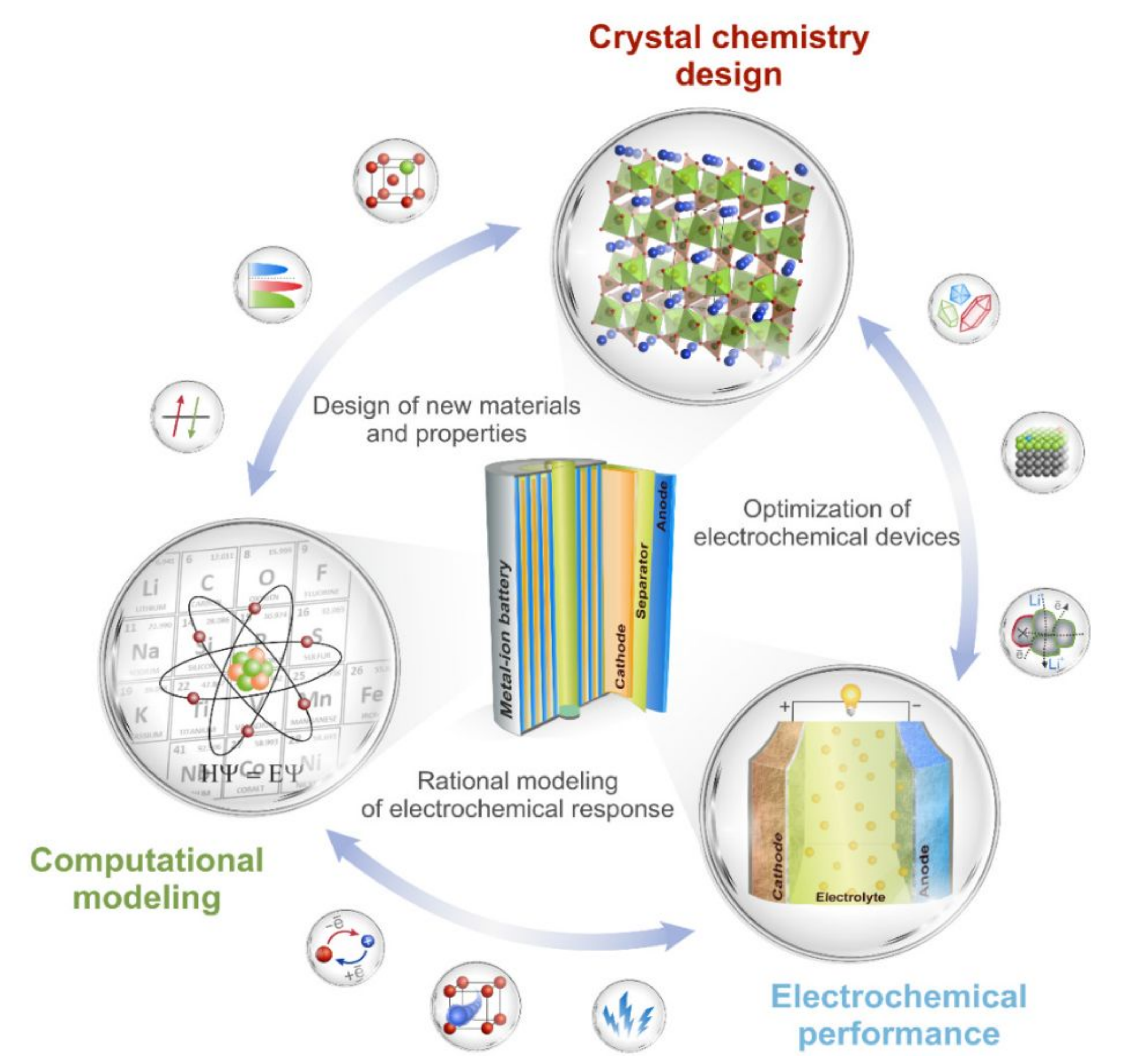
COMPUTATIONAL
SCIENCE
Skoltech
MATERIALS

Russian Science Foundation

Our group

Storion Research Lab

Center for Energy Science and Technology at Skoltech, Moscow



★ MatSolver - a web-service for predicting materials properties.