

On the Balance of Intercalation and Conversion Reactions in Battery Cathodes

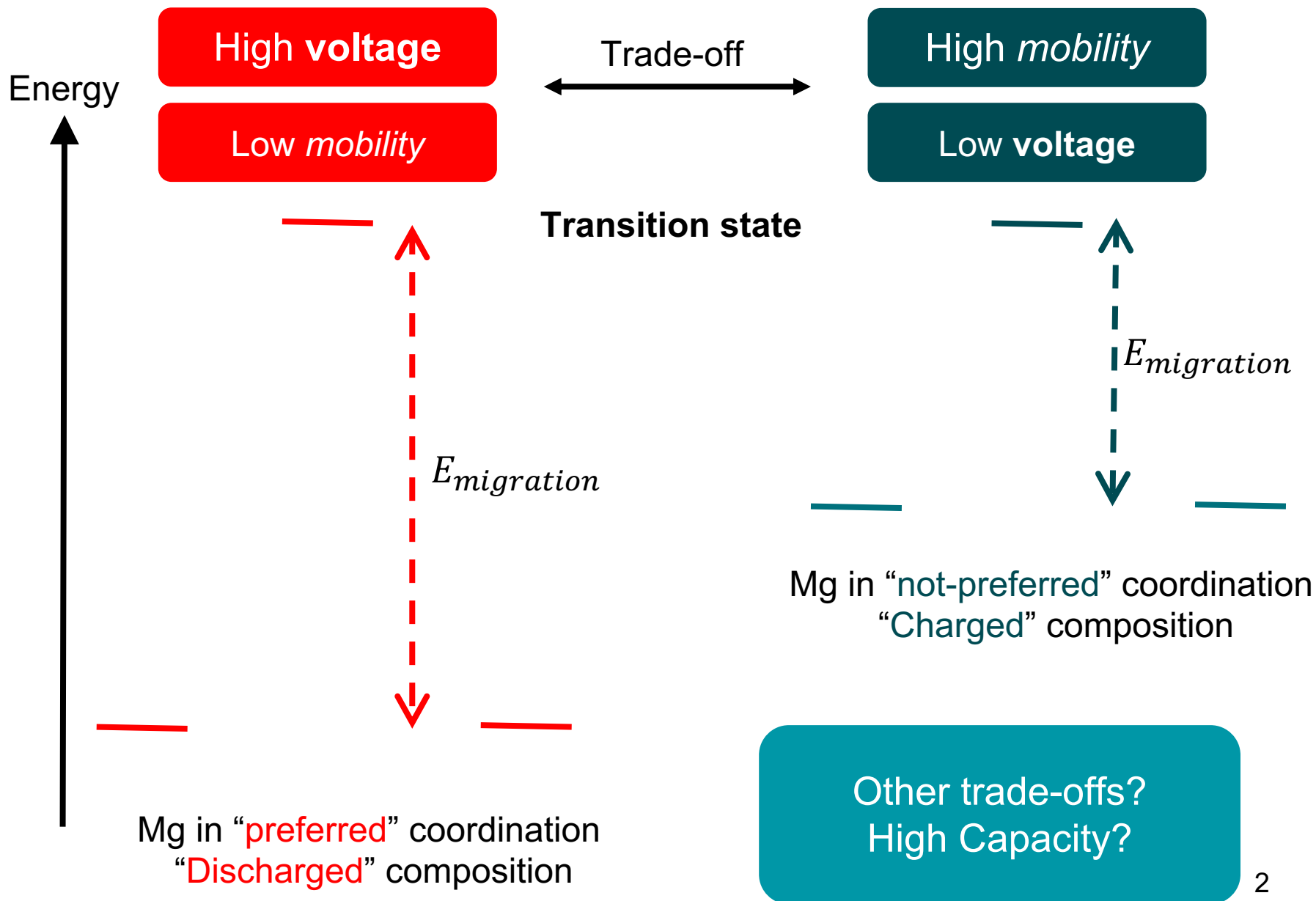
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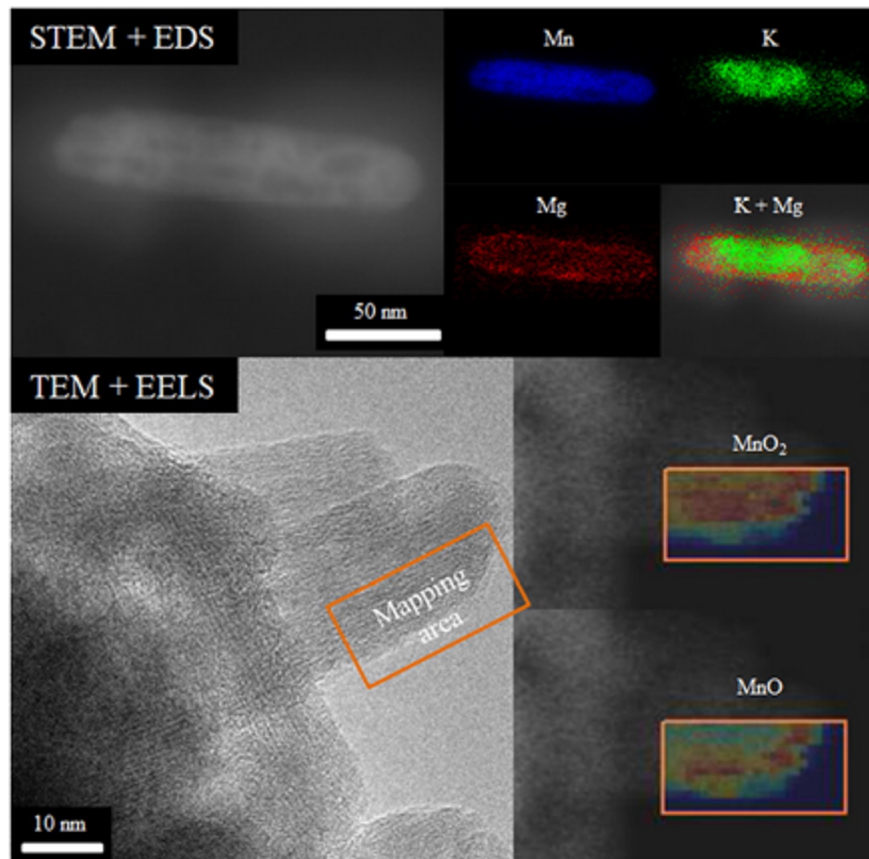
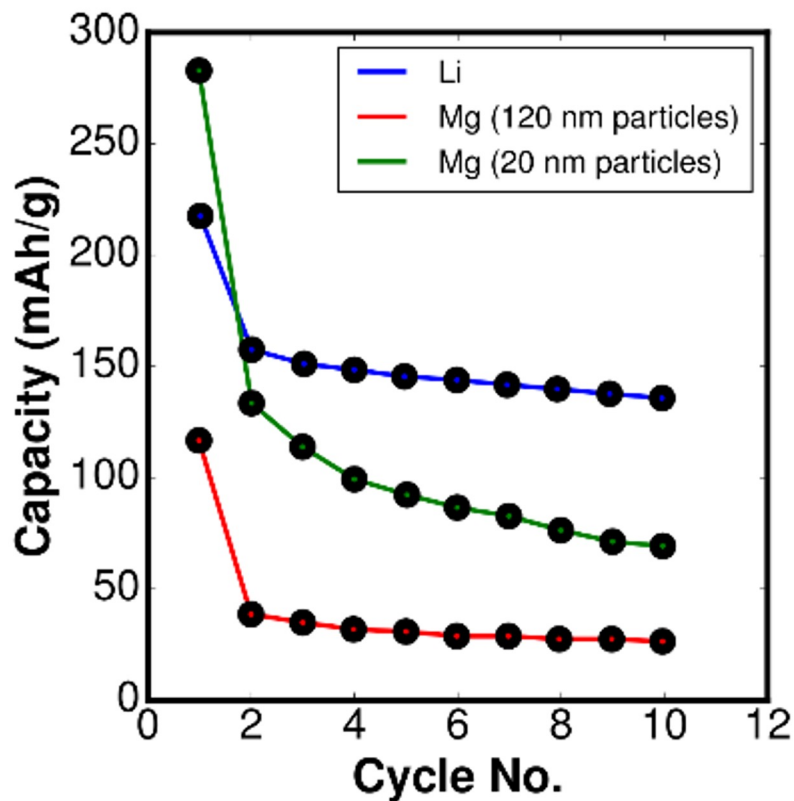
232nd ECS Meeting, National Harbor, MD



The Multivalent cathode design challenge



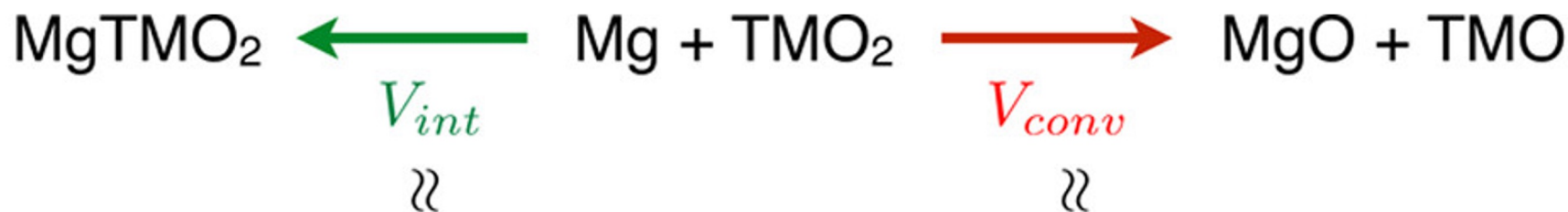
Capacity loss during Mg battery discharge has been attributed to conversion reactions in the cathode



Conversion reactions could seriously limit performance of Multivalent cathodes!

1. M.M. Thackeray, *Prog. Solid St. Chem.* **25**, 71 (1997)
2. T.S. Arthur *et al.*, *ACS Appl. Mater. Interfaces* **6**, 7004 (2014)

Reaction between working ion and cathode host can yield intercalation or conversion



$$-\frac{E_{\text{MgTMO}_2} - E_{\text{TMO}_2} - E_{\text{Mg}}}{2F} < -\frac{E_{\text{MgO}} + E_{\text{TMO}} - E_{\text{TMO}_2} - E_{\text{Mg}}}{2F}$$

Conversion products are *typically*

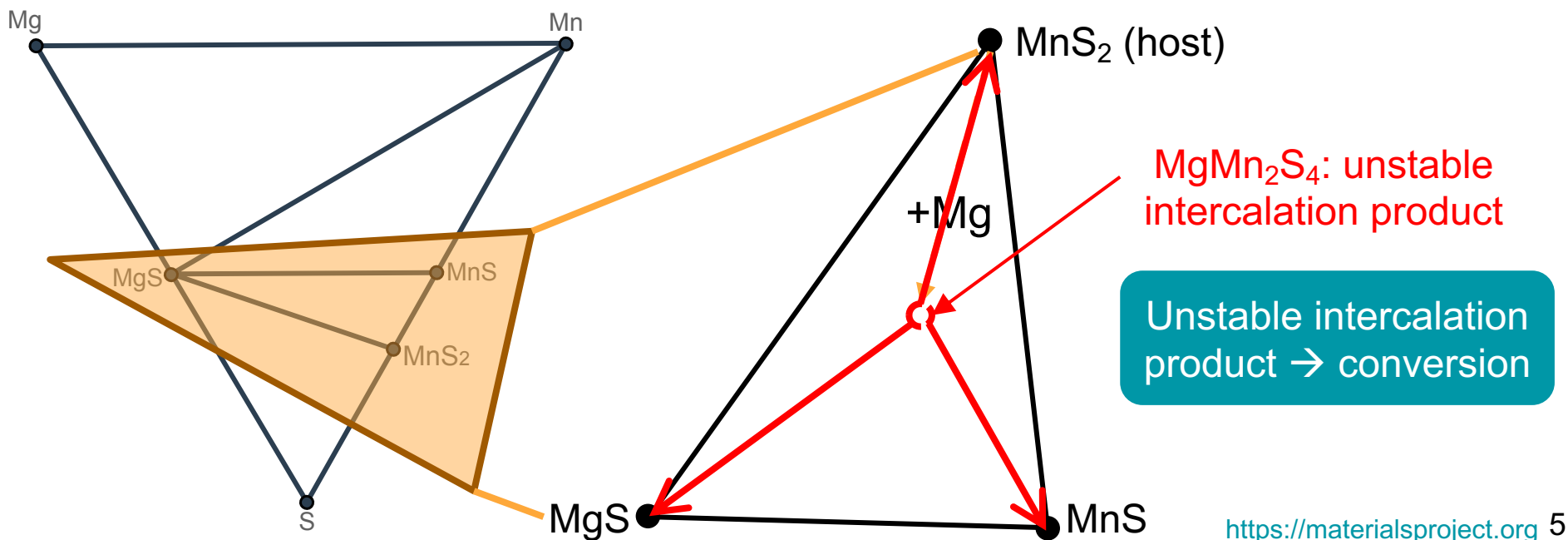
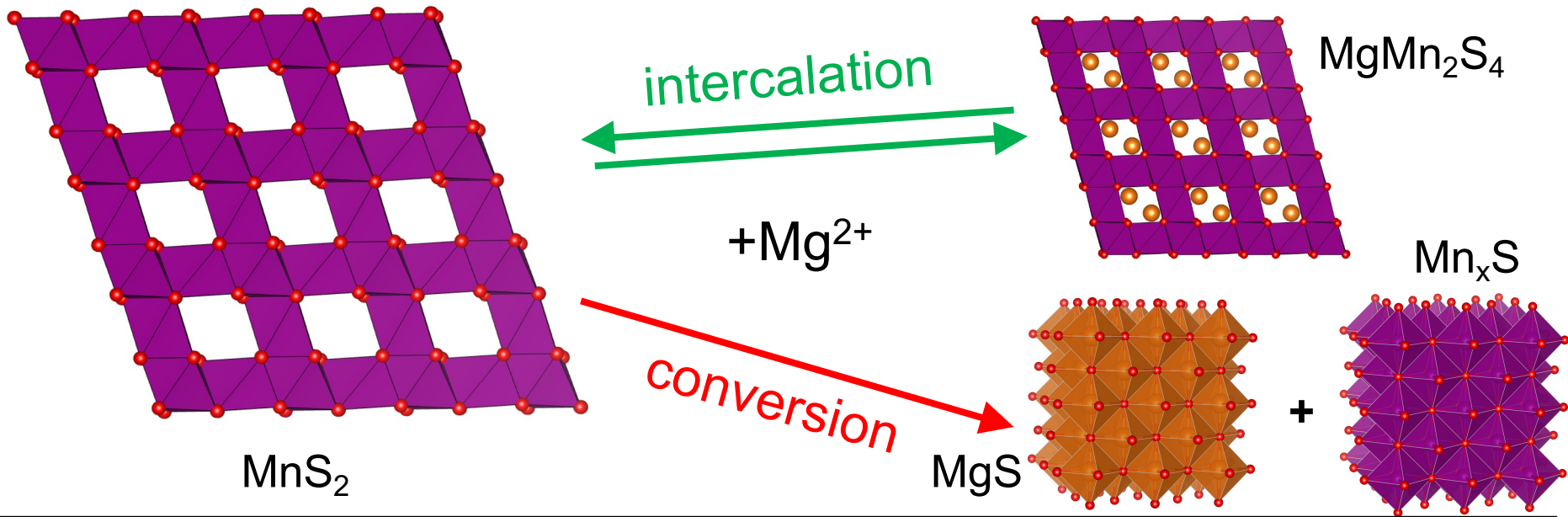
- **Reduced** transition metal oxide forms (ex. $\text{MnO}_2 \rightarrow \text{MnO}$)
- The **intercalant oxide** is one of the products (ex. MgO)
- Typically **irreversible** (ex. Mg can't be removed easily from MgO)



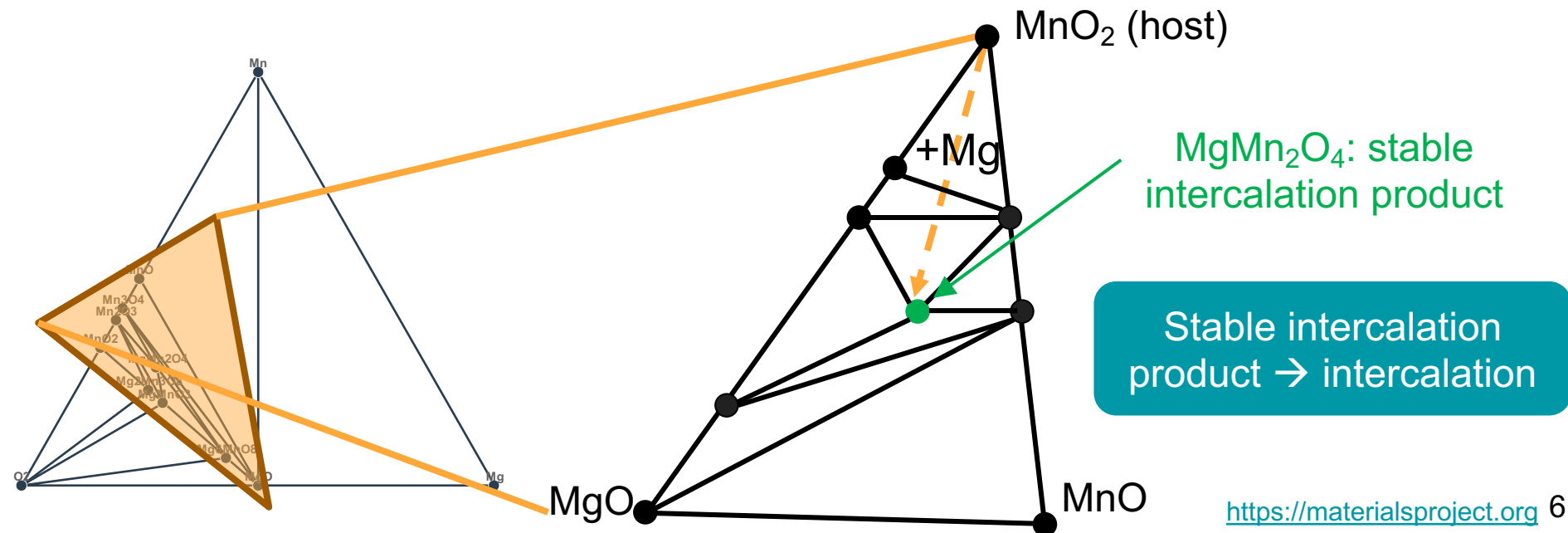
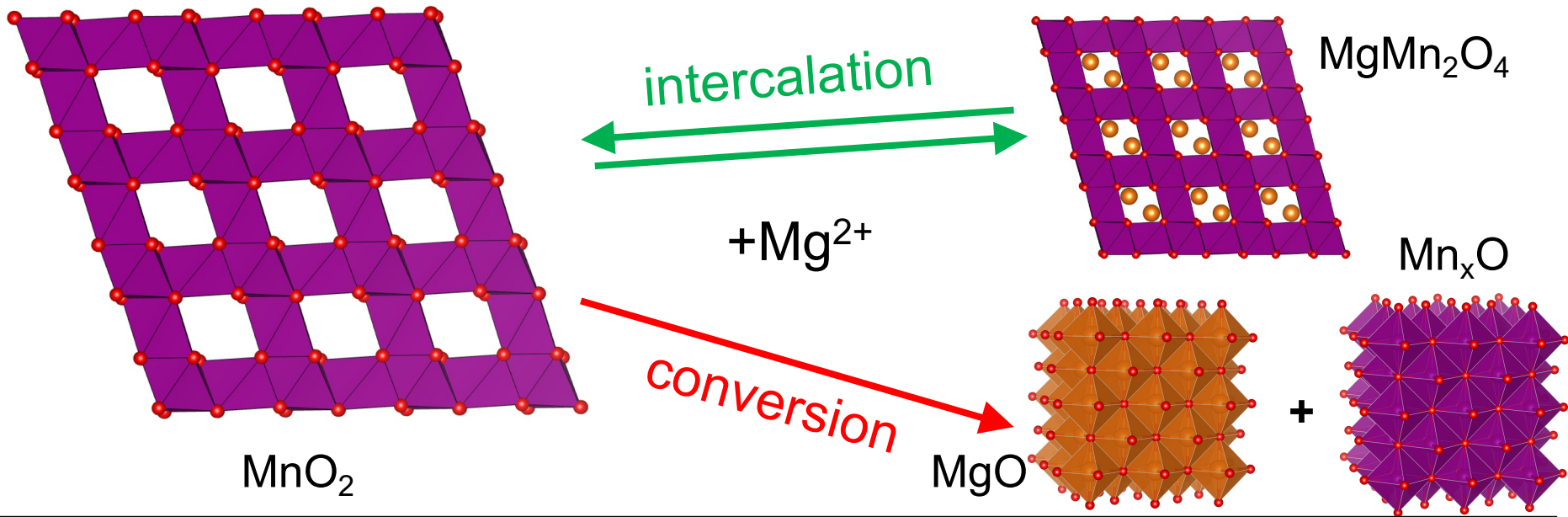
We study the discharge (reduction) reaction → **higher voltage** process drives reaction

Can we screen cathodes that favor intercalation over conversion?

Conversion on a phase diagram: Mg-Mn-S

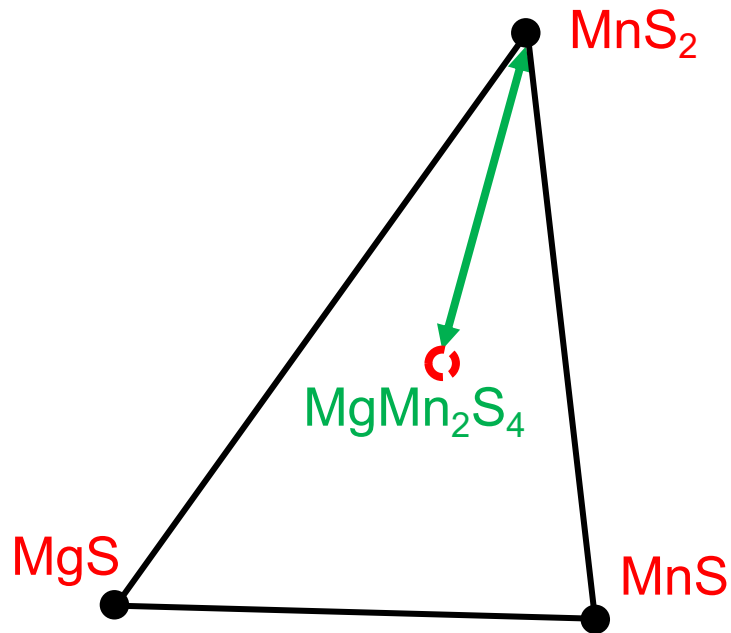


Intercalation on a phase diagram: Mg-Mn-O



But most operating battery materials are metastable!

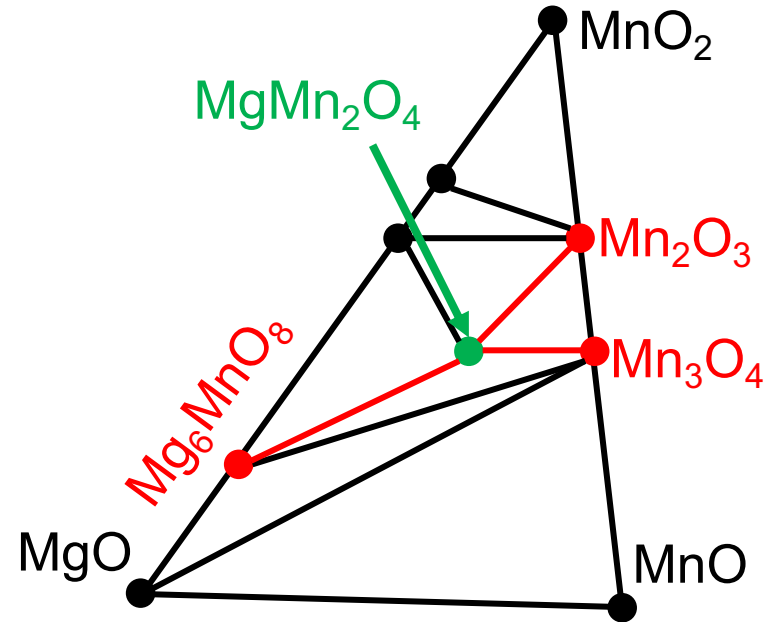
Define a hypothetical **intercalation** voltage in converting systems



$$V_{int}^{hypo} = - \frac{E_{\text{MgMn}_2\text{S}_4} - (2E_{\text{MnS}_2}) - E_{\text{Mg}}}{2F}$$

$$V_{conv} = - \frac{E_{\text{MgS}} + E_{\text{MnS}} - E_{\text{MnS}_2} - E_{\text{Mg}}}{2F}$$

Define a hypothetical **conversion** voltage in intercalating systems



$$V_{conv}^{hypo} = - \frac{E_{\text{Mg}_6\text{MnO}_8} + 4E_{\text{Mn}_2\text{O}_3} + E_{\text{Mn}_3\text{O}_4} - (12E_{\text{MnO}_2}) - 6E_{\text{Mg}}}{12F}$$

$$V_{int} = - \frac{E_{\text{MgMn}_2\text{O}_4} - (2E_{\text{MnO}_2}) - E_{\text{Mg}}}{2F}$$

Magnitude of difference between voltages will indicate tendency to convert/intercalate

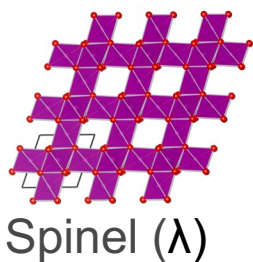
Polymorph selection can determine whether intercalation or conversion occurs

Kim *et al.*, *Adv. Mater.* 27, 3377 (2015)

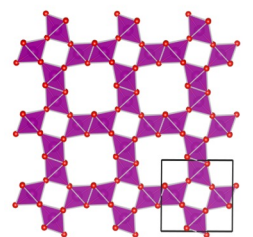
MnO₂ polymorphs

Product of Mg + MnO₂

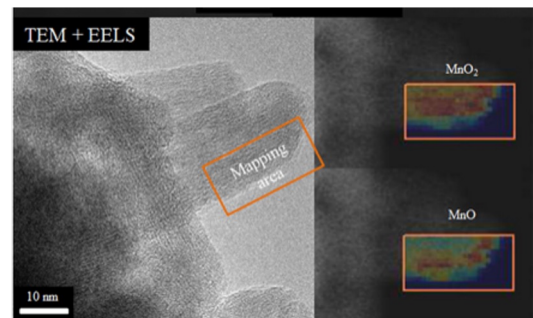
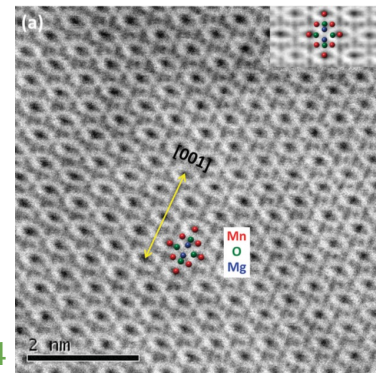
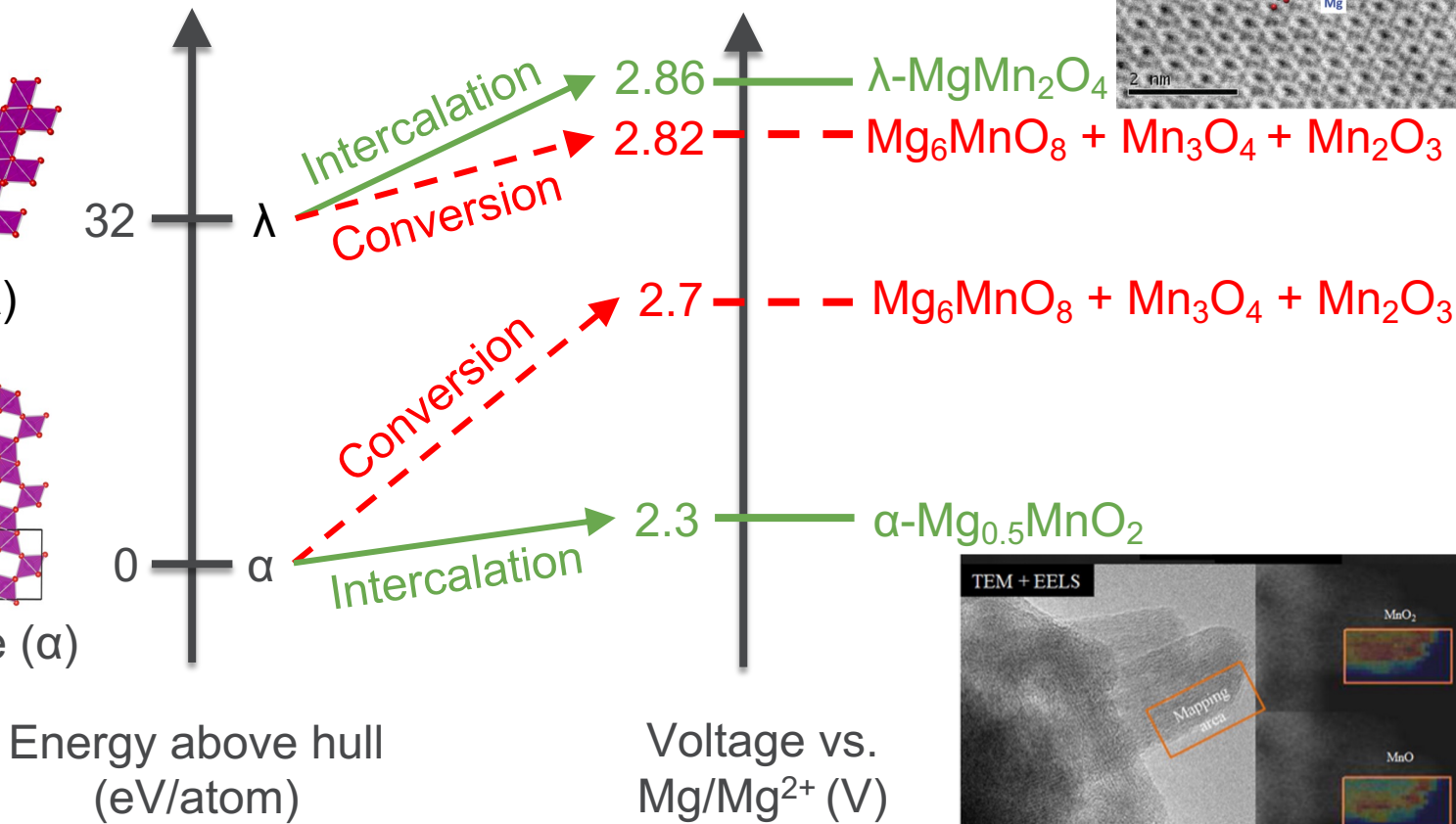
Stable
"discharged"
polymorph



Mg +

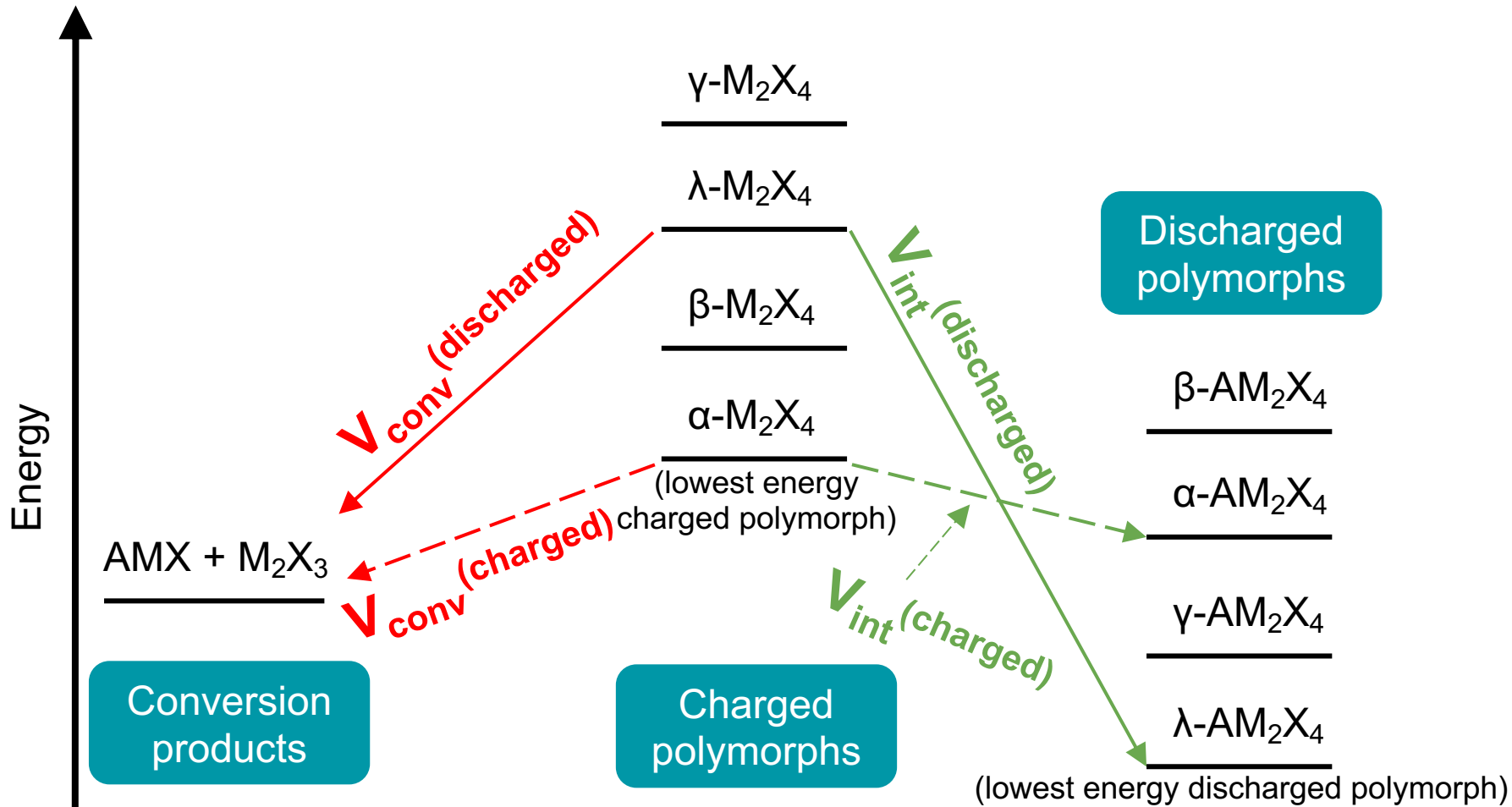


Stable "charged"
polymorph



T.S. Arthur *et al.*, *ACS Appl. Mater. Interfaces* 6, 7004 (2014)

A general thermodynamic framework for assessing conversion vs. intercalation



Conversion

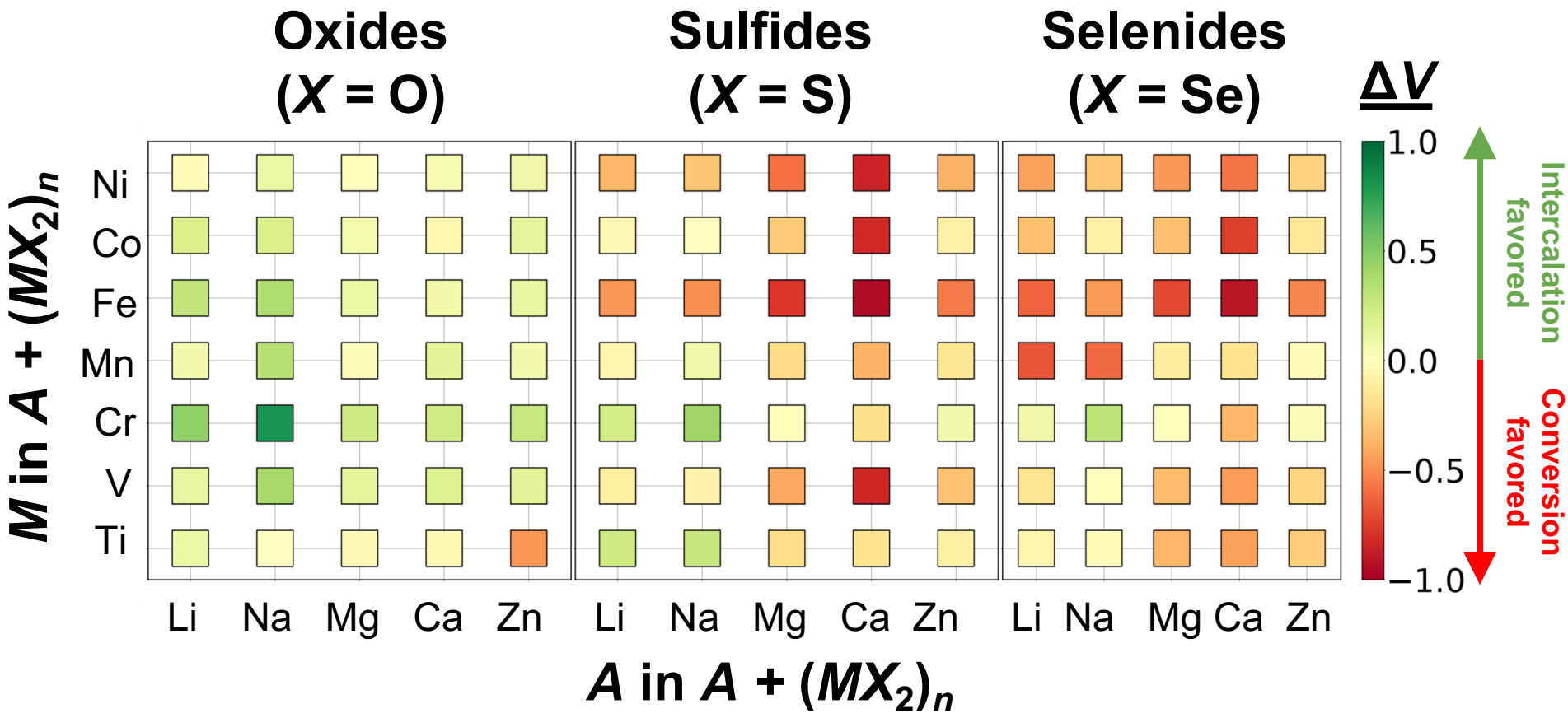


Intercalation



1e⁻ reduction from lowest energy **discharged** polymorph ($V_{\text{int/conv}}^{\text{(discharged)}}$)

"Discharged" polymorph: High voltage, Low Mobility



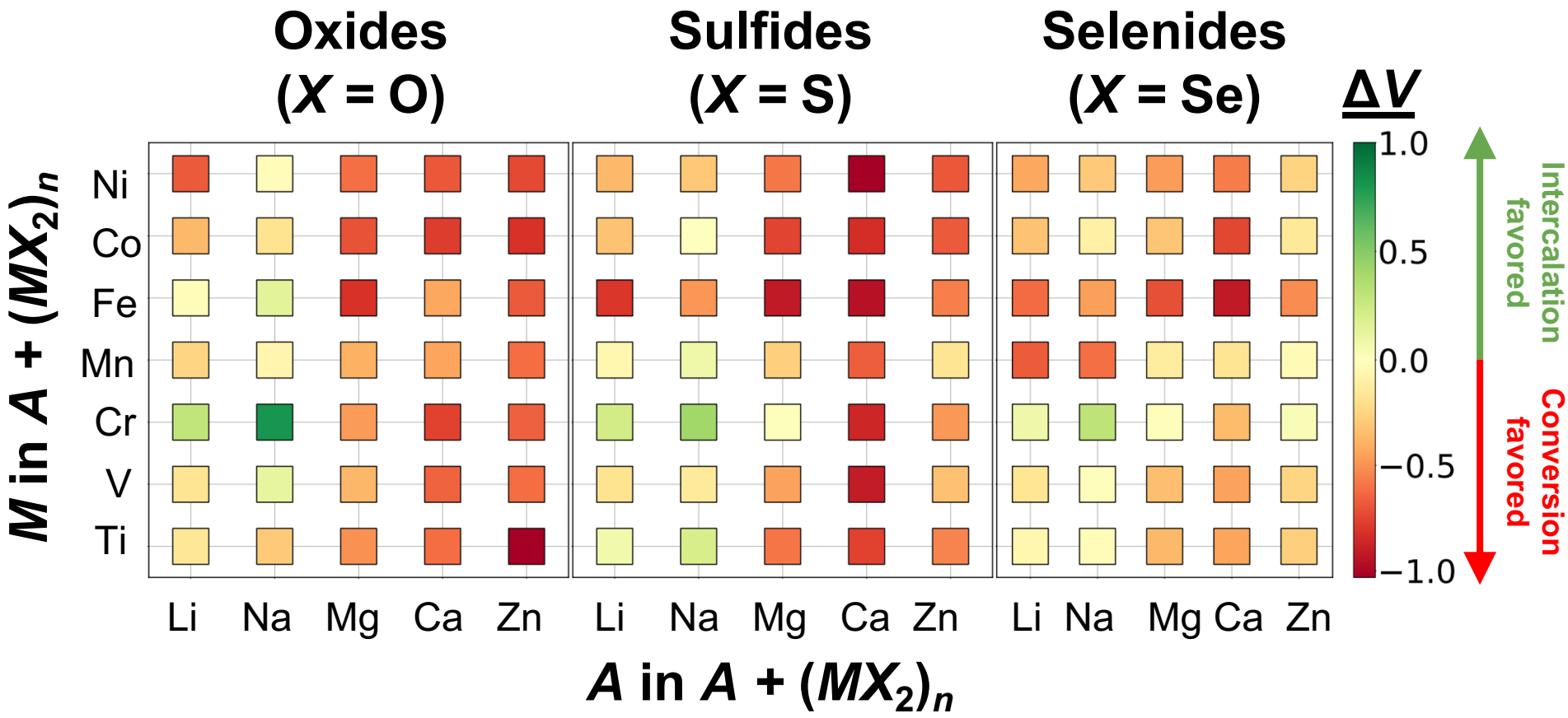
$$\Delta V \text{ (V)} = V_{\text{int}} - V_{\text{conv}}$$

Oxides tend to favor intercalation, while sulfides and selenides are more likely to convert.

1e⁻ reduction in lowest energy **charged** polymorph

($V_{\text{int/conv}}^{\text{(charged)}}$)

"Charged" polymorph: Low voltage, High Mobility

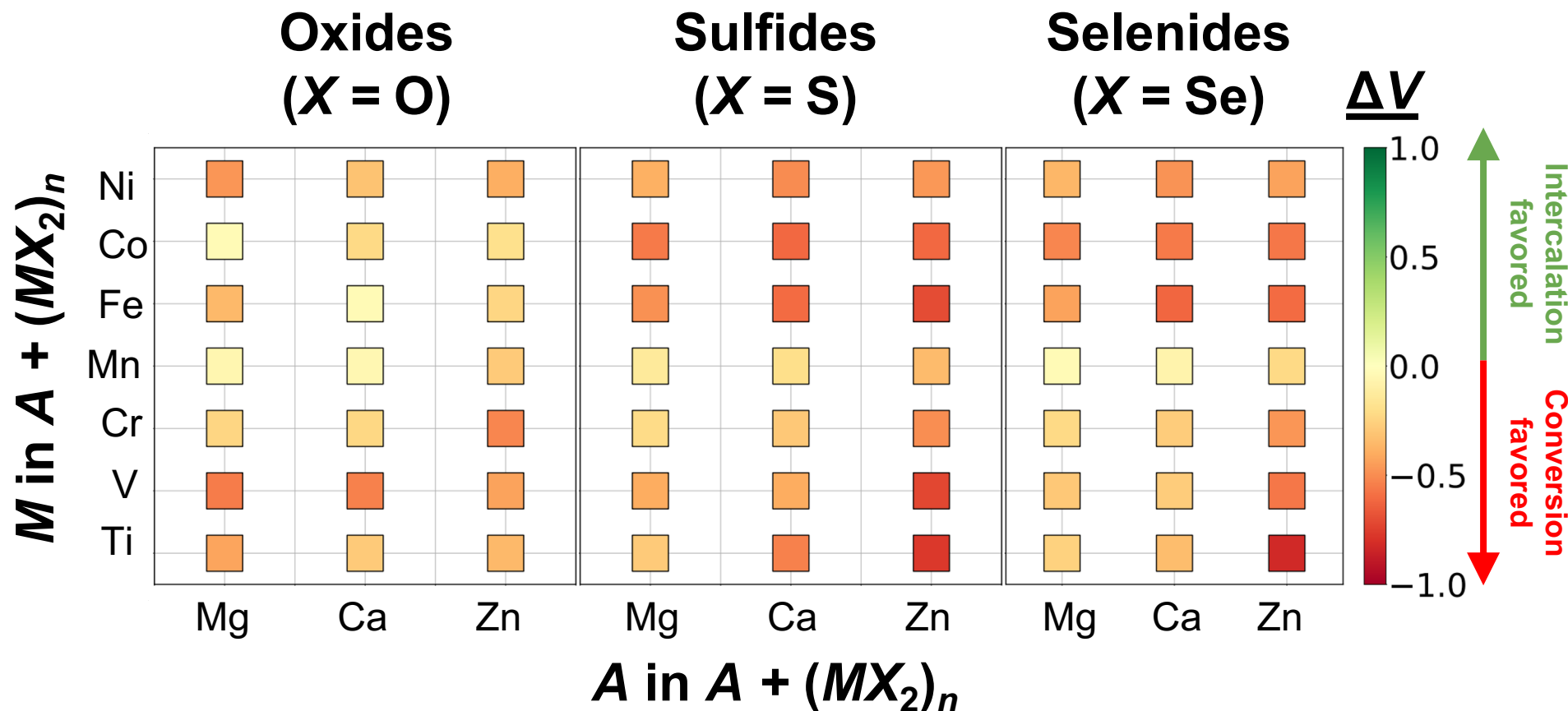


$\Delta V (V) = V_{\text{int}} - V_{\text{conv}}$

Starting with lowest energy charged polymorph tends to yield conversion, even for oxides.

2e⁻ intercalation into MX₂ compounds always favors conversion

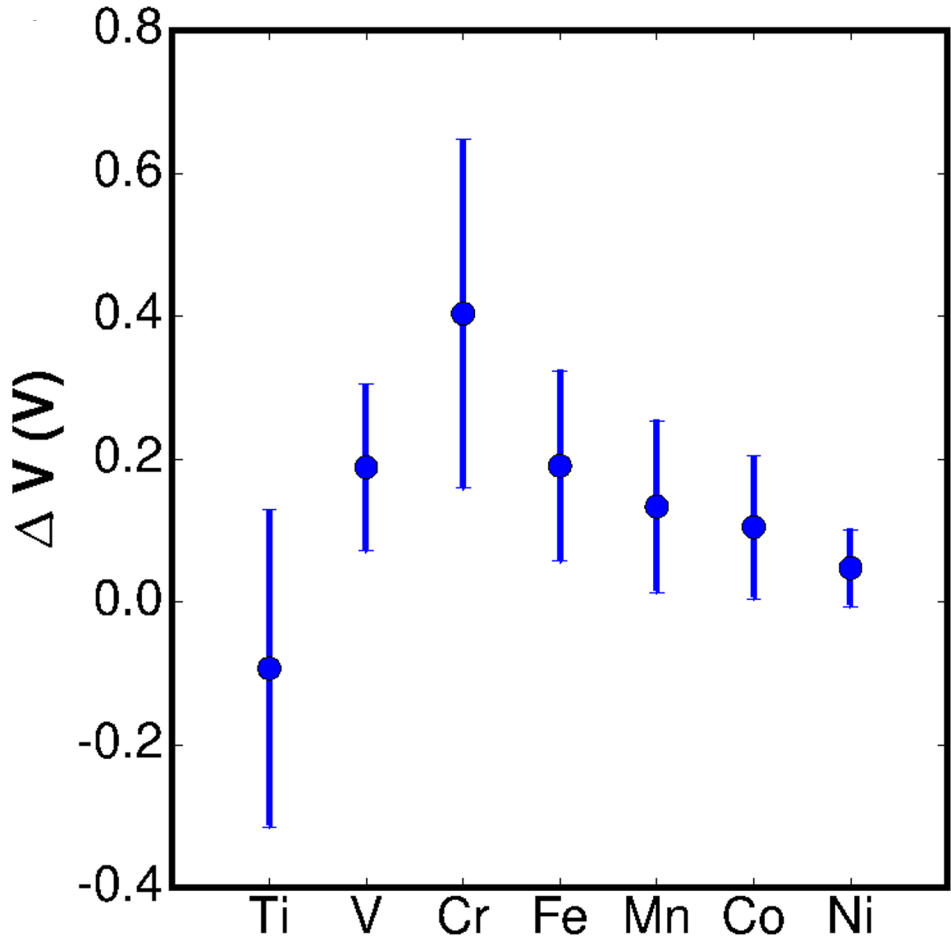
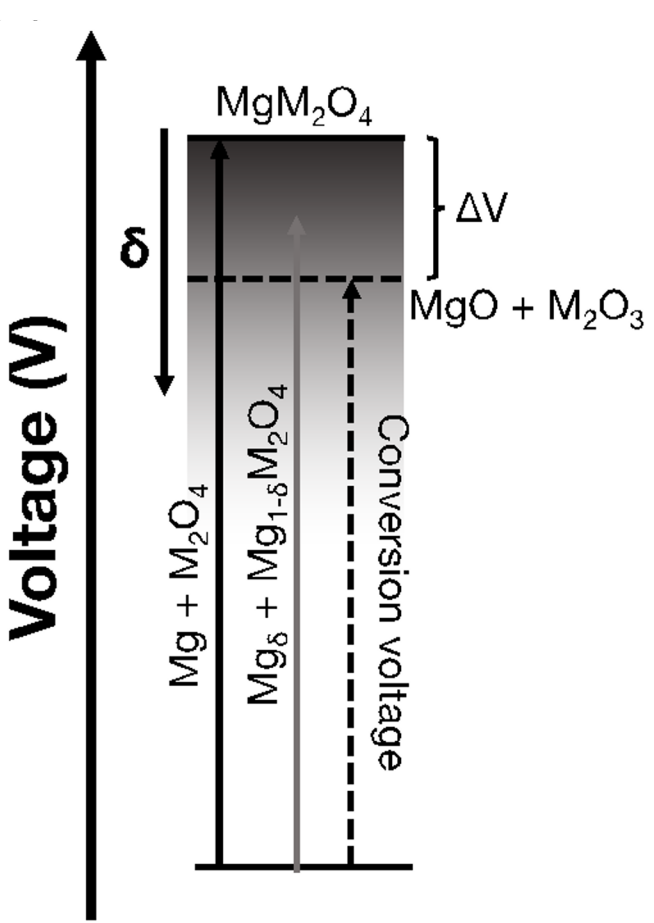
$$\Delta V \text{ (V)} = V_{\text{int}} - V_{\text{conv}}$$



"Conventional" cathode chemistries are not viable for multi-electron redox

The magnitude of $V_{\text{int}} - V_{\text{conv}}$ determines resistance to conversion

Cr-oxides strongly resistant to conversion



ΔV (V) = $V_{\text{int}}^{\text{discharged}} - V_{\text{conv}}^{\text{discharged}}$

Conclusions

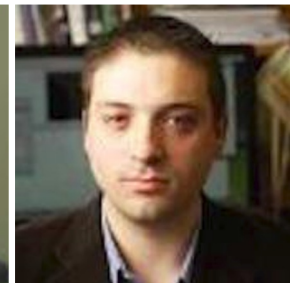
- Implications for battery design:
 - Synthesize in discharged state → Resistance to conversion, high voltage, low mobility
 - Synthesize in charged state → High mobility, more likely to convert, higher mobility
- Cr oxides resist conversion most strongly among the transition metal oxides
- $2e^-$ reduction of cathode requires us to explore stoichiometries with higher transition metal oxidation states (e.g. V_2O_5 and MoO_3)

- D.C. Hannah, G.S. Gautam, P. Canepa and G. Ceder, “*On the balance of intercalation and conversion reactions in battery cathodes*”, in preparation
- P. Canepa, G.S. Gautam, D.C. Hannah *et al.*, **Chem. Rev.** 117, 4287, 2017



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