

# Evaluation of layered oxide frameworks as K-ion cathodes

Pawan Kumar Jha, Sanyam Nitin Totade, Prabeer Barpanda, Sai Gautam Gopalakrishnan

Materials Engineering, Indian Institute of Science

[saigautamg@iisc.ac.in](mailto:saigautamg@iisc.ac.in); <https://sai-mat-group.github.io>

# Acknowledgments



Group picture in May 2023

Dereje

Vijay

Reshma

Pawan

Sanyam



Prof. Prabeer Barpanda



Pawan



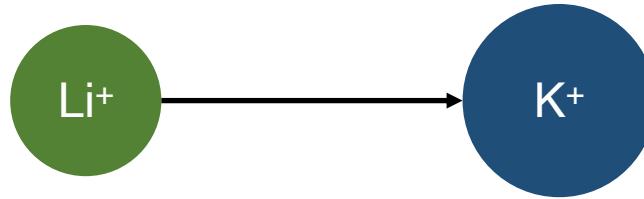
SERC (IISc)



# Why K-ion batteries?

Next generation of electric devices will benefit from higher energy density storage systems

- Li-ion technology approaching fundamental limits
  - Safety, supply-chain constraints; limits on achievable energy densities



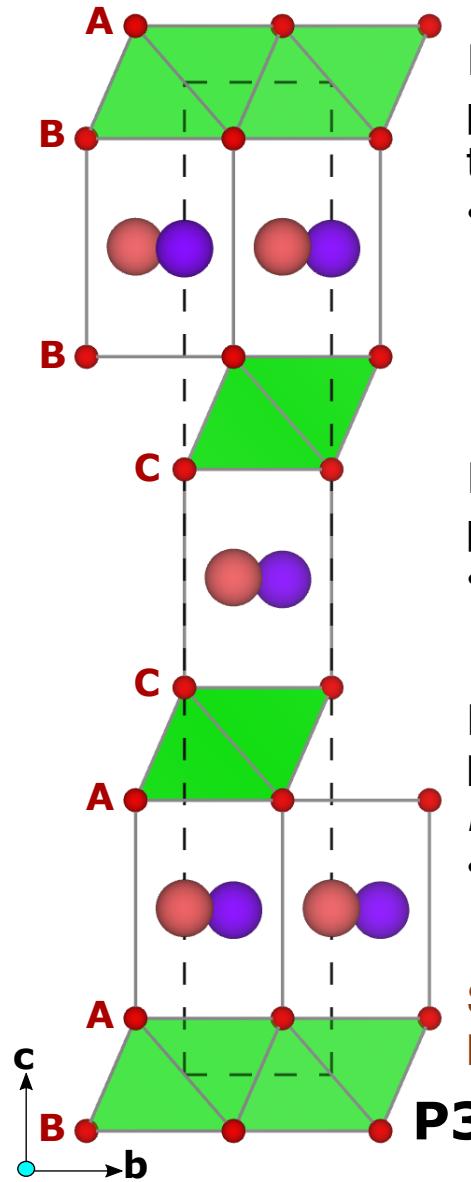
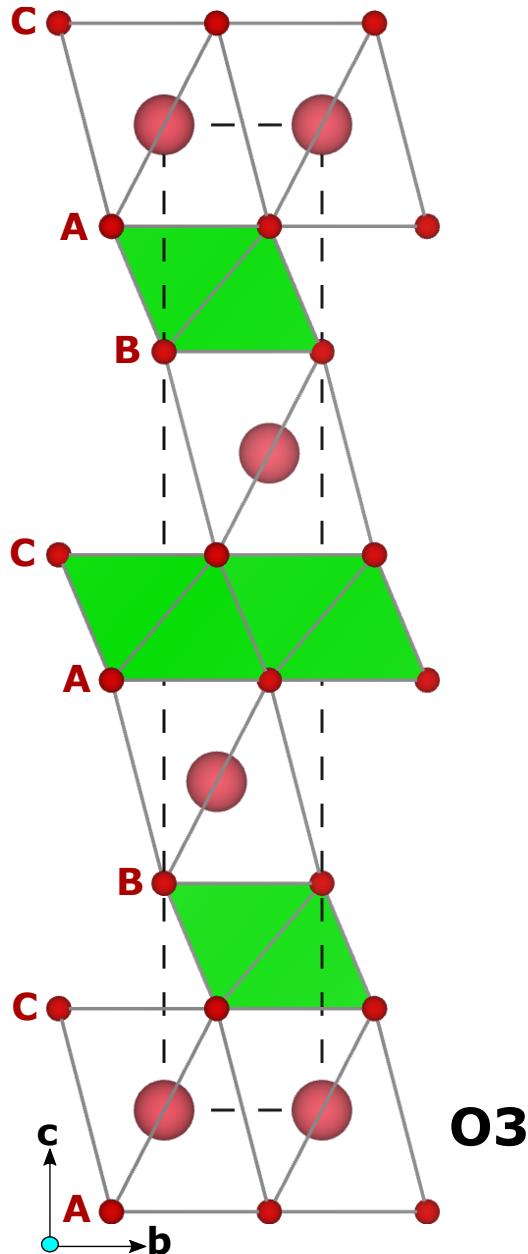
## Why K?

- Graphite as anode: similar to existing Li-ion
- Similar standard reduction potential for K (-2.94 V vs. SHE) vs. Li (-3.04 V)
- Natural abundance of K: relevant for grid-scale

Need good positive electrode (cathode) materials

- Layered transition metal oxides: high energy and power densities (theoretically)

# Prismatic vs. octahedral



Intercalant ion in either octahedral or prismatic coordination in layered transition metal (TM) oxides

- Function of intercalant concentration, transition metal (oxidation state+identity)

In  $K_xTMO_2$ , octahedral at  $x \sim 1$ , prismatic at intermediate  $x$

- Prismatic is typical at  $x \sim 0.5$

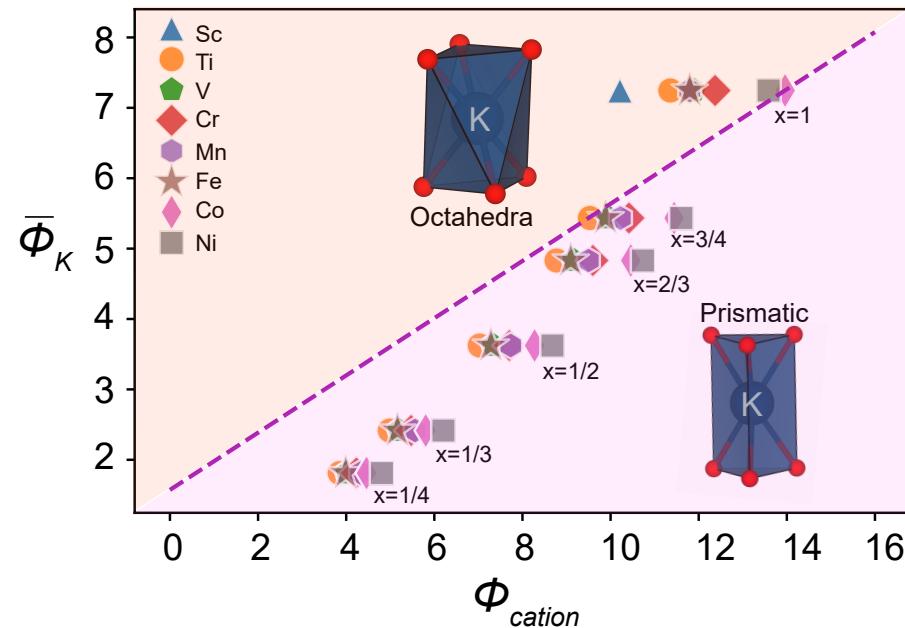
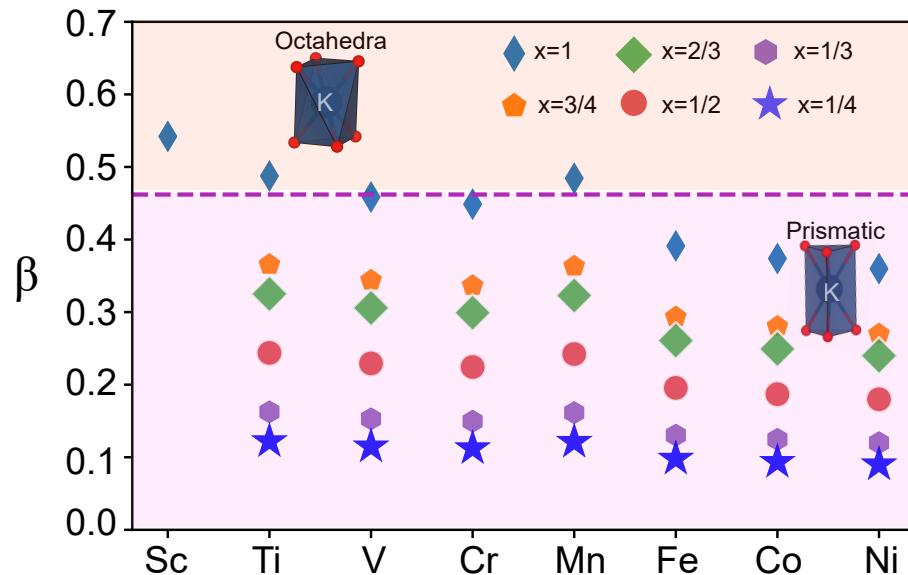
Prismatic coordination can exhibit higher rate performance [*Adv. Energy Mater.* **8**, 1703415 (2018)]

- But results in lower capacity

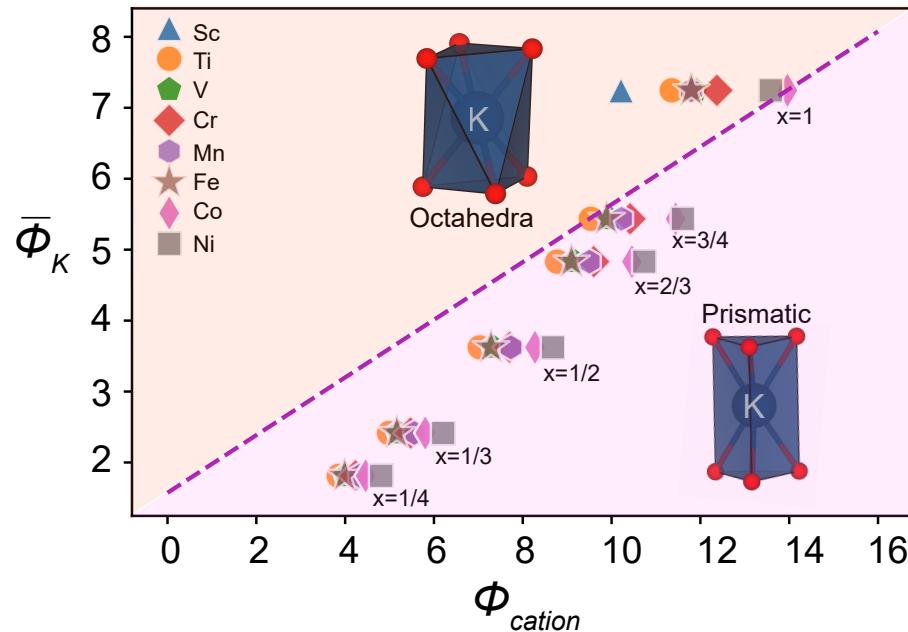
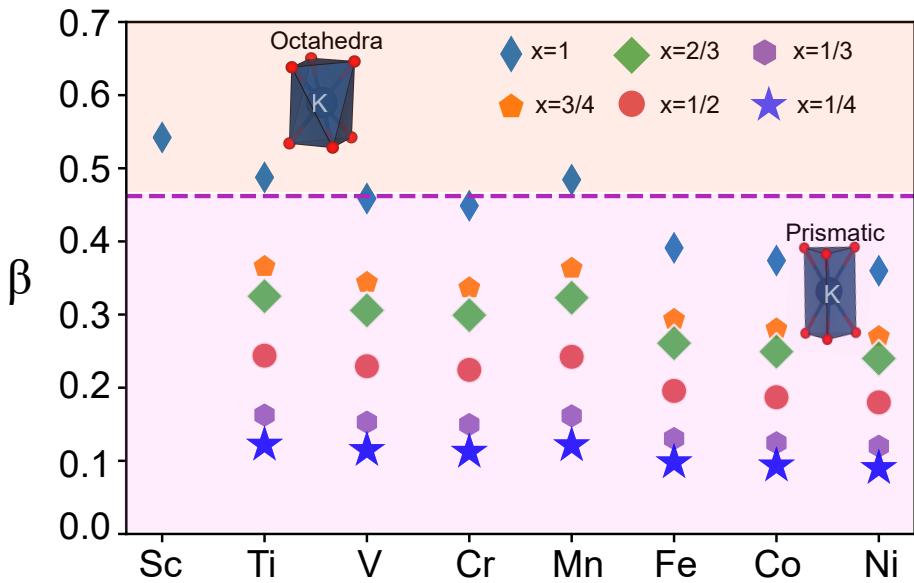
Systematic studies on prismatic layered TM oxides with K: missing

1. Deb and Sai Gautam, *J. Mater. Res.* **37**, 3169-3196 (2022)
2. Delmas et al., *Physica B+C* **99**, 81-85 (1980)

# Empirical models: prismatic more favorable than octahedral



# Empirical models: prismatic more favorable than octahedral

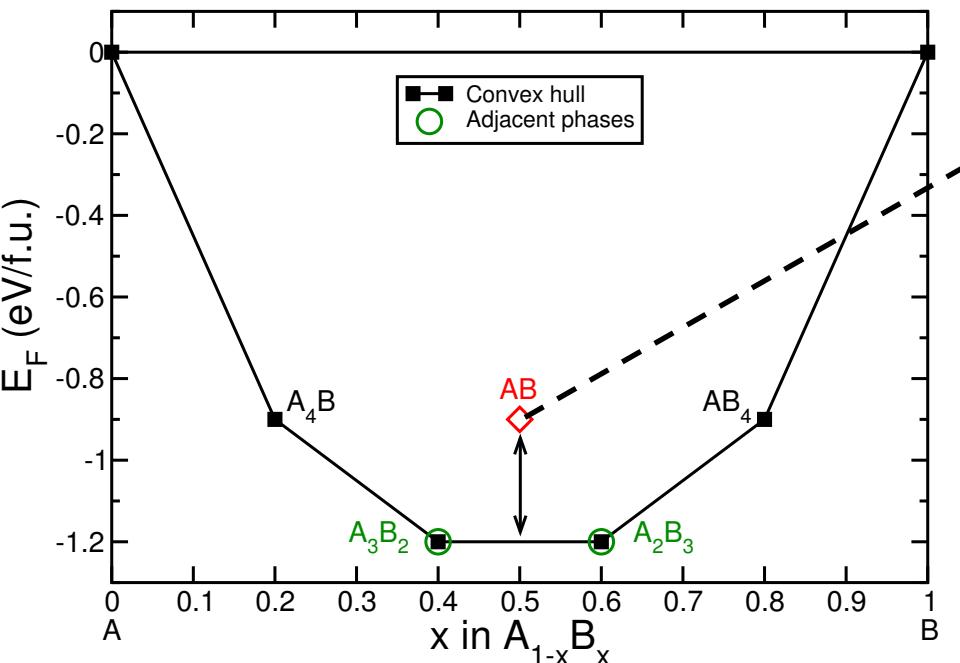


Evaluate P3-K<sub>0.5</sub>TMO<sub>2</sub> and P3-TMO<sub>2</sub>, for Ti, V, Cr, Mn, Co, and Ni via computations

- Choice of TM: ability to access +4 oxidation state reversibly
- Experimental evidence of P3-phases observed in Mn, Co, and Cr
  - [J. Electrochem. Soc. **163**, A1295 (2016); Adv. Mater. **29**, 1702480 (2017); Chem. Commun. **53**, 3693-3696 (2017); Energy Environ. Sci. **11**, 2821-2827 (2018)]

# Density functional theory and 0 K thermodynamics

- Calculations done using Vienna ab initio simulation package
- Exchange-correlation: Hubbard  $U$  corrected strongly constrained and appropriately normed (SCAN+ $U$ ) functional
- Initial structures: inorganic crystal structure database ( $2\times2\times1$  supercell)



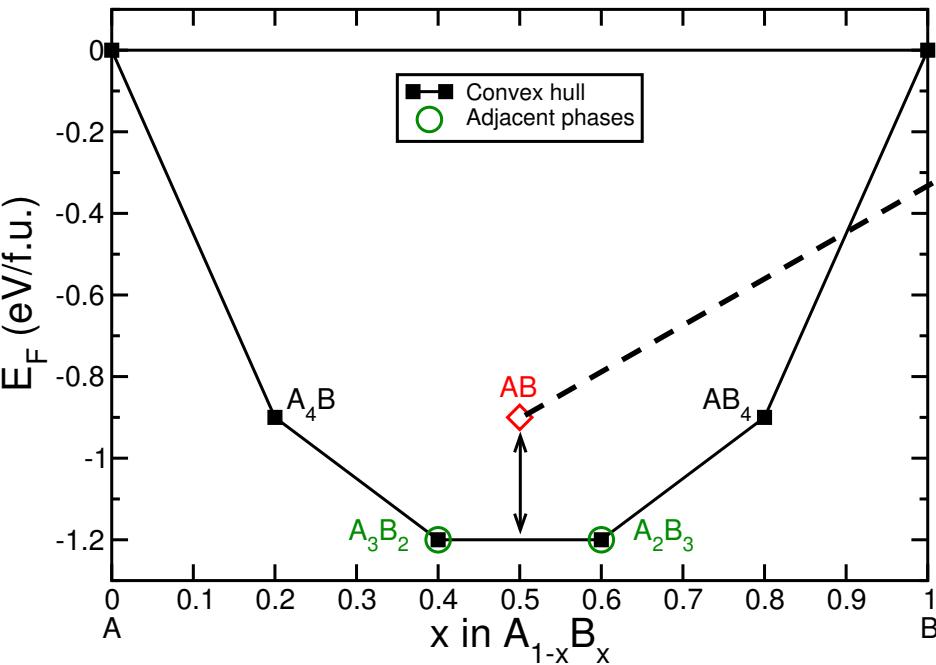
Positive  $E^{hull}$ : metastable (< 25-50 meV/atom) or unstable (>50 meV/atom)

- Largest energy release via decomposition of AB

$E^{hull}$ : measure of **stability** of a given structure+composition combination (at 0 K)

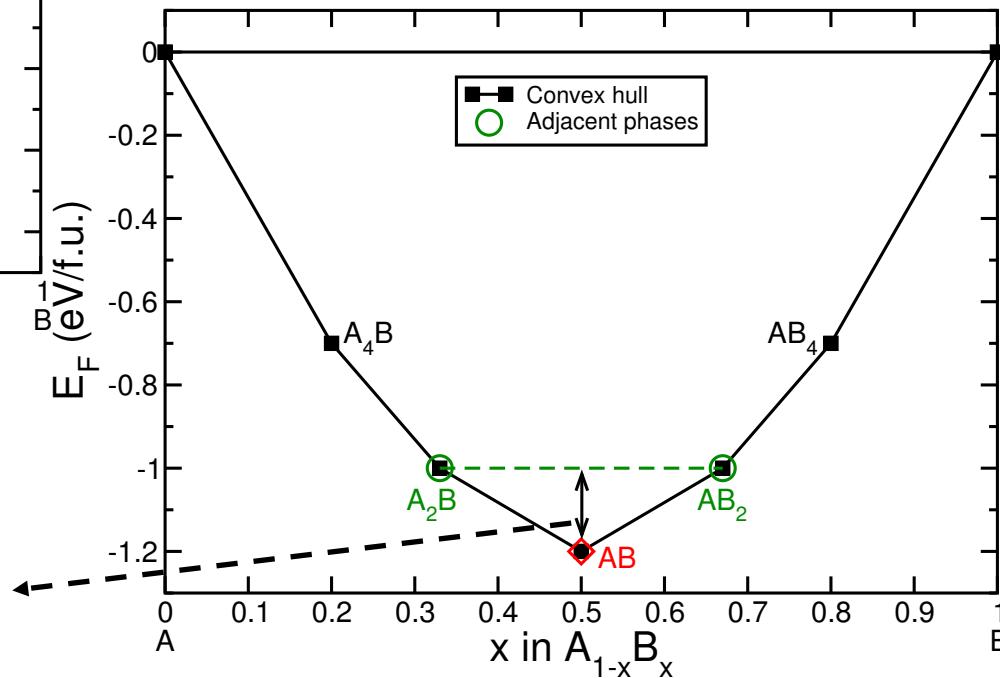
# Density functional theory and 0 K thermodynamics

- Calculations done using Vienna ab initio simulation package
- Exchange-correlation: Hubbard  $U$  corrected strongly constrained and appropriately normed (SCAN+ $U$ ) functional
- Initial structures: inorganic crystal structure database ( $2 \times 2 \times 1$  supercell)



Positive  $E^{hull}$ : metastable (< 25-50 meV/atom) or unstable (>50 meV/atom)

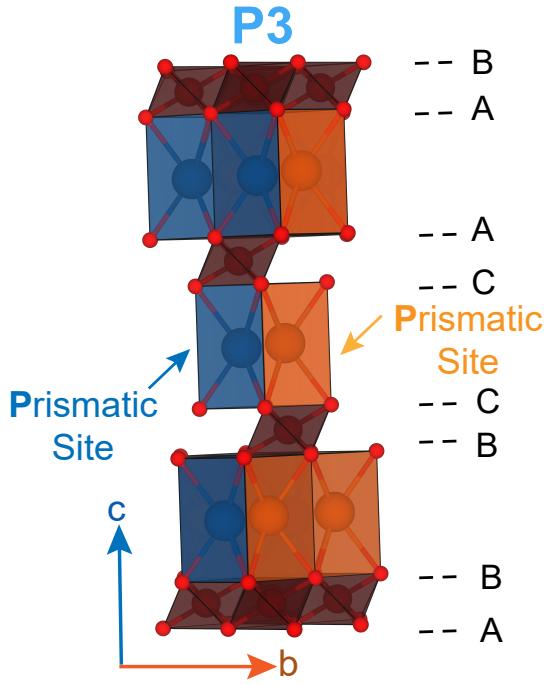
- Largest energy release via decomposition of AB



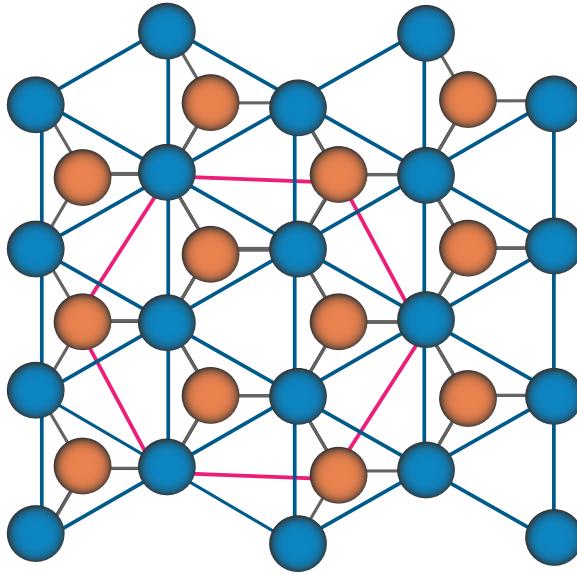
Negative (or zero)  $E^{hull}$ : stable

- Lowest energy release via formation of AB

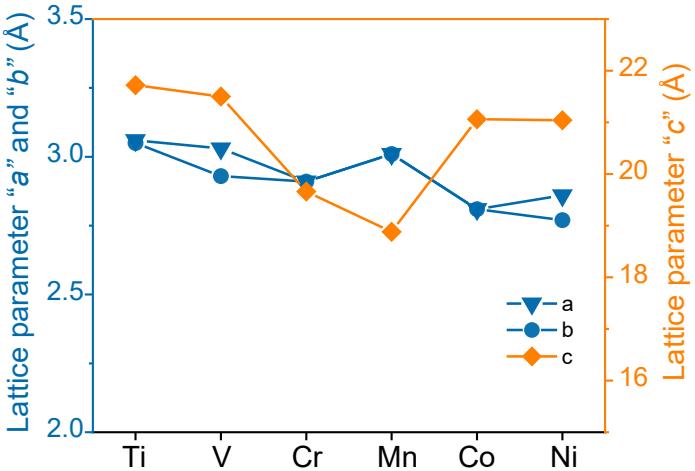
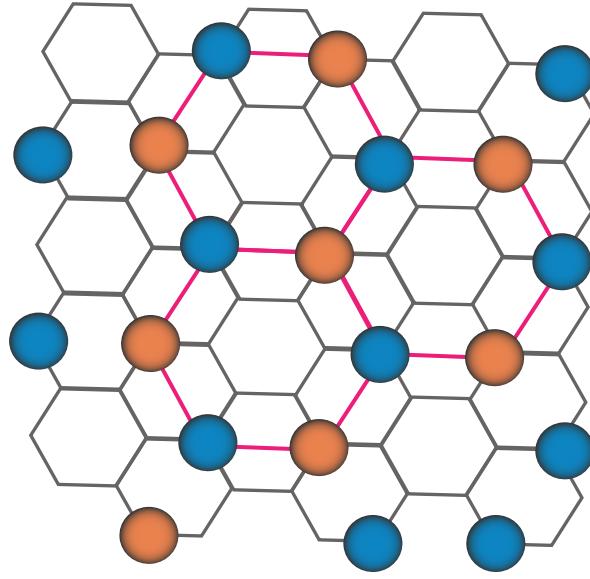
# K-vacancy ground state configuration identical for all TM



Two trigonal prismatic sites



"Honeycomb" arrangement  
K ion ordering at  $x=1/2$



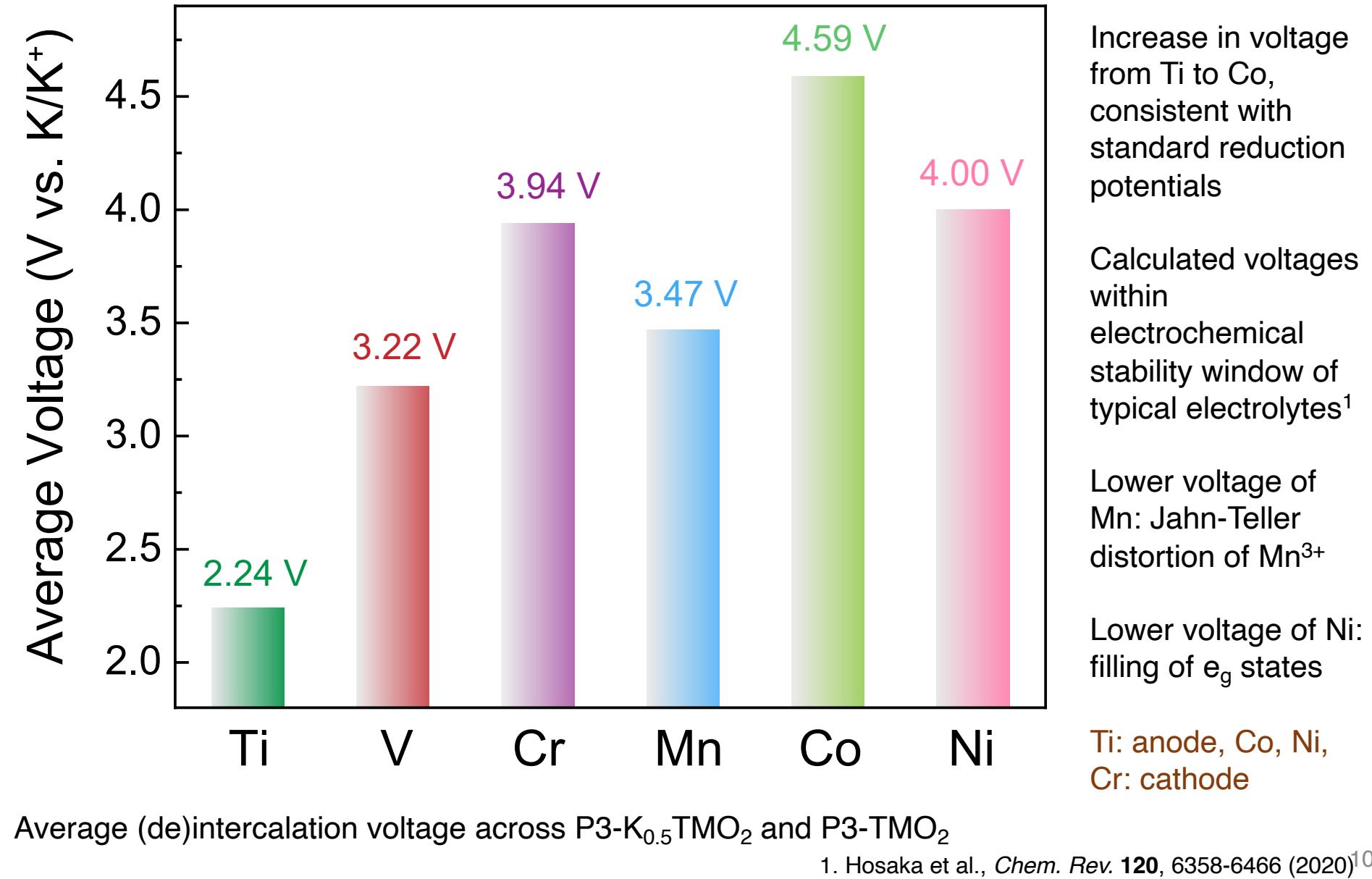
Calculated lattice parameters for  $P3-K_{0.5}TMO_2$

< 5% deviation from known experimental values

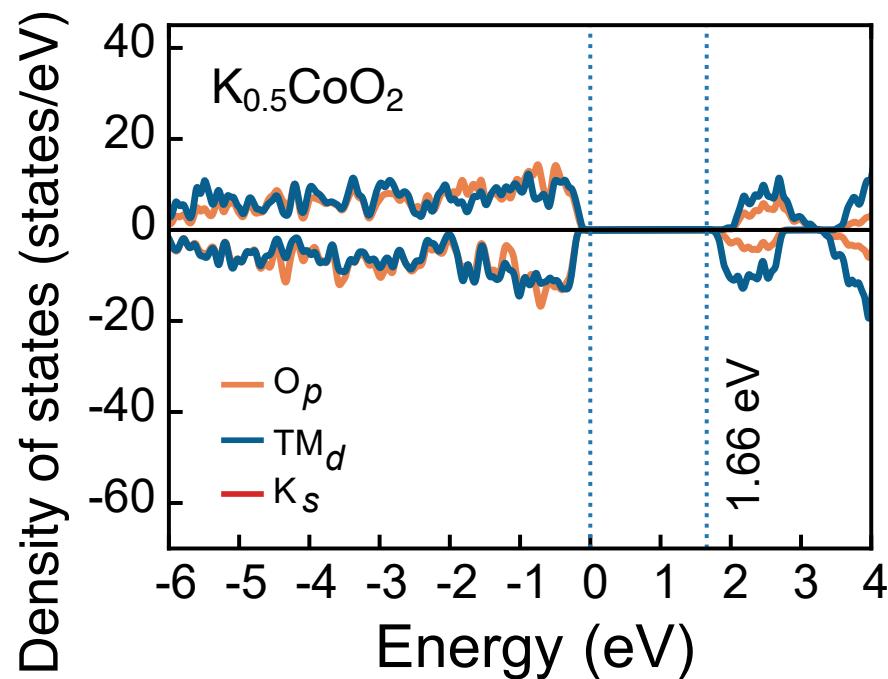
Parameters  $a$  and  $b$  increase with TM

- Anomalous trends in Mn and Ni due to Jahn-Teller
- $c$  parameter in  $K_{0.5}CoO_2$ : overestimated computationally

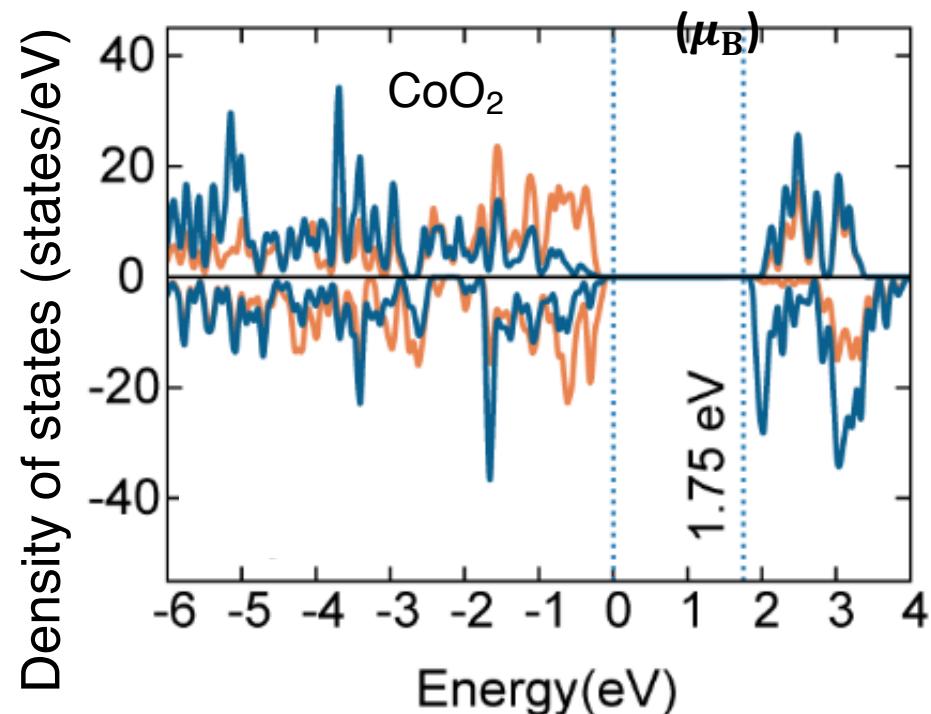
# Average voltage: Co is promising



# Electronic structure: TM is redox-active



Co  $d$  and O  $p$  contribute to valence band edge



Co  $d$  states shift to conduction band with K removal

# Electronic structure: TM is redox-active

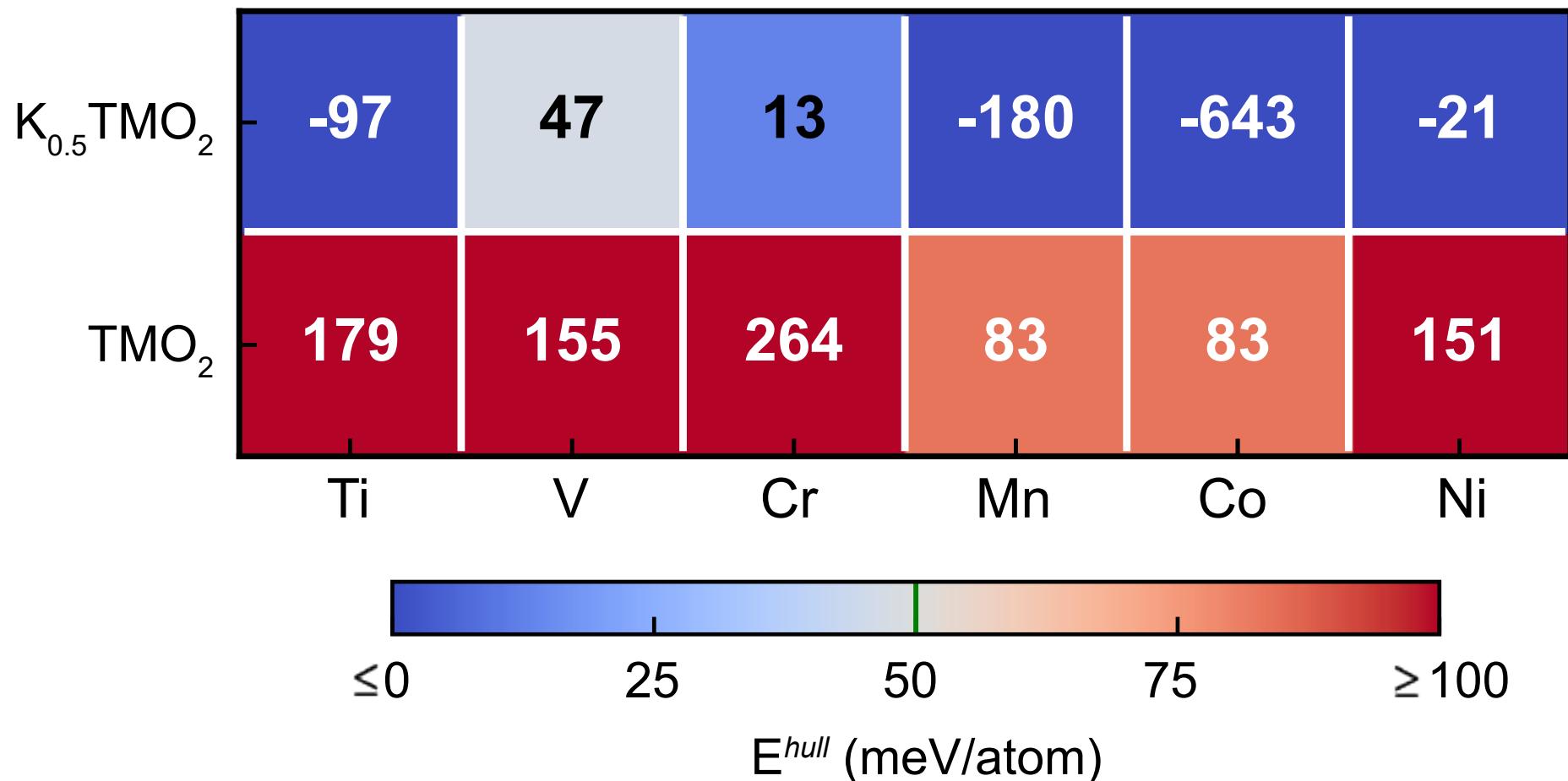
TM	Calculated on-site magnetic moments ( $\mu_B$ )	
	$K_{0.5}TMO_2$	$TMO_2$
Ti	0.88 (3 <sup>+</sup> ) & 0.06 (4 <sup>+</sup> )	0.00 (4 <sup>+</sup> )
V	1.74 (3 <sup>+</sup> ) & 1.16 (4 <sup>+</sup> )	1.15 (4 <sup>+</sup> )
Cr	2.51 (3 <sup>+</sup> /4 <sup>+</sup> )	2.24 (4 <sup>+</sup> )
Mn	3.84 (3 <sup>+</sup> ) & 3.03 (4 <sup>+</sup> )	3.07 (4 <sup>+</sup> )
Co (Low spin)	0.01 (3 <sup>+</sup> ) & 1.00 (4 <sup>+</sup> )	1.06 (4 <sup>+</sup> )
Ni (Low spin)	0.99 (3 <sup>+</sup> ) & -0.01 (4 <sup>+</sup> )	0.00 (4 <sup>+</sup> )

Calculated on-site magnetic moments: clear indication that TM is redox-active  
• Both  $K_{0.5}CrO_2$  and  $CrO_2$  are metallic

Electronic structure + magnetic moments → TM redox-activity

# 0 K stability: Co and Mn are reasonable

All elemental, binary, and ternary ‘ordered’ structures considered for stability calculations

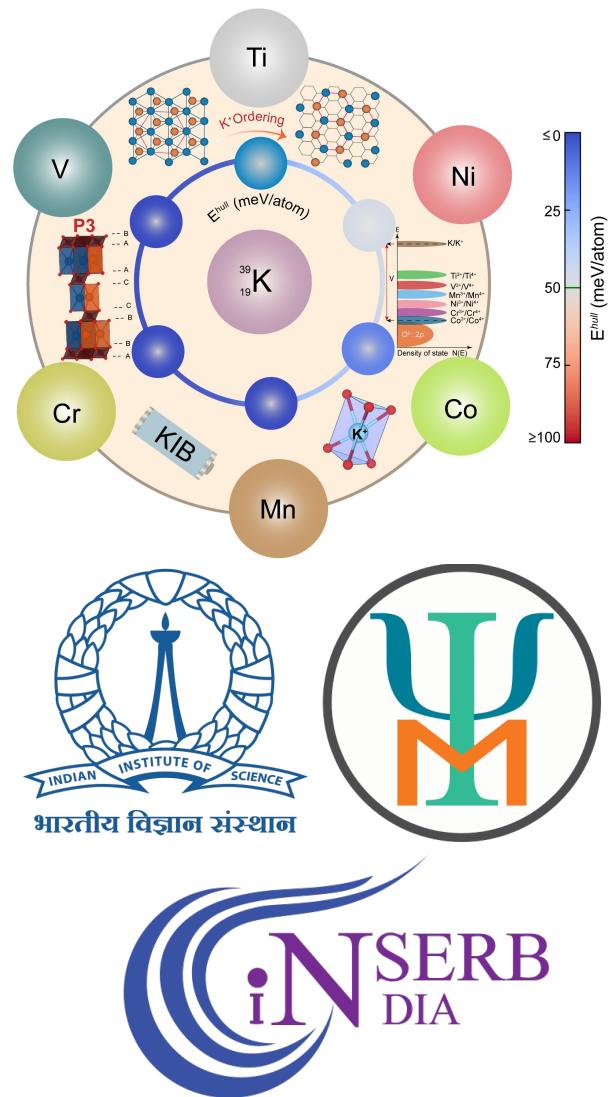


- High instability of P3-TMO<sub>2</sub> structures in Ti, V, Cr, and Ni
- P3-TMO<sub>2</sub> with Mn and Co metastable: may be accessible electrochemically

Voltage + stability: Co is optimal

# Conclusions

- K-ion batteries can act as a substitute for Li-ion batteries
  - Need good cathode materials
- Layered transition metal oxides are good candidates for K-ion cathodes
  - Empirical models suggest prismatic coordination is more favorable than octahedral
- Evaluated P3-type  $K_{0.5}TMO_2$  and  $TMO_2$  compositions using computations
  - TM = Ti, V, Cr, Mn, Co, and Ni
  - Co: offers high voltage with reasonable metastability



“Evaluation of P3-type layered oxides as K-ion battery cathodes”, P.K. Jha, S.N. Totade, P. Barpanda, and G. Sai Gautam, [arXiv 2305.04299](https://arxiv.org/abs/2305.04299) (2023). *Under review*