JCESR JOINT CENTER FOR ENERGY STORAGE RESEARCH

Exploration of the Multivalent Chemical Space for Higher Energy Density Batteries

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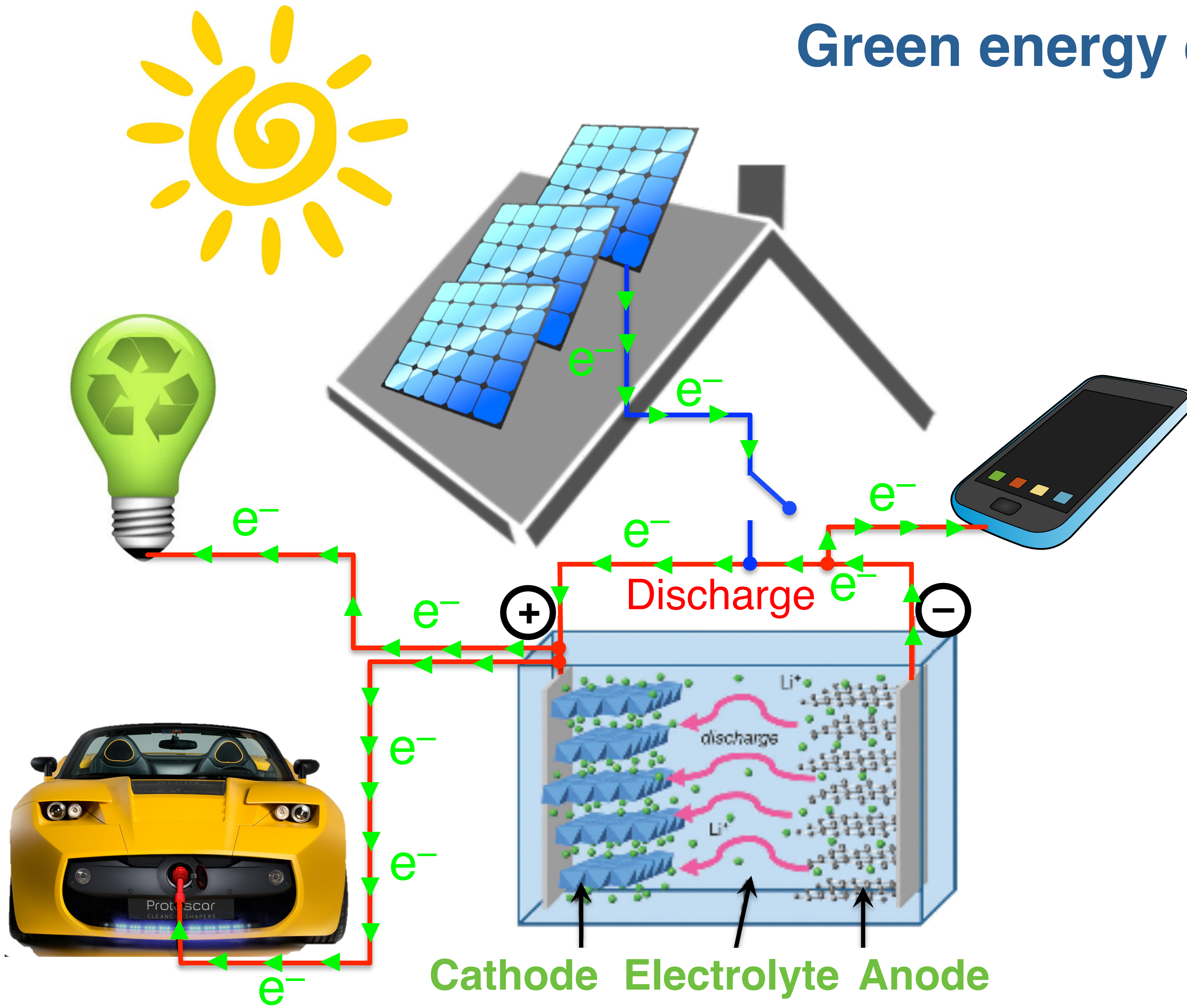
Batteries to store energy

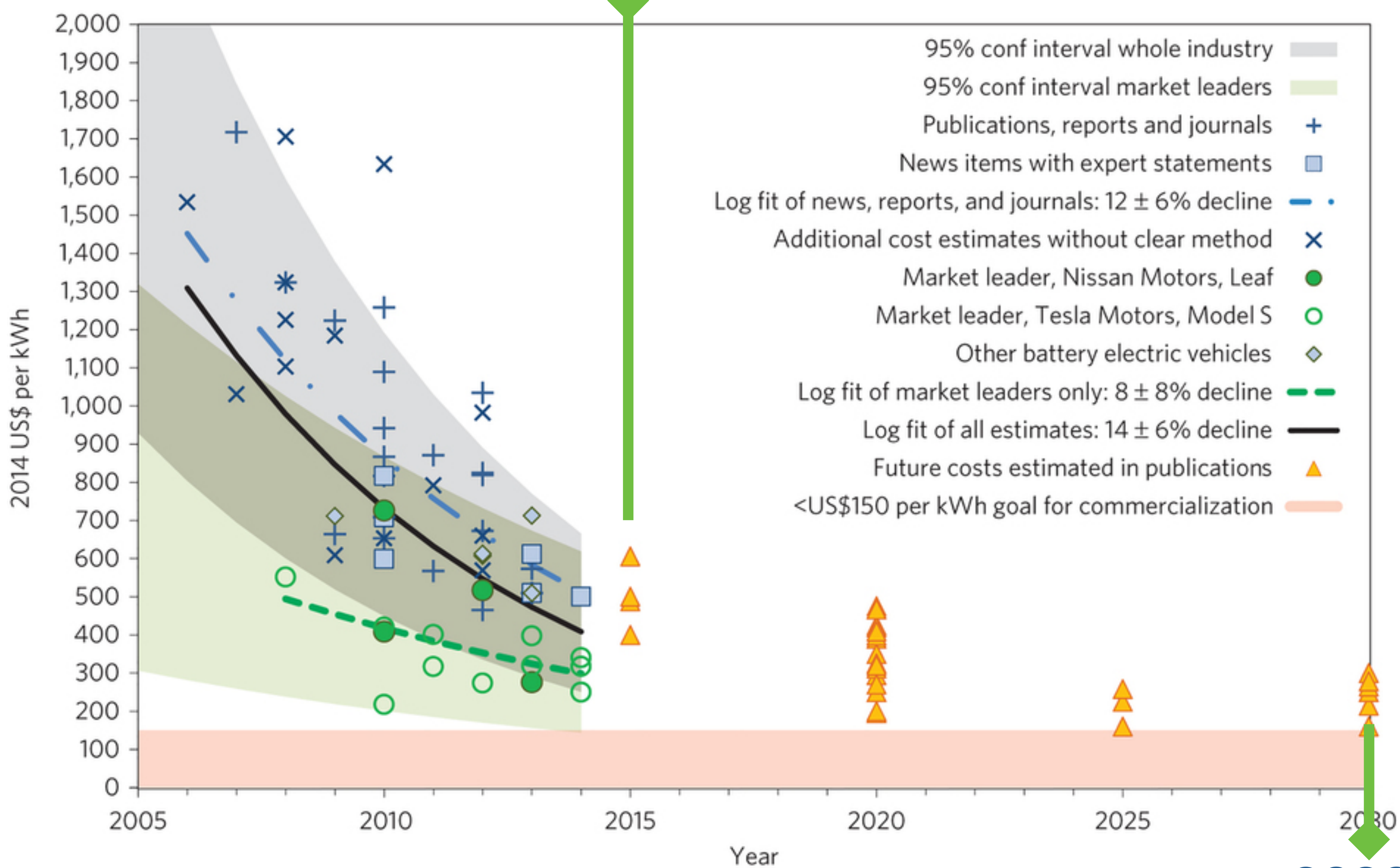
Green energy economy



Li-ion batteries: one way to store and re-distribute energy.

Falling cost of intercalation batteries

2015: 400–600 $/kWh

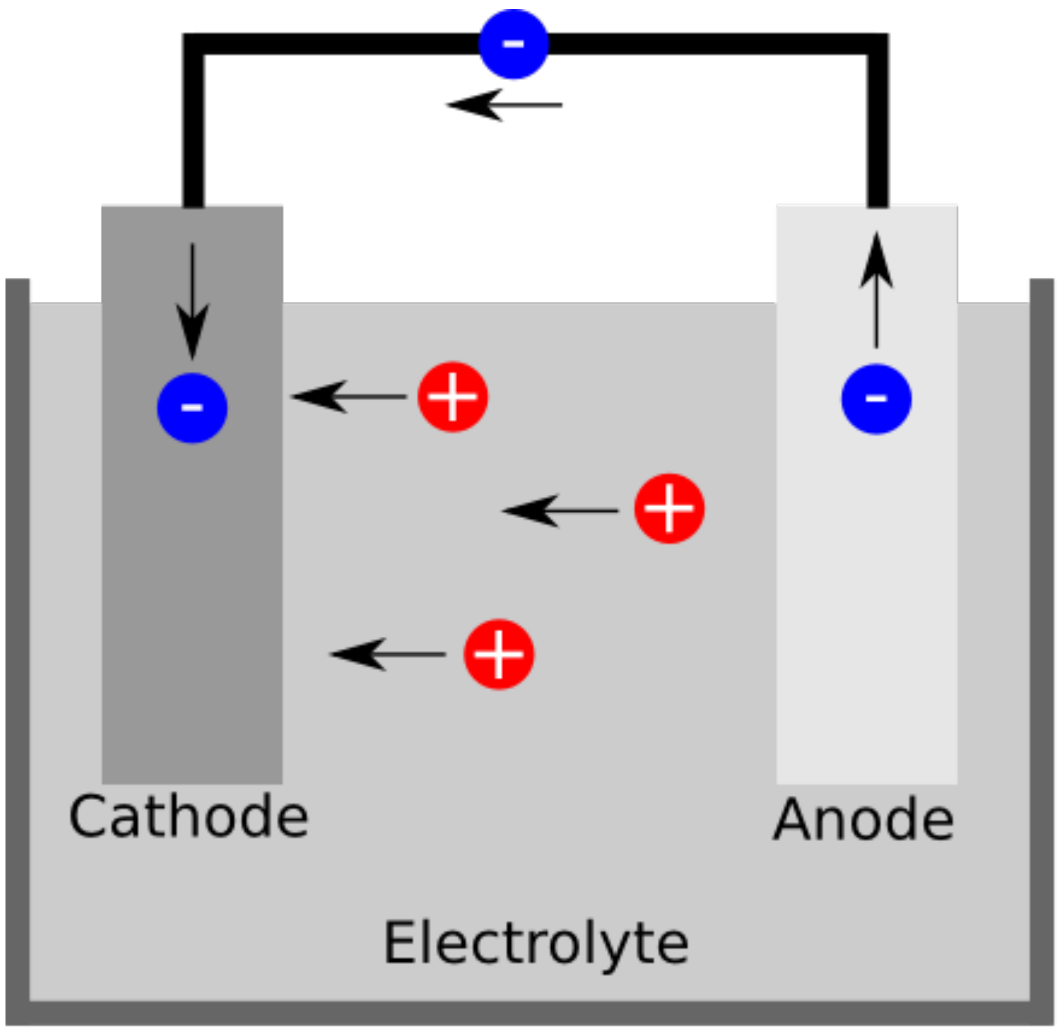


2030: 200–400 $/kWh

B. Nykvist and M. Nilsson, Nature Climate Change **5**, 329–332 (2015).

How does an intercalation battery work?

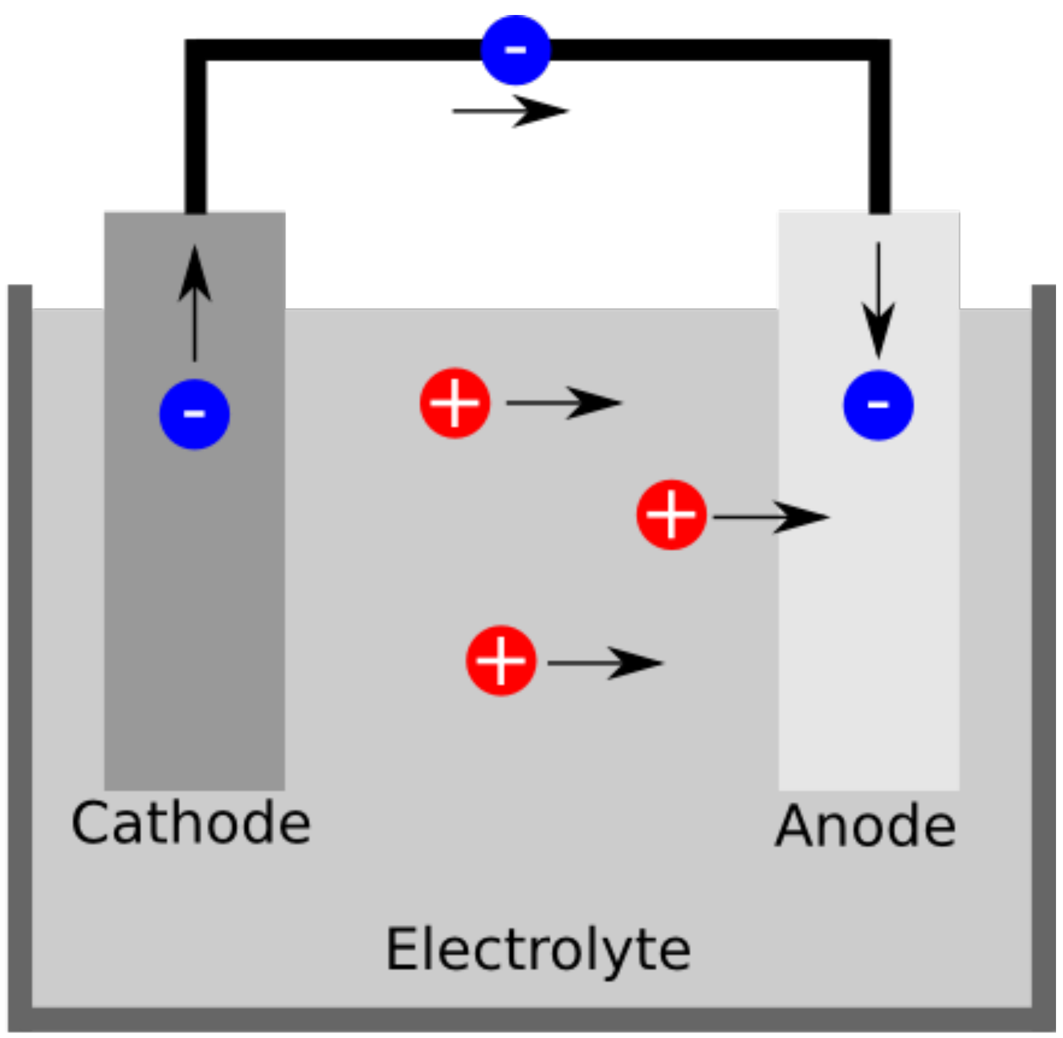
Discharge



The chemical potential difference of Li between the two electrodes triggers Li motion from the anode to the cathode.

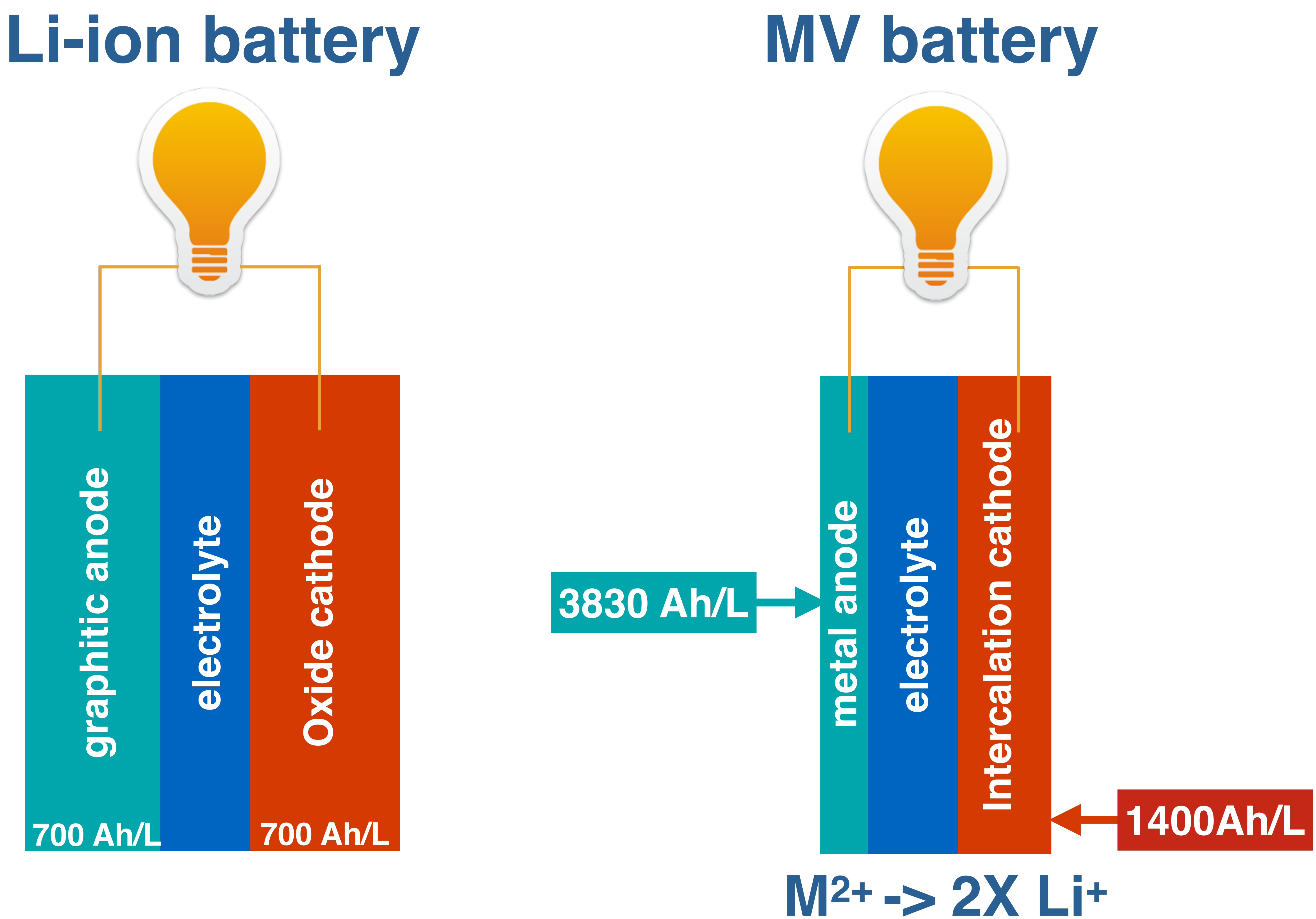
How does an intercalation battery work?

Charge



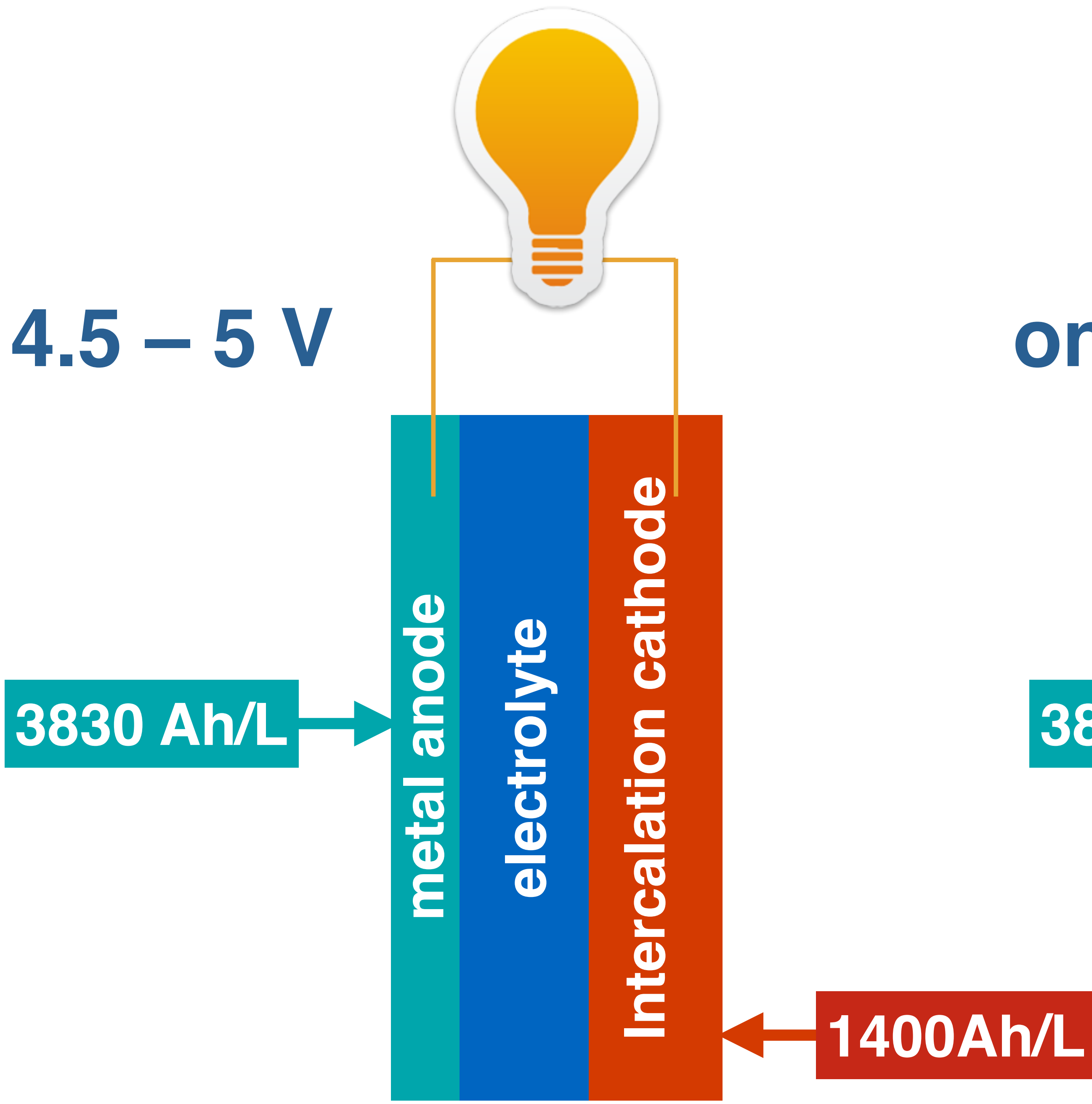
An external electrical potentials reverts the spontaneous process recharging the battery.

Targeting higher energy densities: multivalent batteries

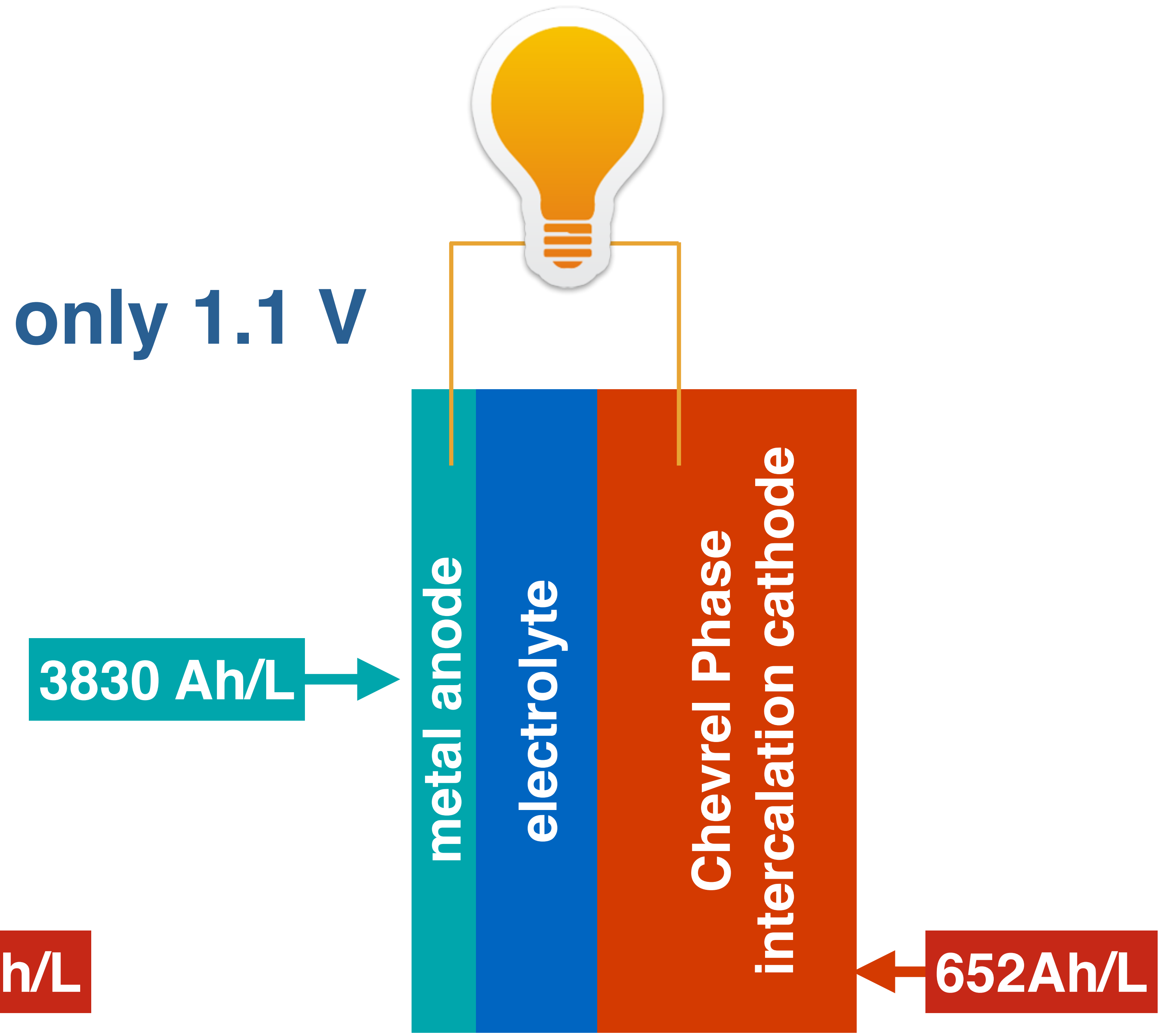


Targeting higher energy densities: multivalent batteries

Dream MV battery



State-of-the-art Mg-ion



Chevrel-phase $Mg_2Mo_6S_8$

D. Aurbach et al., Nature **407**, 724-727 (2000).

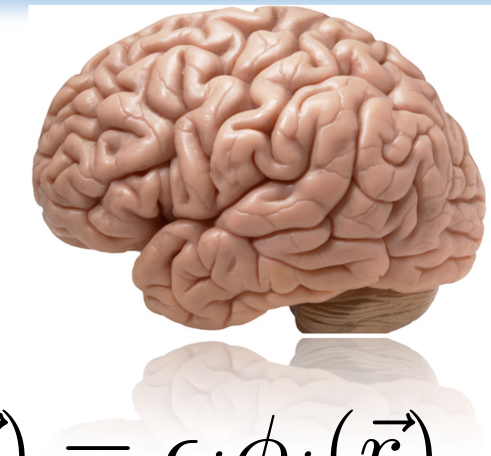
Challenges of multivalent batteries

1. Poor lattice mobility of MV ions eg., Mg^{2+}, Zn^{2+}, Ca^{2+} and Al^{3+} compared to Li^{+} and Na^{+}.
2. Lack of high voltage intercalation cathodes.
3. Lack of electrolytes withstanding high voltage cathode electrodes.

How do we search the chemical space? Strategy

python mongoDB

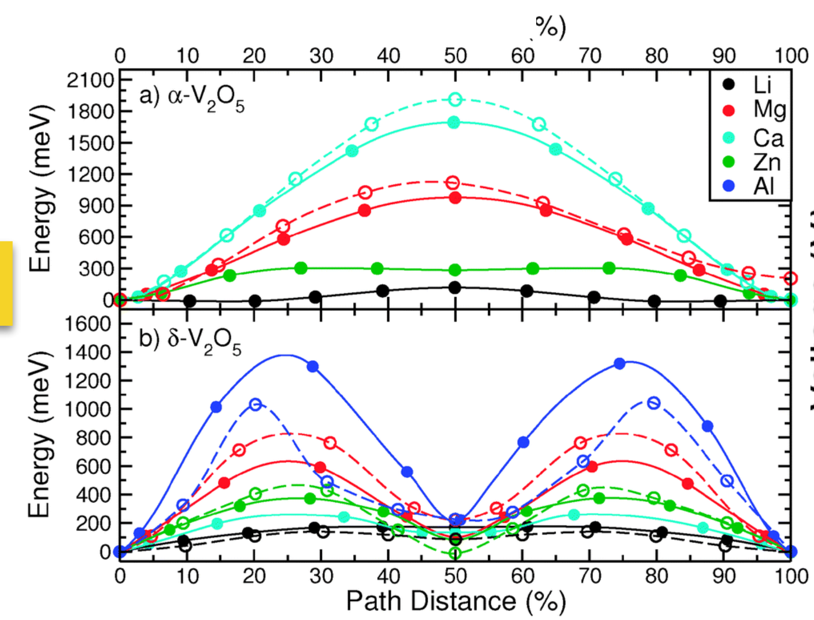
DFT and DFT + *U* + NEB



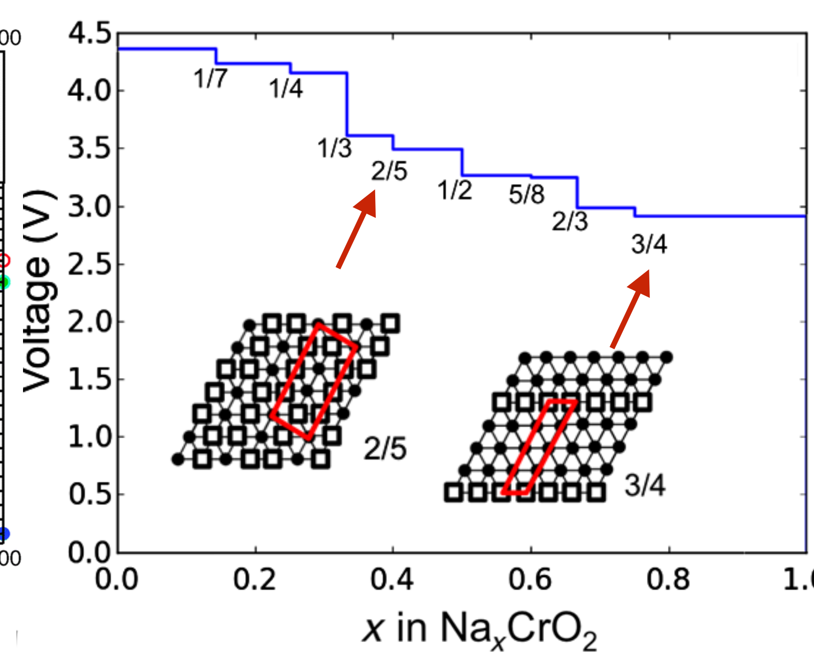
$$\left[-\frac{\hbar^2}{2m}\nabla^2 + V_s(\vec{r})\right]\phi_i(\vec{r}) = \epsilon_i\phi_i(\vec{r})$$

http://www.materialsproject.org

Ion Diffusivities



Voltage Curves



A. J. Toumar et al., Phys. Rev. B **4**, 064002 (2015).
G.S. Gautam, P. Canepa et al., Chem. Commun. **51**, 13619-13622 (2015).

Quantify Ionic Mobility in materials

To ensure high mobility, we need a small MV migration barrier *E_m* in the host structure.

3 Å ~ 3x10^{-8} cm^2

$$D \approx v \cdot a^2 exp\left(- \frac{E_m}{k_b T} \right)$$

10^{12} s^{-1}

0.0256 eV

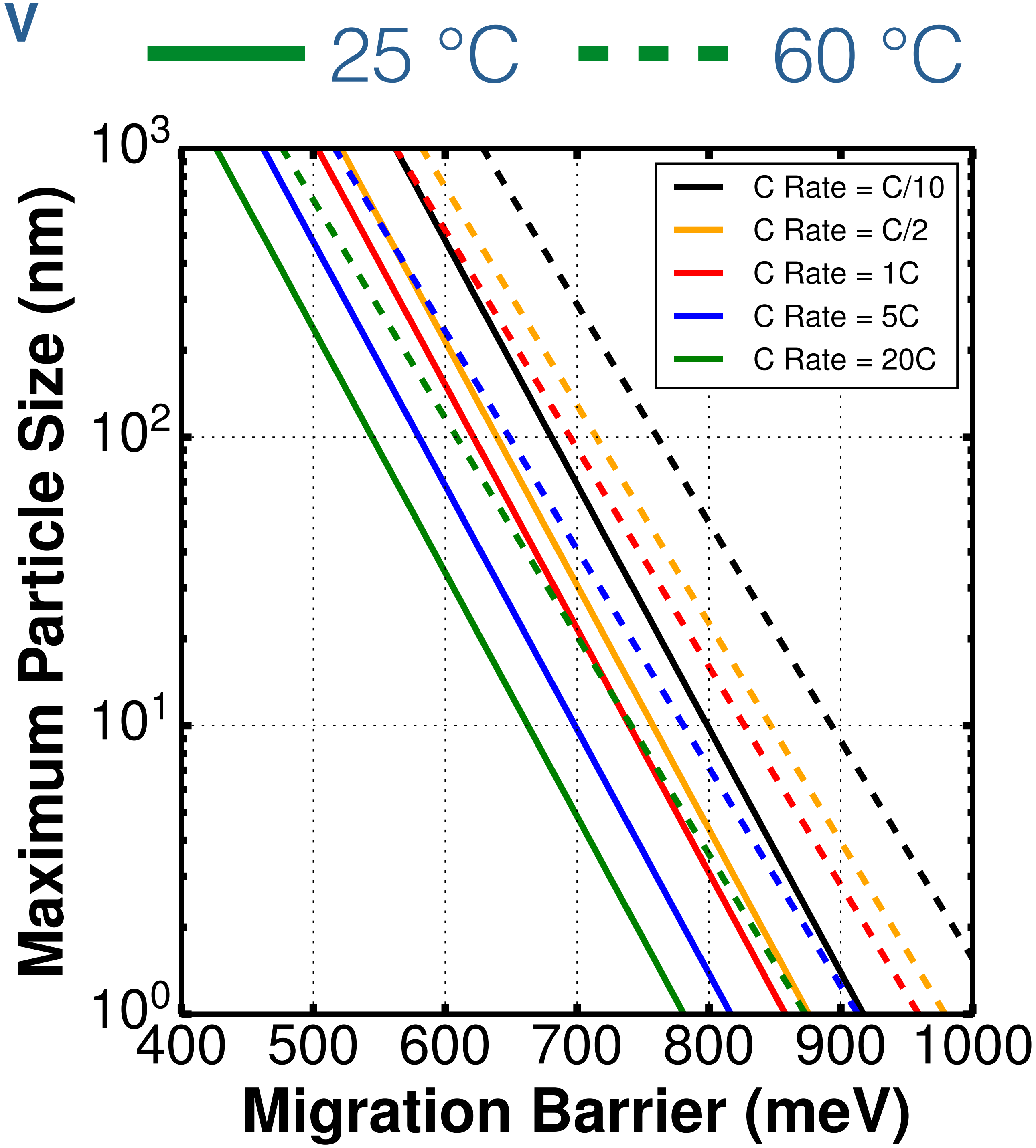
Determining the *E_m*

particle size (1 μm = 10^{-4} cm)^2

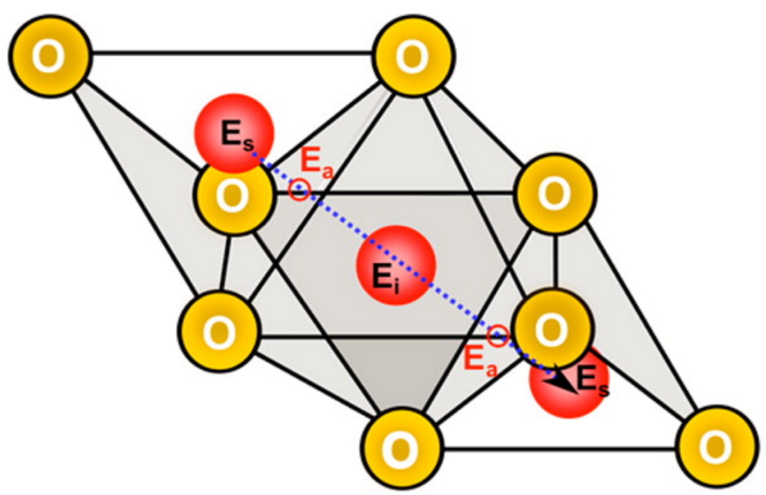
$$D \approx \frac{x^2}{t} \sim 10^{-12} cm^2/s$$

7200s (C/2)

525 meV

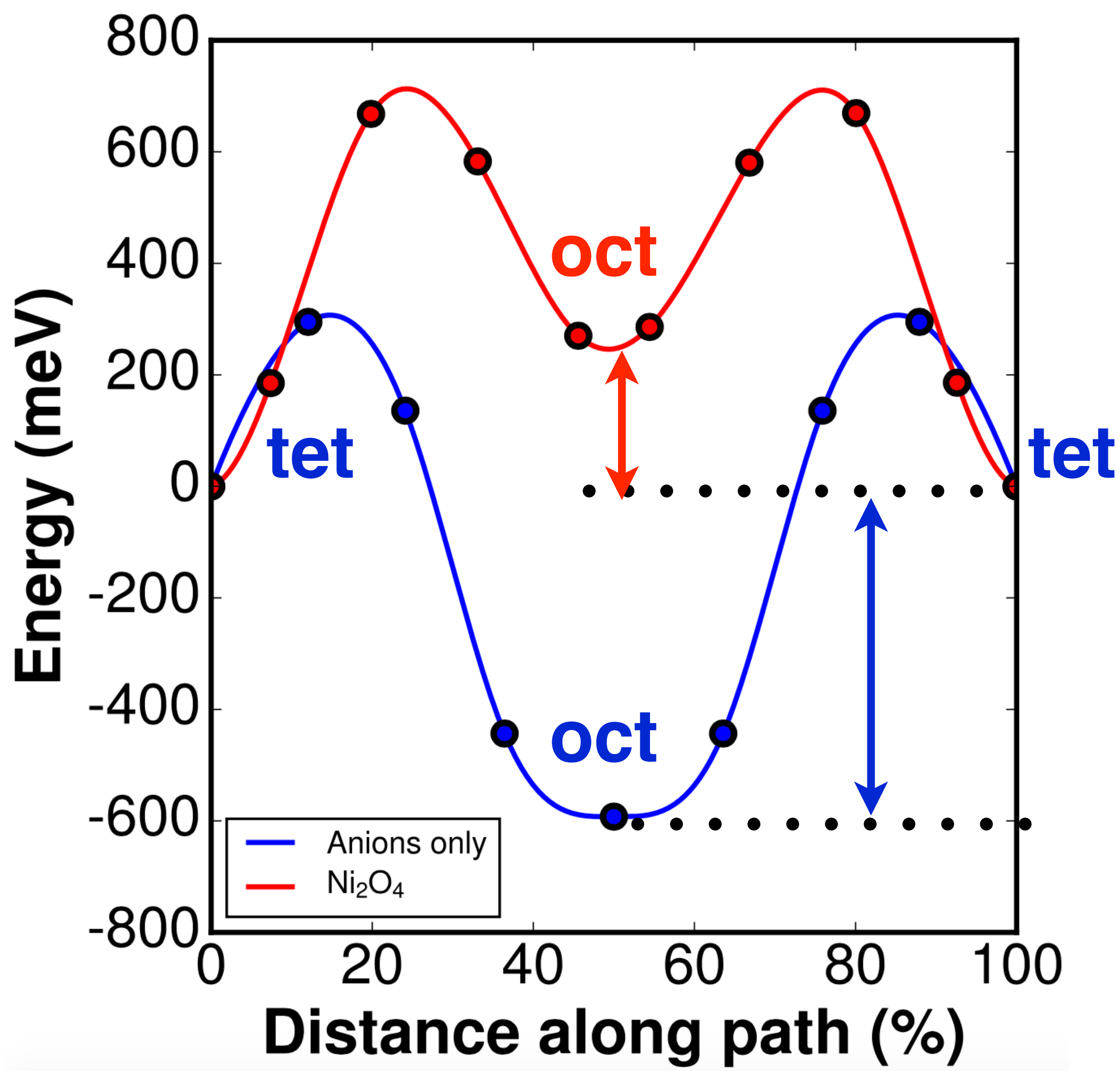


For energy dense cathodes, Can we intercalate MV in close-pack structures?



Can we intercalate Mg in a spinel structure? For example $MgTM_2X_4$

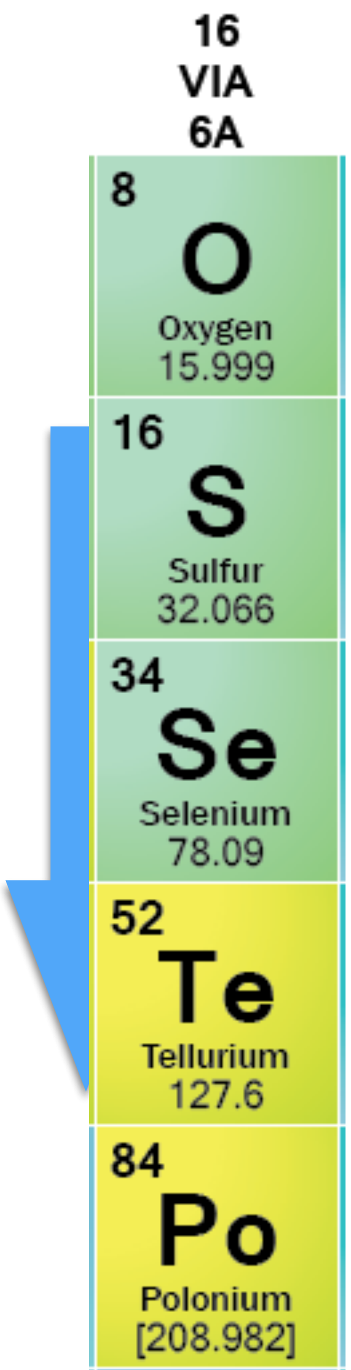
1. Transition metals (TM) reduces the site energy difference helping MV mobility!



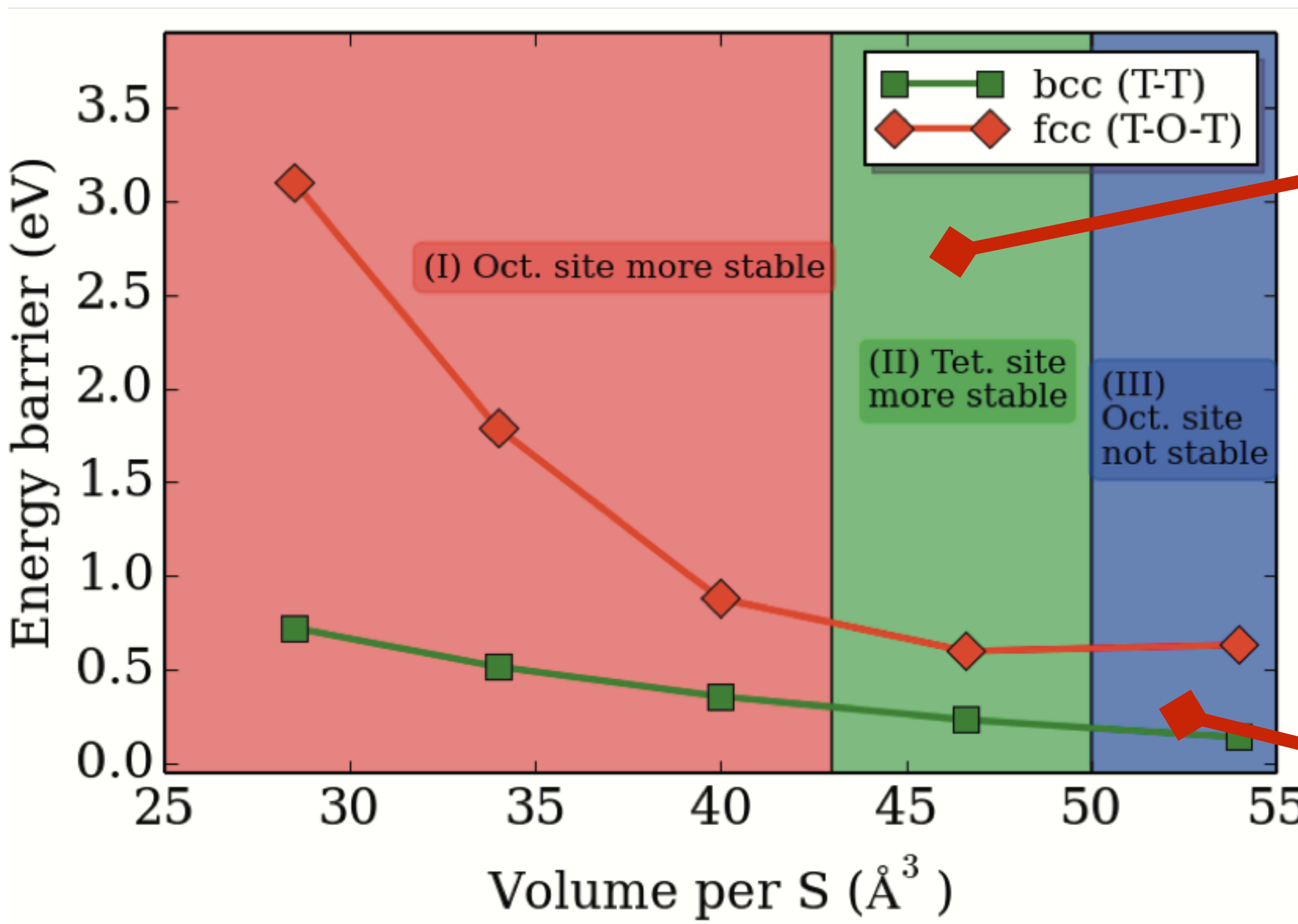
2. Careful Choice of TM can flatten the migration landscape further.

Z. Rong, R. Malik, P. Canepa, G.S. Gautam et al., Chem. Mater. **27** (17), 6016–6021 (2015).
M. Liu, Z. Rong, R. Malik, P. Canepa et al., Energy Environ. Sci. **8** 964-974 (2015).

Increasing Volume per anion helps MV mobility!



Mg migration barriers in sulfur lattices

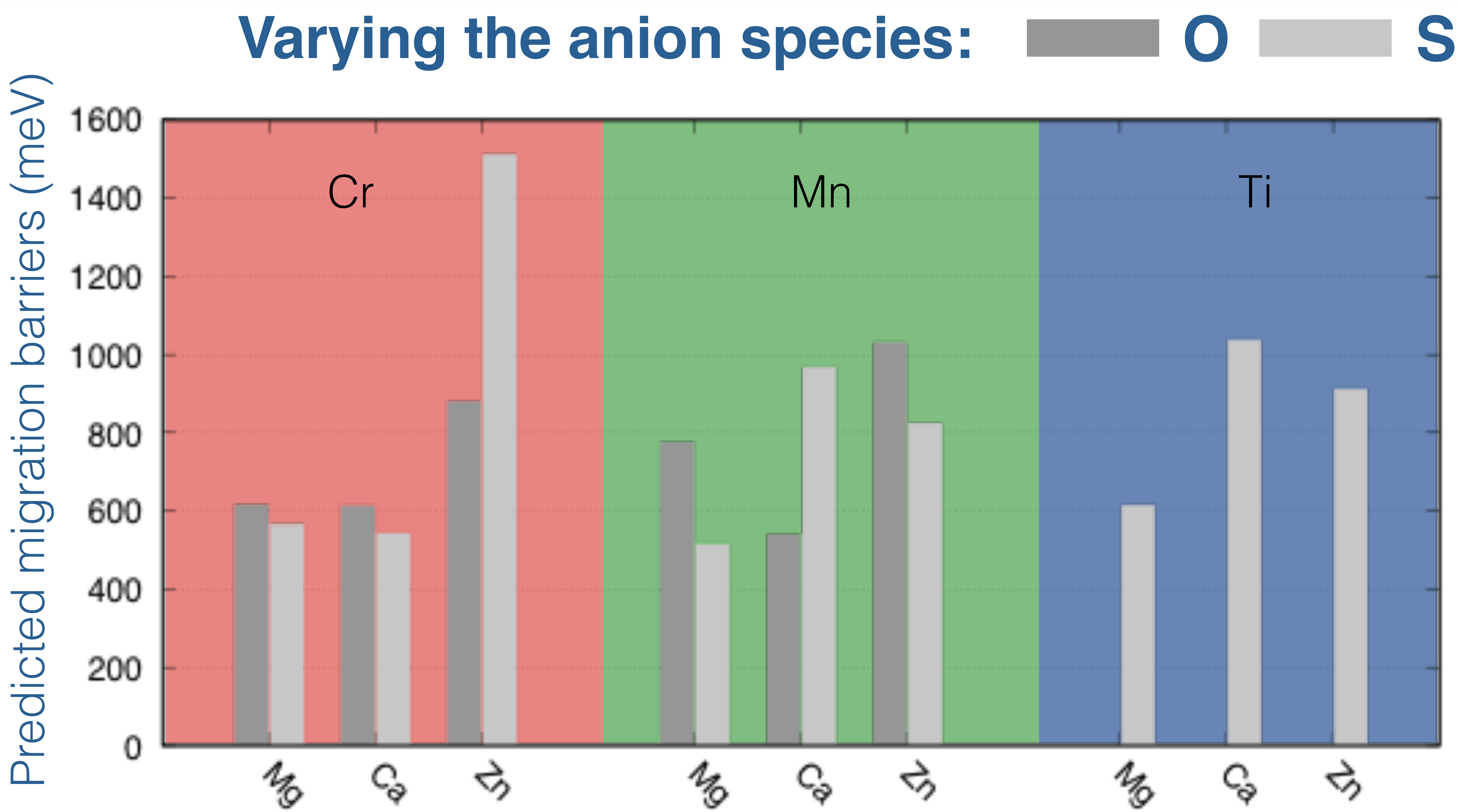


Materials with critical volume per anion

Large anions seem also promising

Y. Wang, et al., Nature Materials **14**, 3733–3742 (2015)

Sulfides as an alternative to Oxides

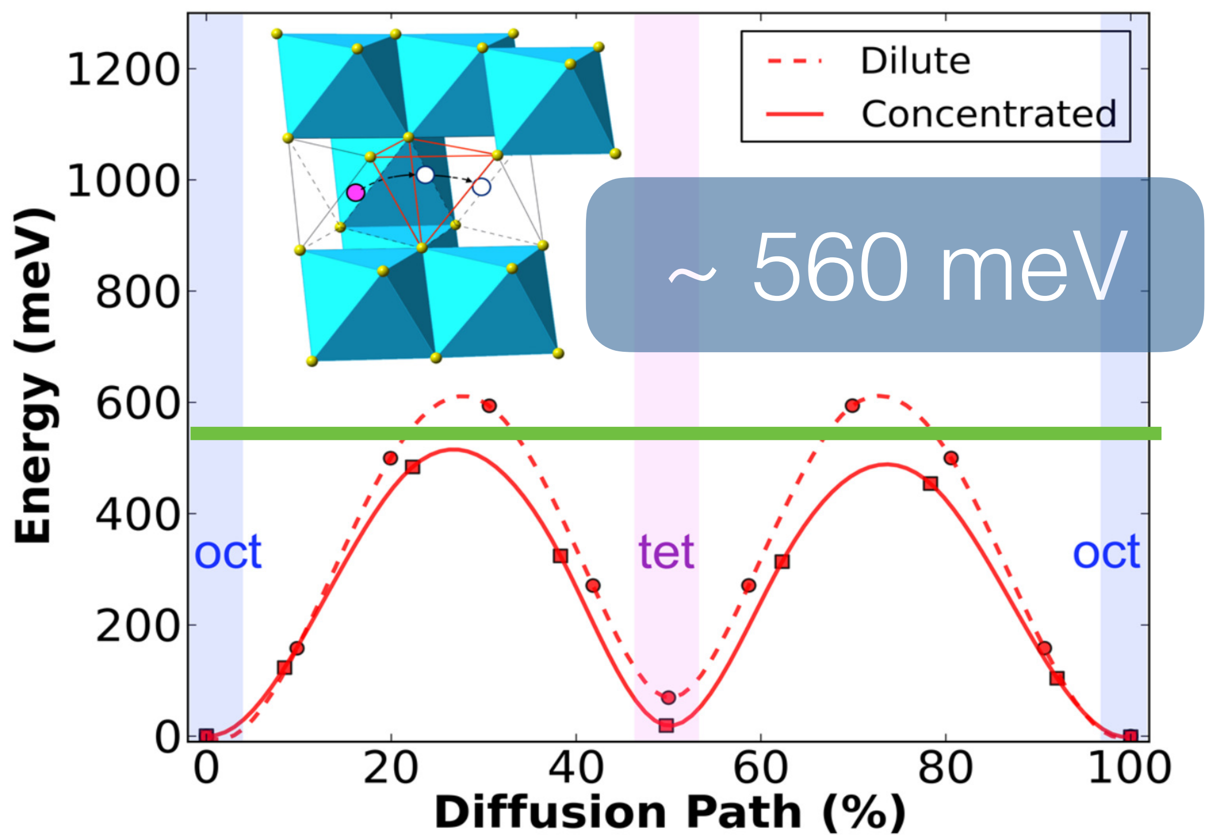


1. Sulfides are more covalent than oxides
2. Most sulfides show better MV than oxides

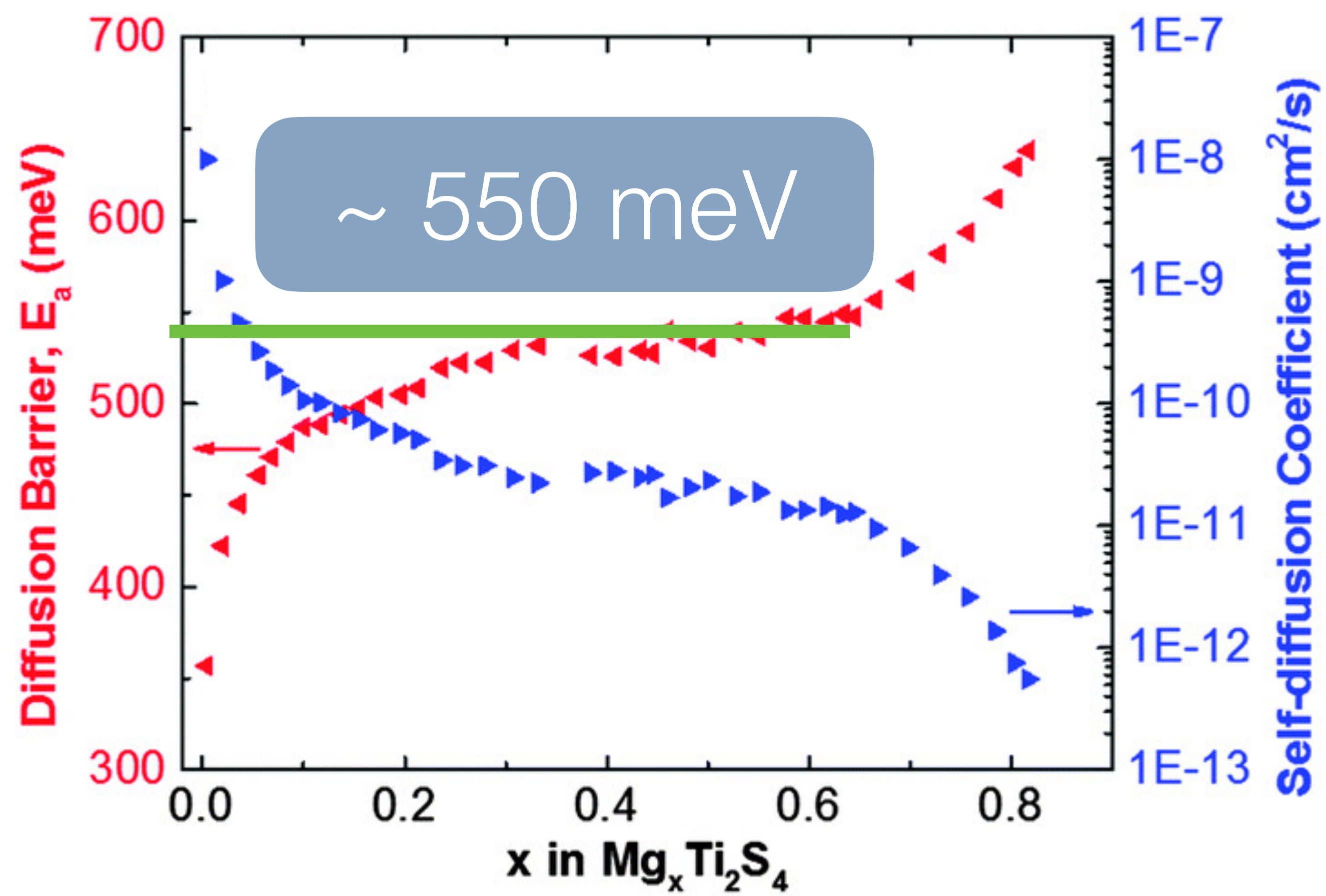
M. Liu, …, P. Canepa et al., Evaluation of sulfur spinel compounds for multivalent battery cathode applications, accepted in Energy Environ. Sci. (2016).

Sulfides at work Theory *vs.* Experiment

Theory – NEB



Experiment – GITT



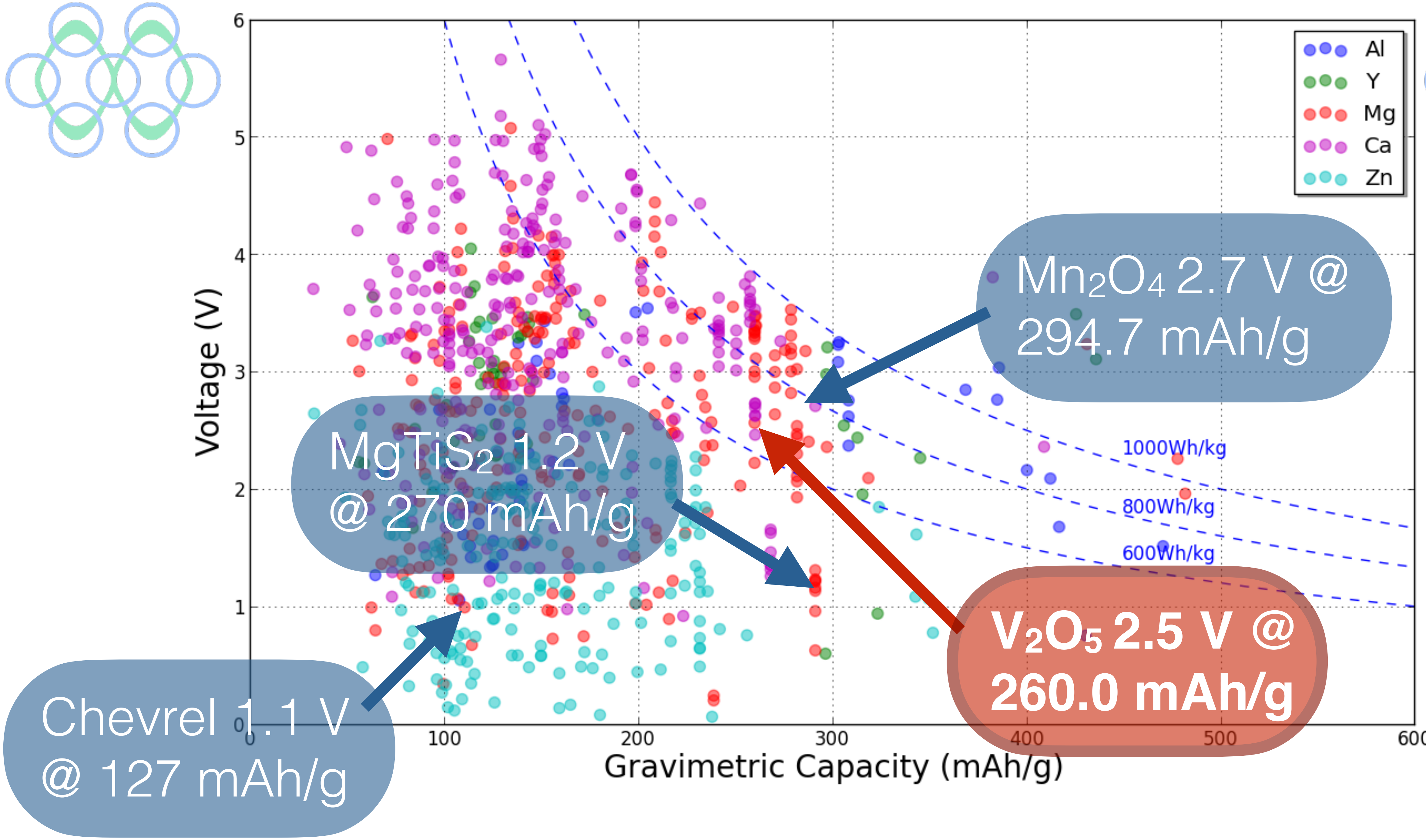
First-principles Mg migration barriers support the experimental data suggesting facile Mg diffusion in the close packed lattice of $MgTi_2S_4$. <u>Close packed frameworks can access higher energy densities that the Chevrel phase.</u>

X. Sun et al., Energy Environ. Sci. **9**, 2273-2277 (2016).

Sulfides do not meet the energy density requirements to compete with current Li-ion technology

High-throughput can help with MV Voltages

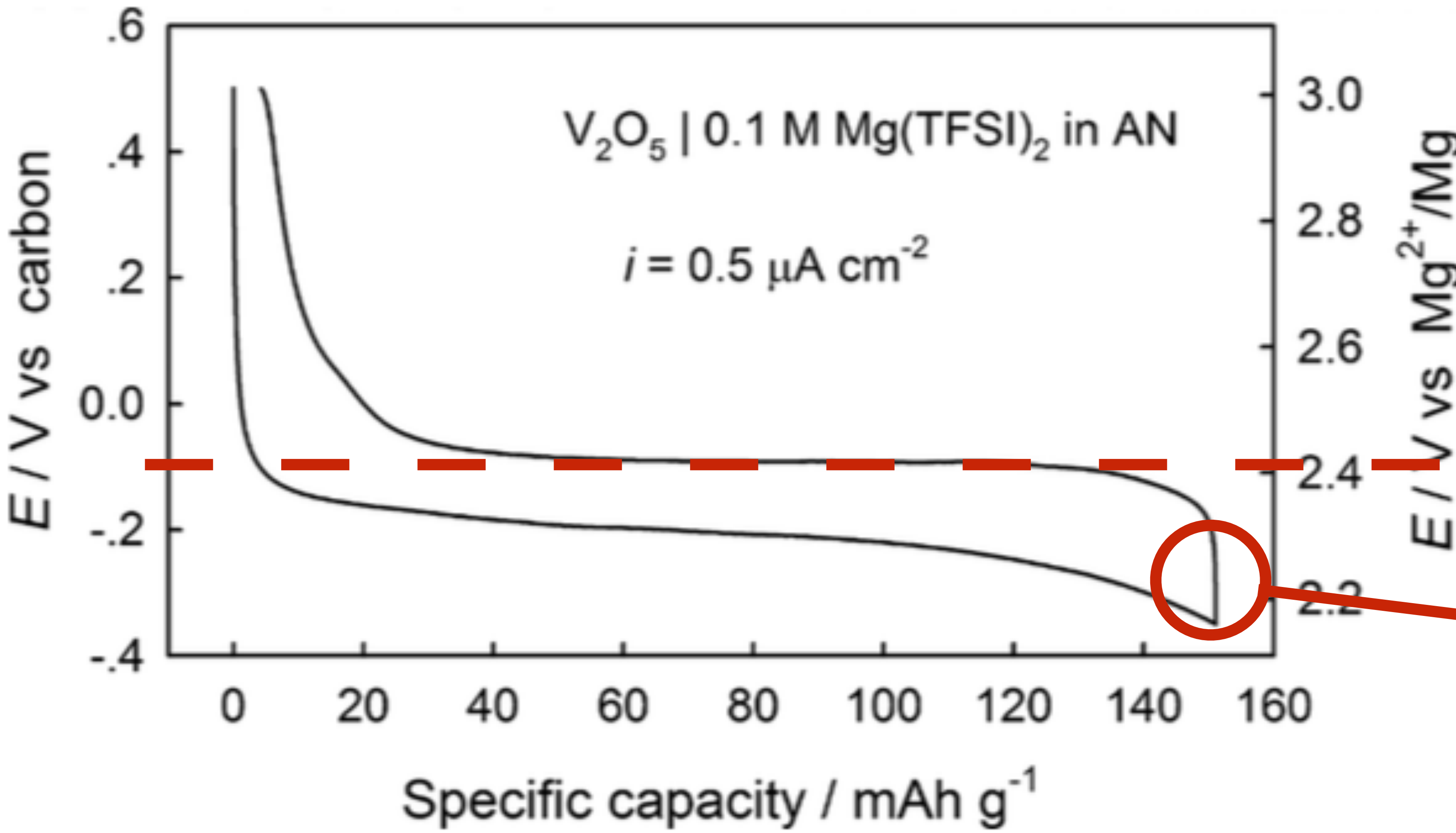
High-throughput can generate voltages for hundred of materials per day



M. Liu, Z. Rong, R. Malik, P. Canepa et al., Energy Environ. Sci. **8** 964-974 (2015).

Cycling Mg in V_2O_5

Theoretical V_2O_5 2.5 V @ 294.7 mAh/g



Mg cycled with empty V_2O_5

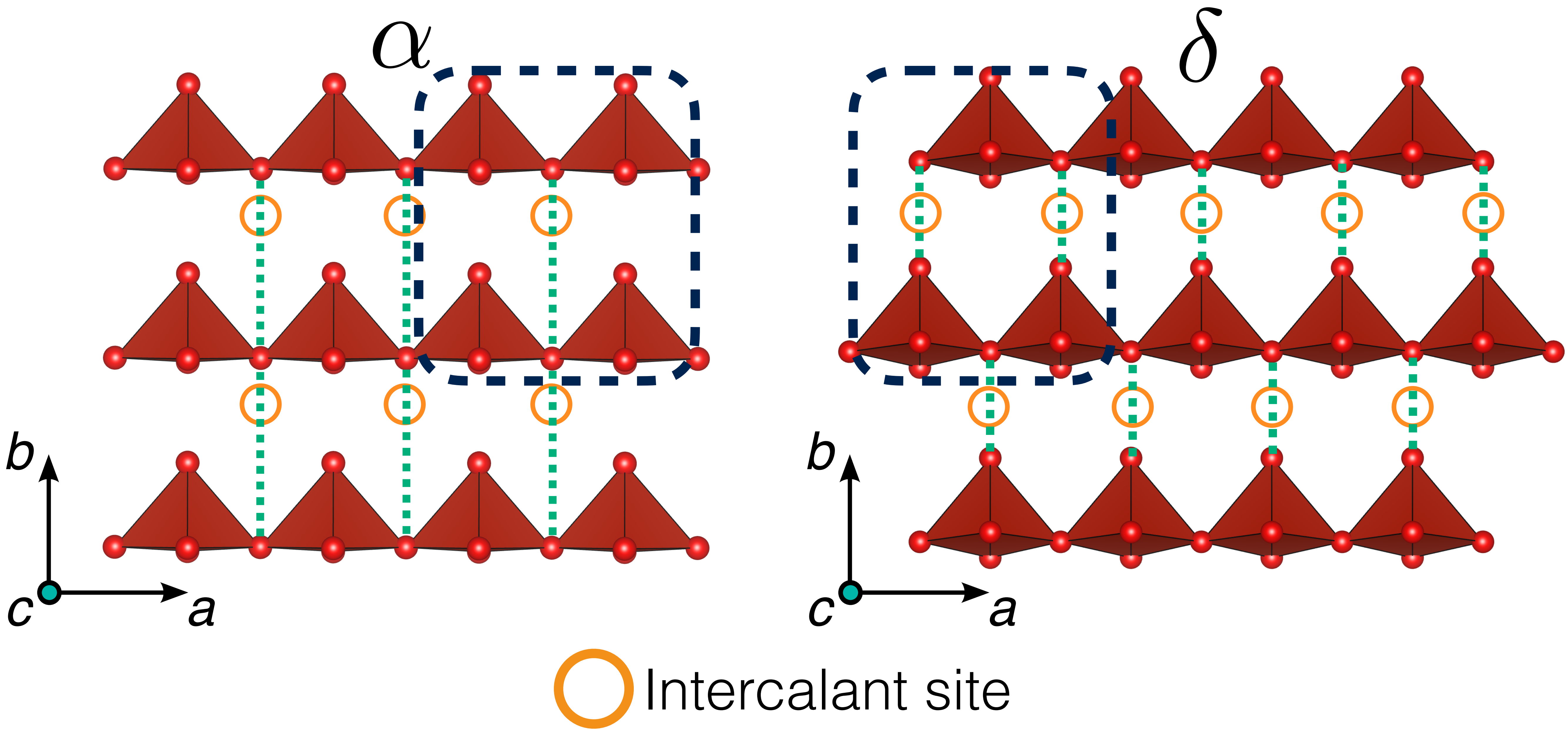
Average voltage ~2.35 V

Voltage drop at x_{Mg}~0.5

Can we benchmark the experimental voltage curves with theoretical predictions?

G. Gershinsky et al., Langmuir **29** (34), 10964–10972 (2013).

α and δ polymorphs

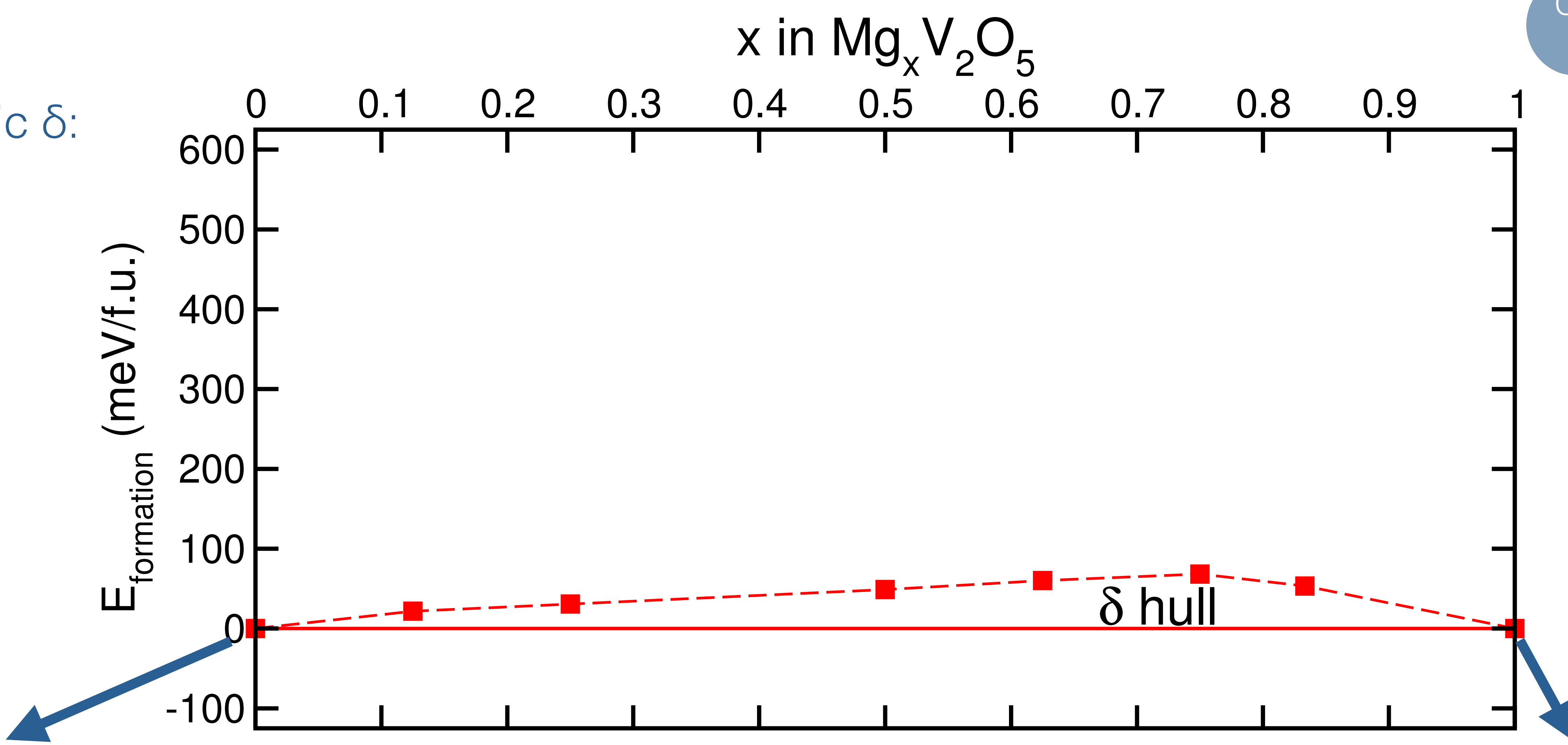


G.S. Gautam, P. Canepa et al., Chem. Mater. **27** (10), 3733–3742 (2015).

Building the phase diagram of V_2O_5 at 0 K using DFT+U

Convex hull for the expert

Topatactic δ: 2-phase



Empty δ-V_2O_5

Magnesiated δ-V_2O_5

G.S. Gautam, P. Canepa et al., *Chem. Mater.* **27** (10), 3733–3742 (2015).

Building the phase diagram of V_2O_5 at 0 K using DFT+*U*

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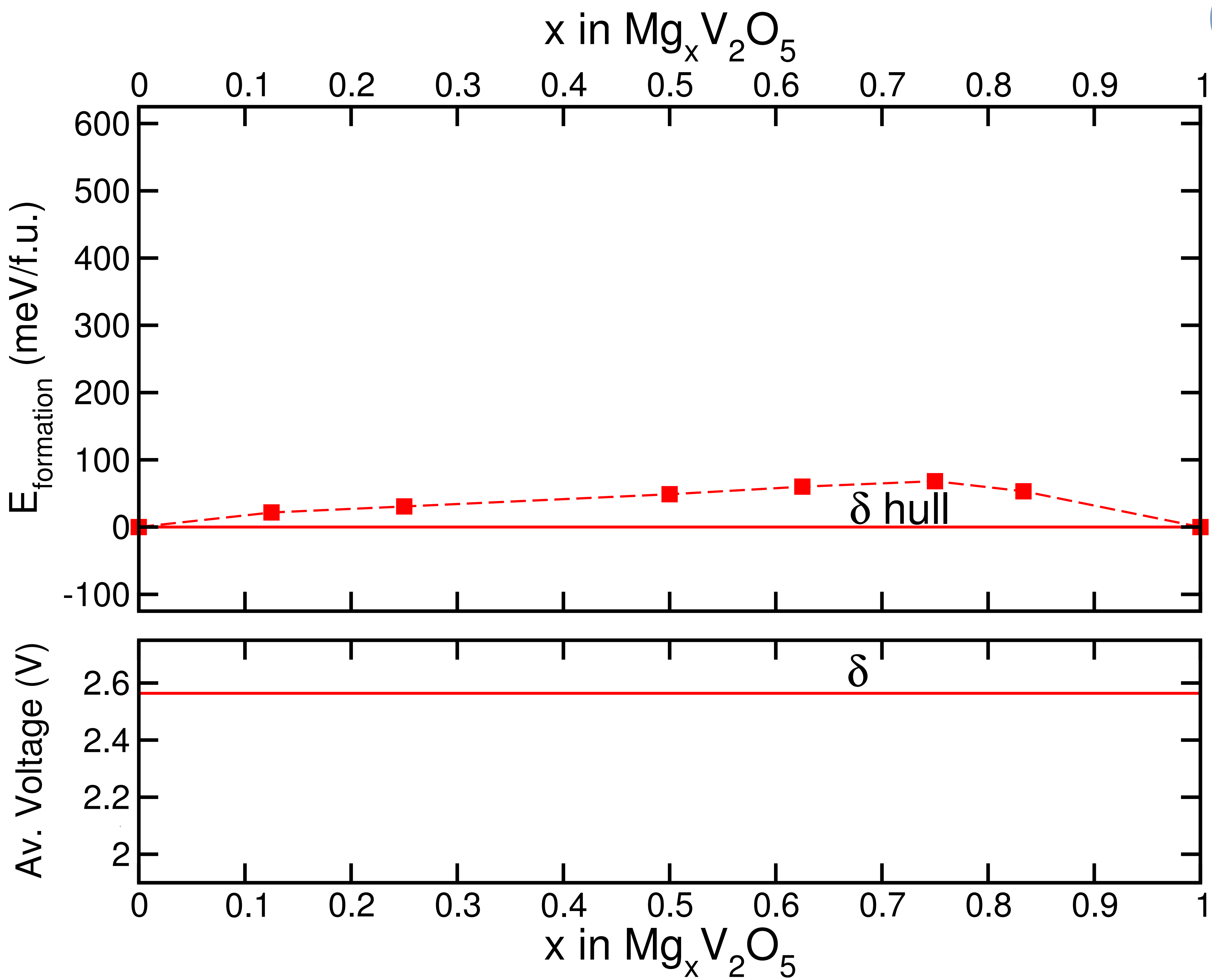
Topatactic δ: 2-phase



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G.S. Gautam, P. Canepa et al., Chem. Mater. **27** (10), 3733–3742 (2015).

Building the phase diagram of V_2O_5 at 0 K using DFT+*U*

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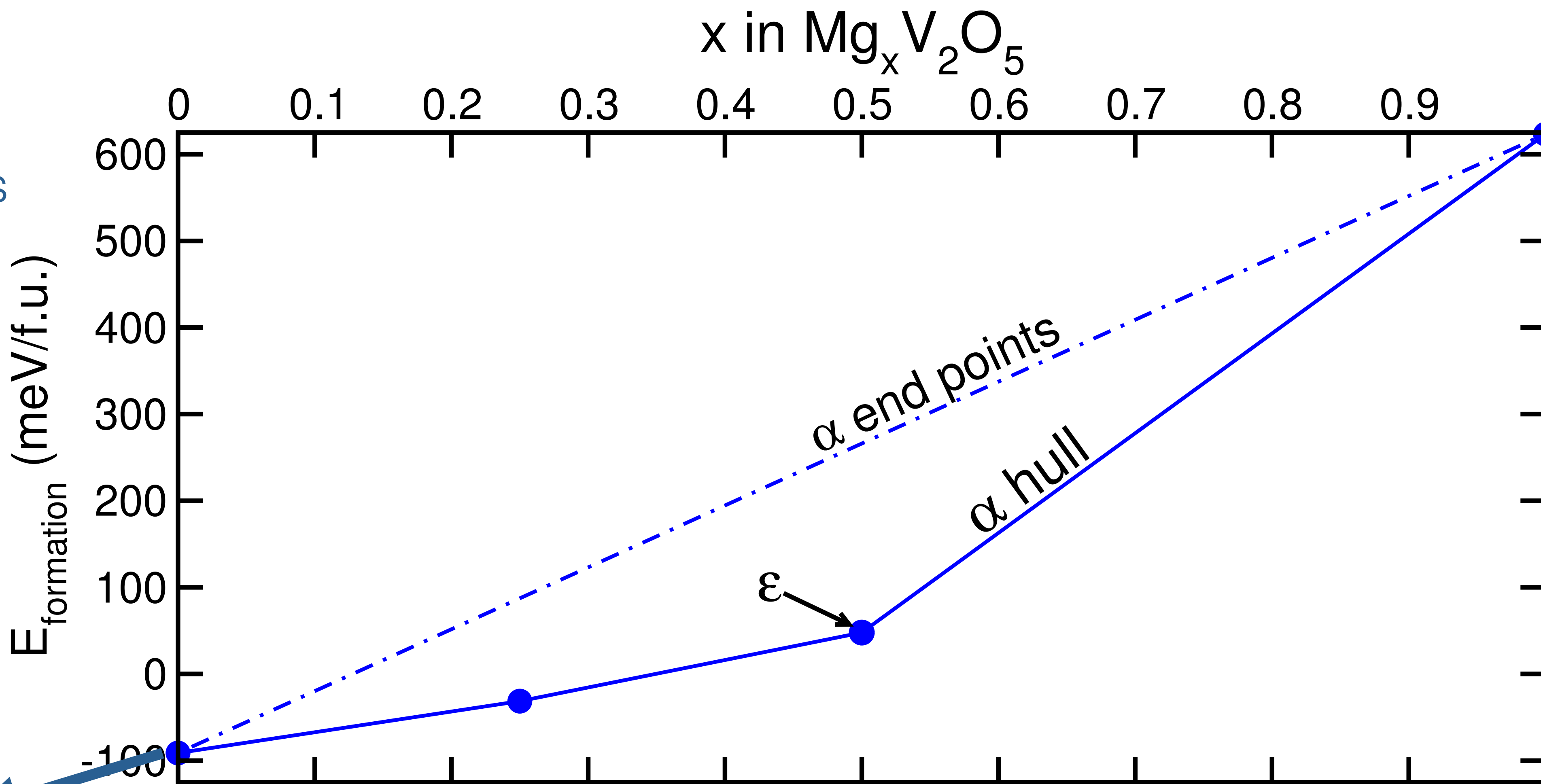
Topatactic α: Intermediates



Magnesiated α-V_2O_5

Empty α-V_2O_5

G.S. Gautam, P. Canepa et al., *Chem. Mater.* **27** (10), 3733–3742 (2015).

Building the phase diagram of V_2O_5 at 0 K using DFT+*U*

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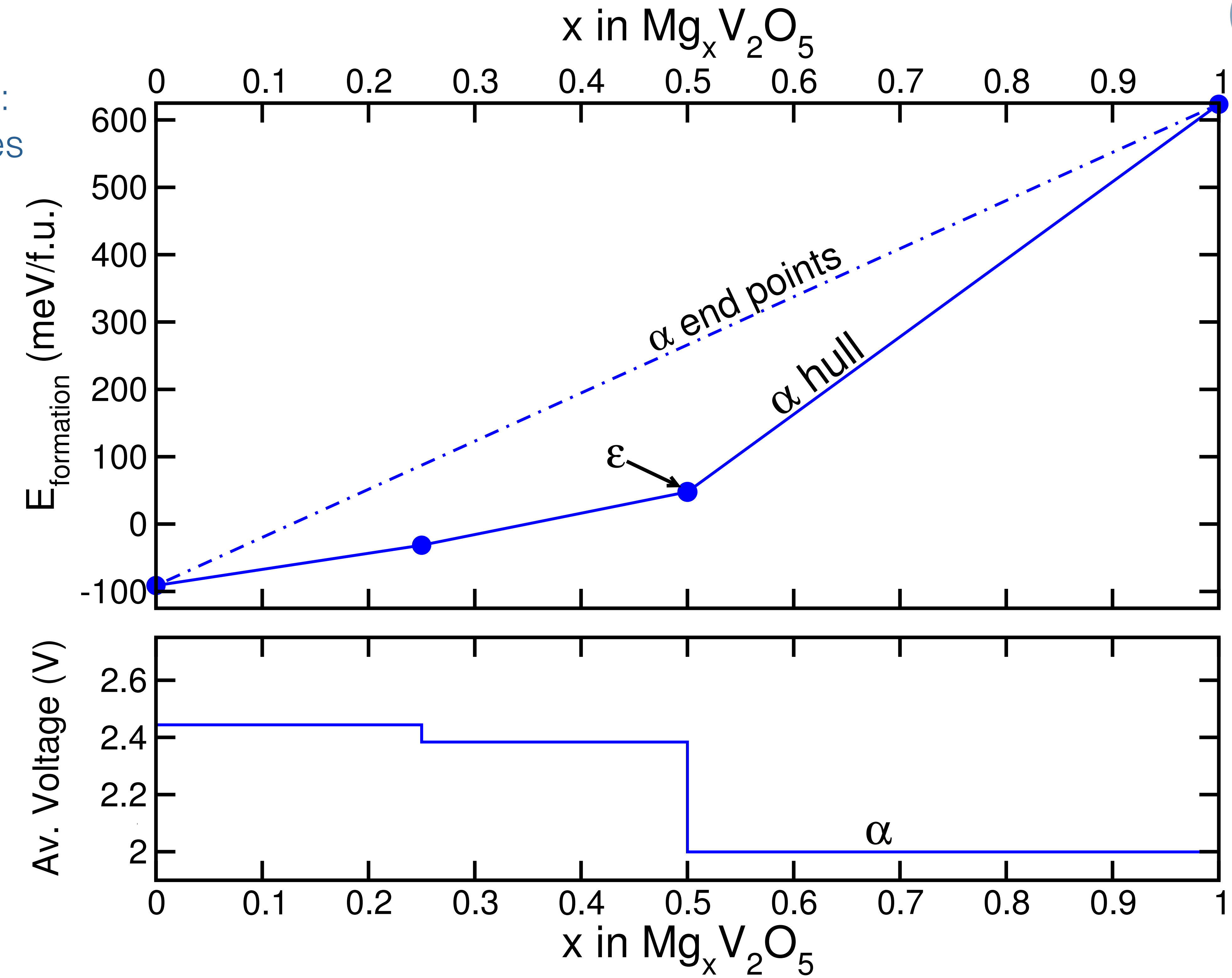
Topatactic α: Intermediates



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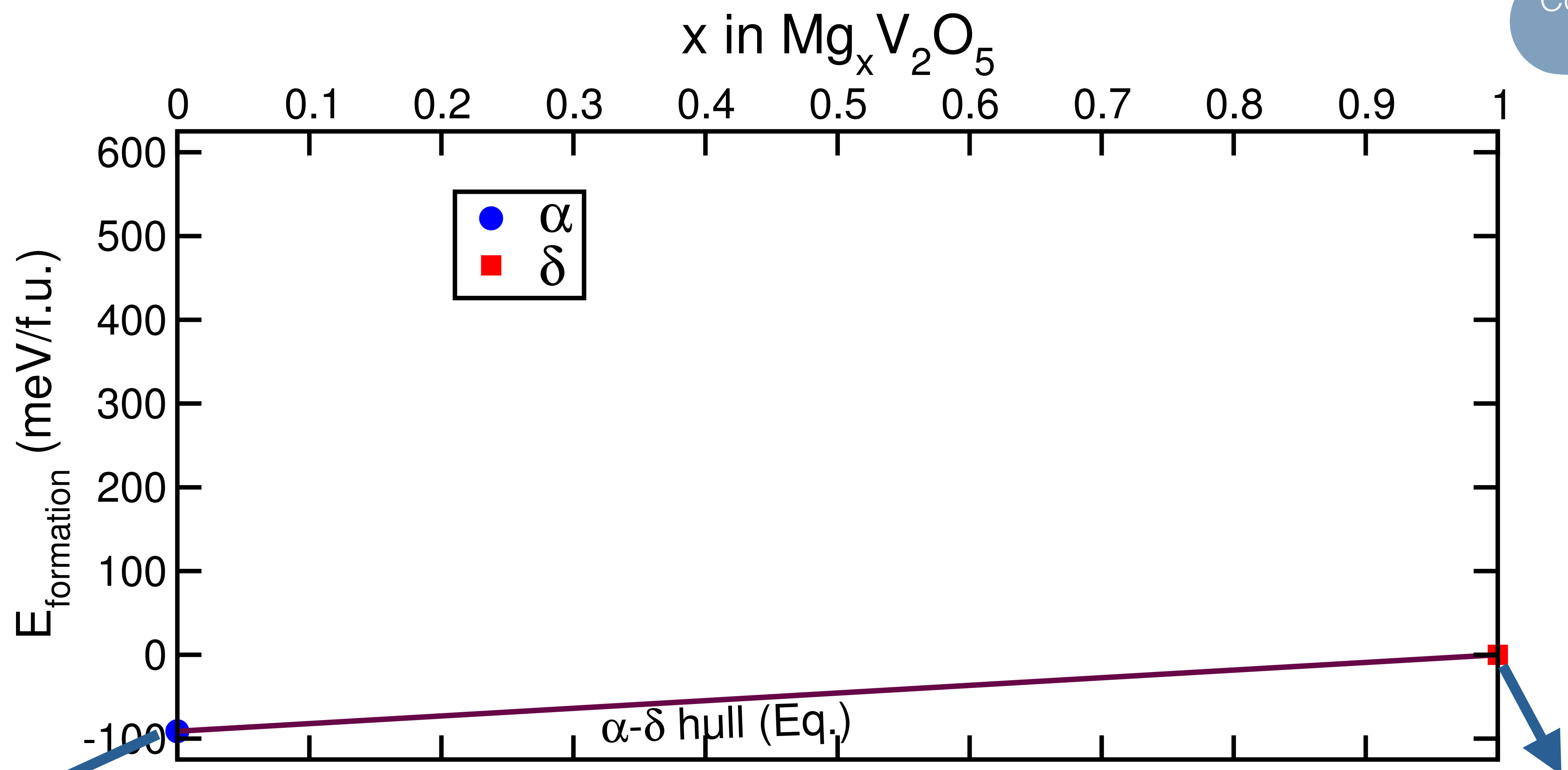


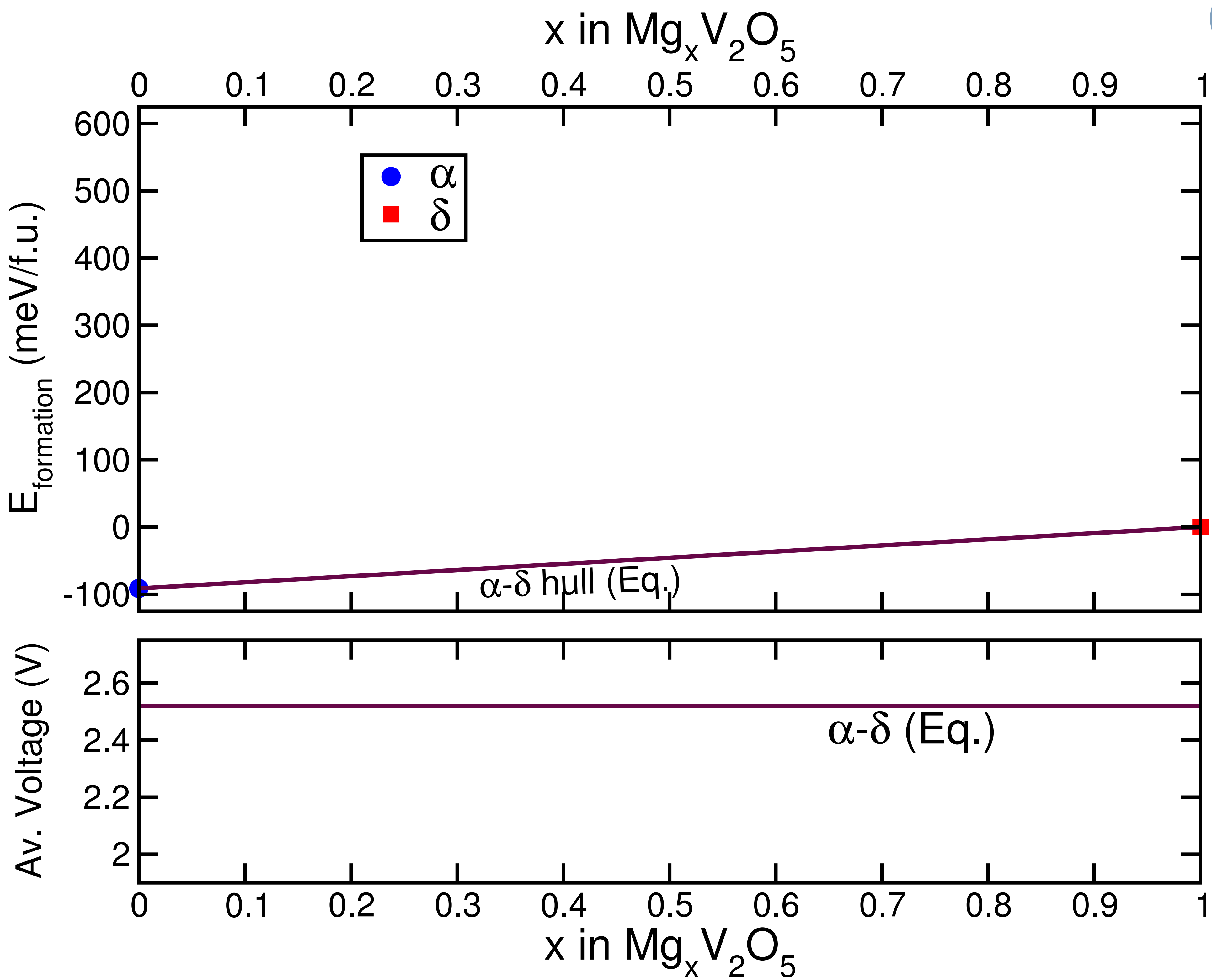
Empty
α-V_2O_5

Magnesiated
δ-V_2O_5

G.S. Gautam, P. Canepa et al., *Chem. Mater.* **27** (10), 3733–3742 (2015).

Building the phase diagram of V_2O_5 at 0 K using DFT+*U*

Convex hull for the expert



G.S. Gautam, P. Canepa et al., Chem. Mater. **27** (10), 3733–3742 (2015).

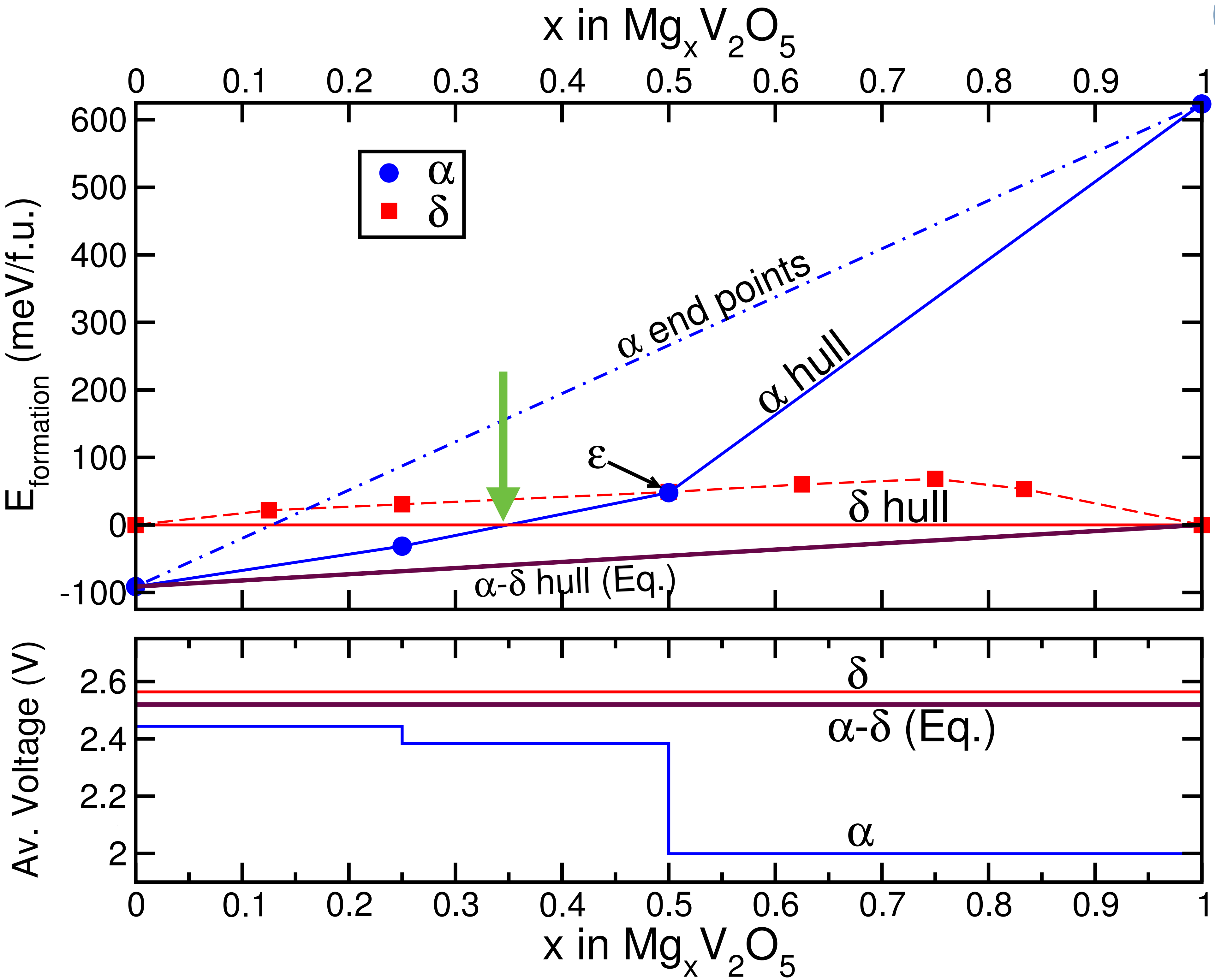
Building the phase diagram of V_2O_5 at 0 K using DFT+*U*

Convex hull for the expert

Topatactic δ: 2-phase

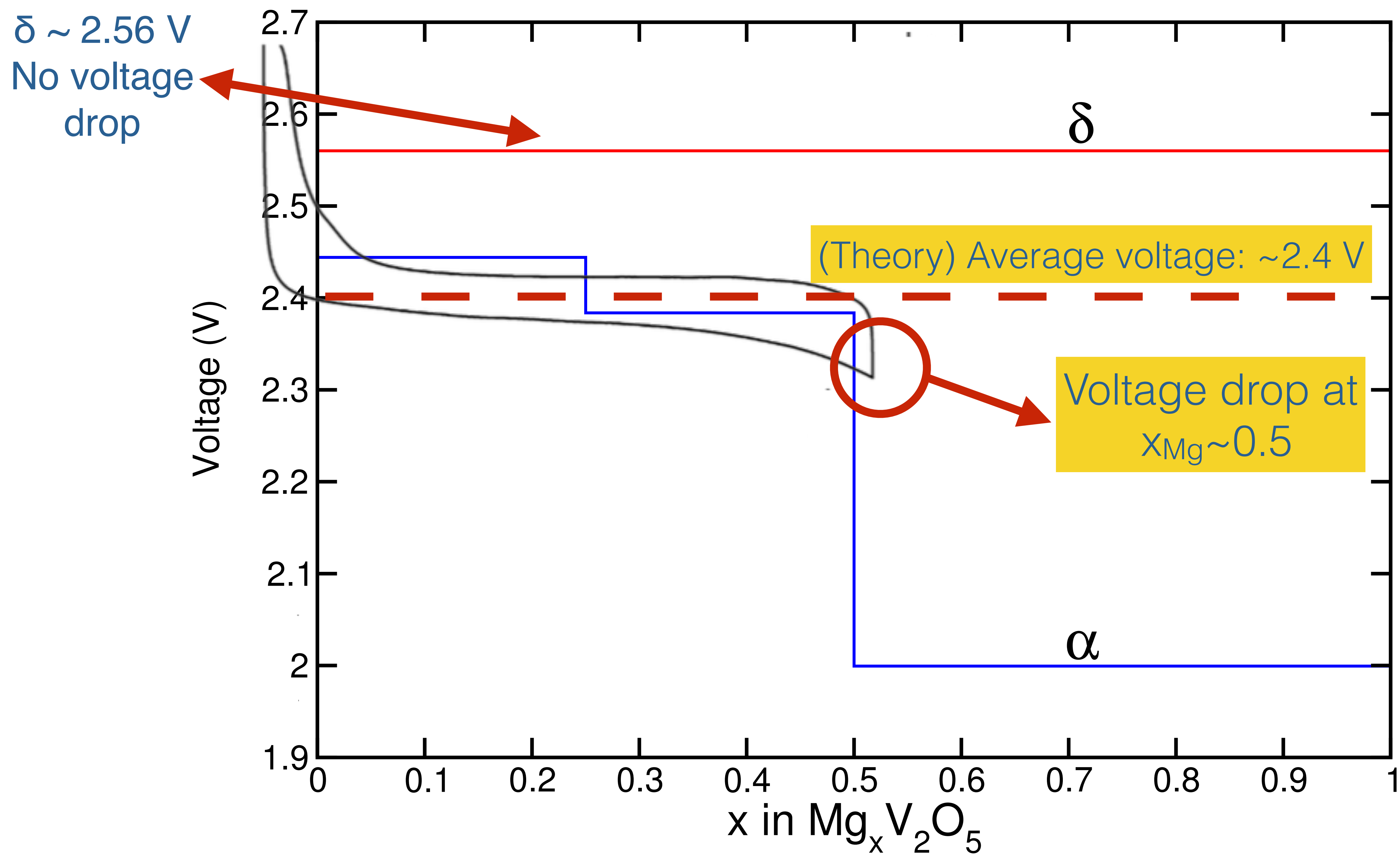
Topatactic **α**: Intermediates

Low Mg: **α**
High Mg: δ



G.S. Gautam, P. Canepa et al., *Chem. Mater.* **27** (10), 3733–3742 (2015).

V_2O_5 at work: Theory *vs.* Experiment

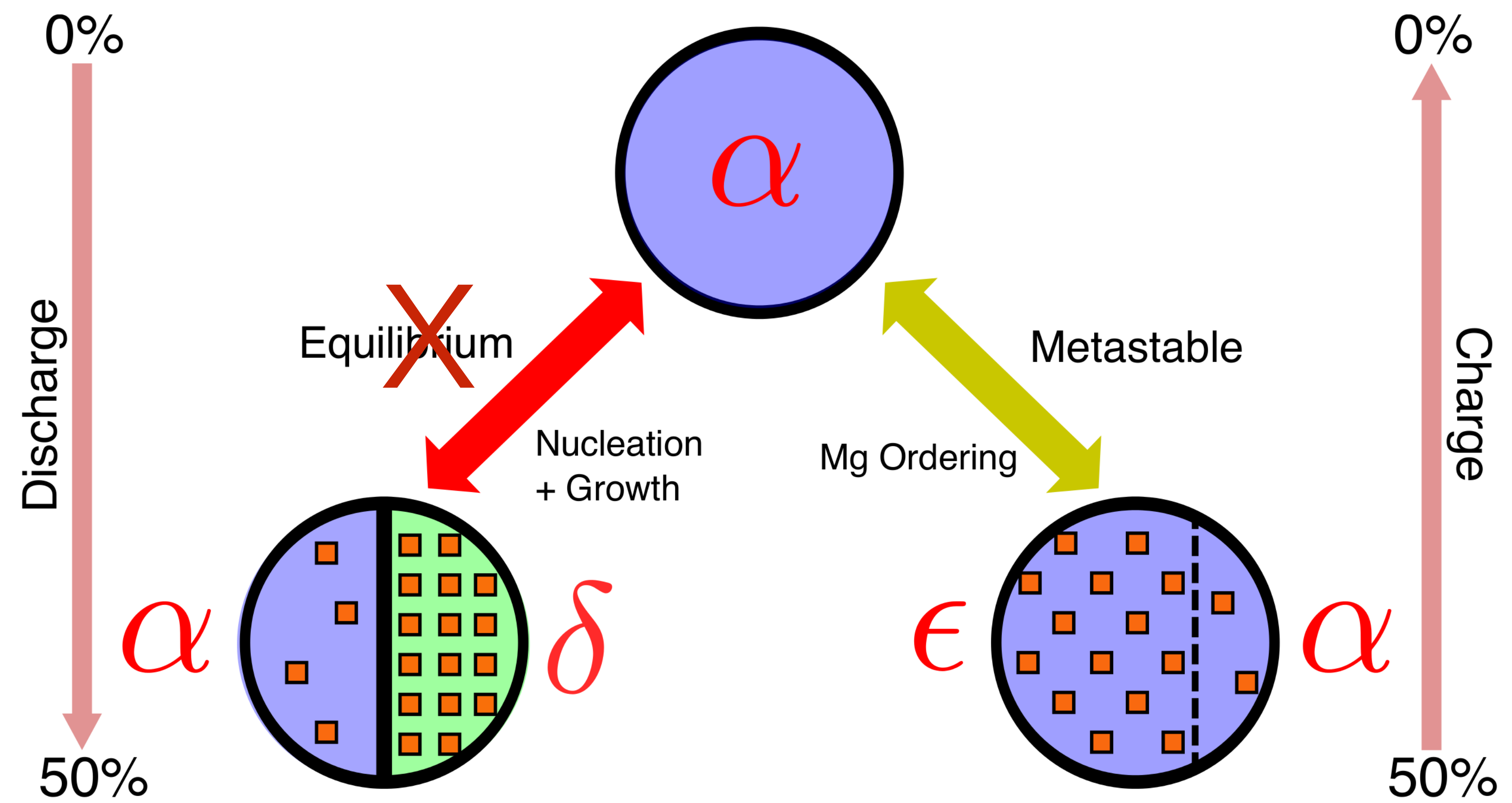


G.S. Gautam, *P. Canepa et al., Chem. Mater.* **27** (10), 3733–3742 (2015).
G. Gershinsky et al., Langmuir **29** (34), 10964–10972 (2013).

Key understandings from the V_2O_5 phase-diagram

When Mg cycling begins in empty (charged) V_2O_5, α is retained

- Experimental voltage curve benchmarks with predicted curve for **α**

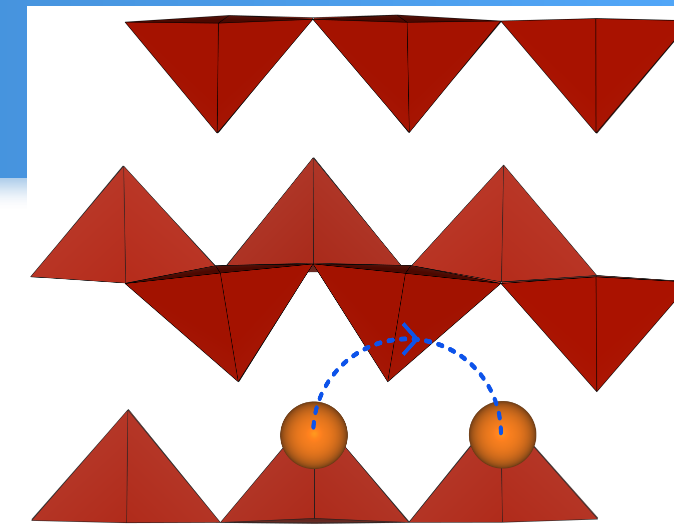


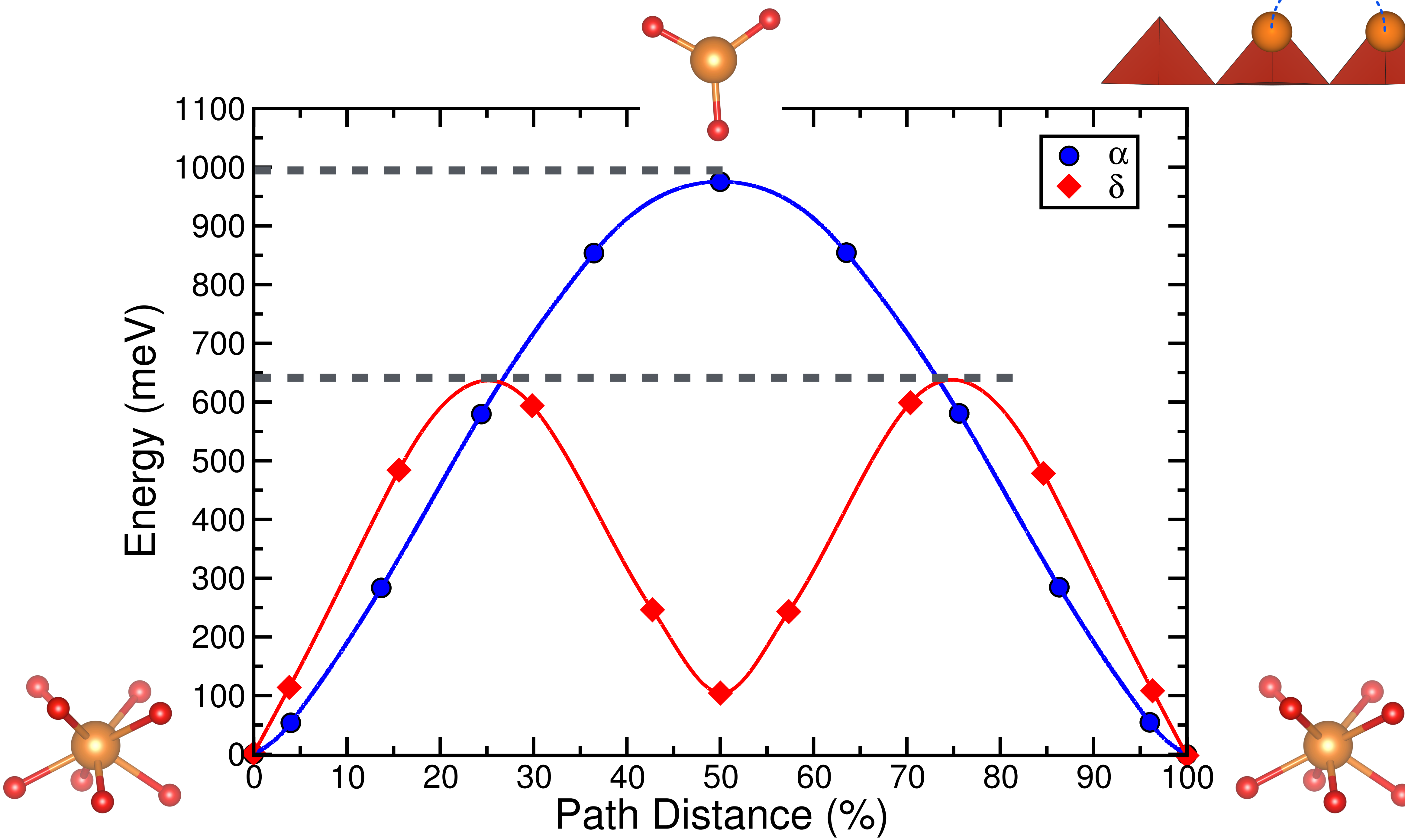
α→δ transformation could be kinetically hindered

- Since **α** remains upon magnesiation and transformation to δ-V_2O_5 requires structural arrangement
- δ-V_2O_5, if accessed, could be metastable upon Mg charge
- Starting from δ-MgV_2O_5, which has been experimentally synthesized

G. S. Gautam, P. Canepa et al., Chem. Mater. **27** (10), 3733–3742 (2015).

δ has better mobility: scope for improvement





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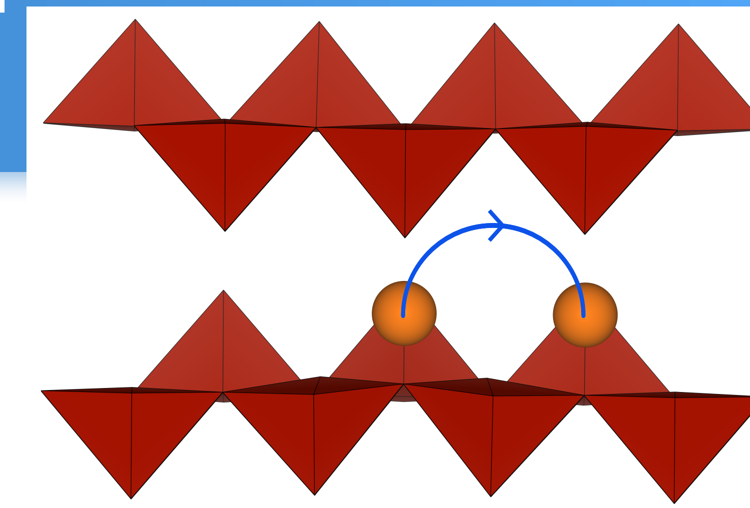
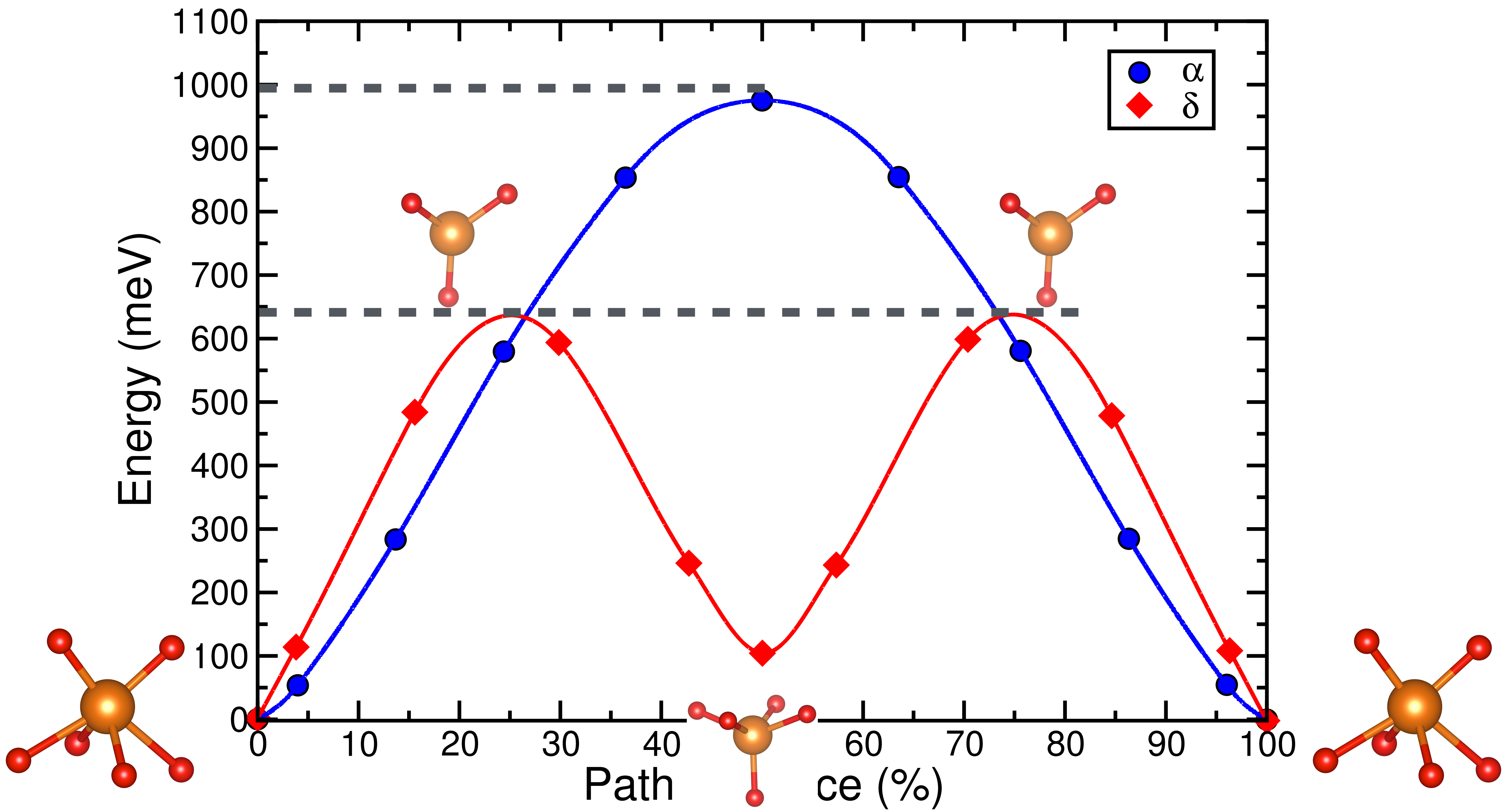
δ has better mobility: scope for improvement



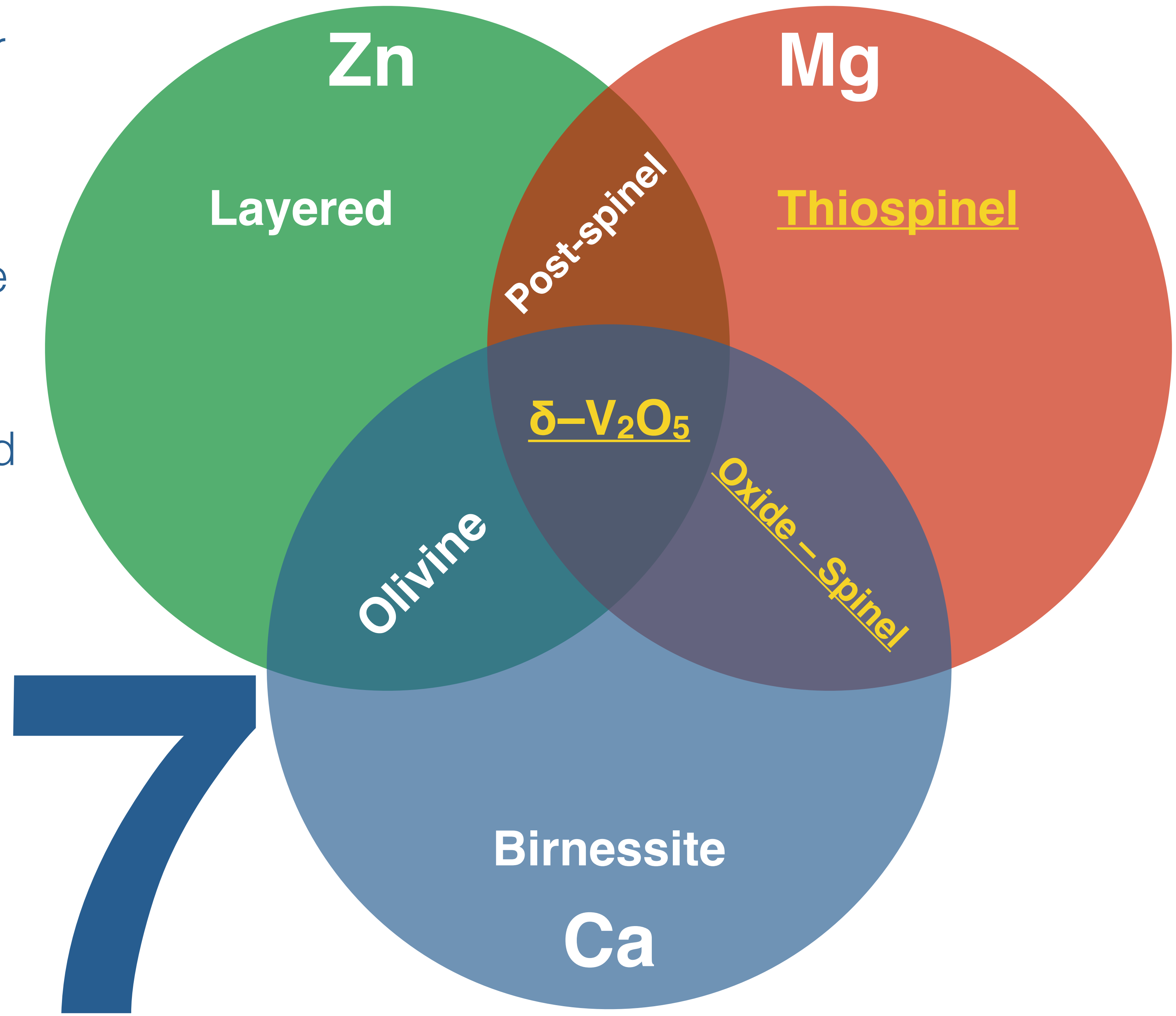
Coordination change for screening



G. S. Gautam, P. Canepa et al., Chem. Mater. **27** (10), 3733–3742 (2015).

DFT Screening for MV cathodes yields 7 novel compounds

1. DFT can asses mobility (slow) and voltages (fast) for MV cathode materials
2. Thiospinels show “fast” Mg mobility and facile reversible intercalation.
3. Larger volume per anion and an appropriate choice of TM can increase MV mobility.
4. V_2O_5 can provide “high” voltage with relatively high mobility for Mg.
5. MV Mobility depends on coordination changes of the MV species.



Thank you!

Cathode papers

- *M. Liu, Z. Rong, R. Malik, P. Canepa et al., Energy Environ. Sci.* **8** 964-974 (2015). **—> HT screening on Spinel materials for MV**
- *G.S. Gautam, P. Canepa et al., Chem. Mater.* **27** (10), 3733–3742 (2015). **—> V_2O_5 Phase Diagram**
- *G.S. Gautam, P. Canepa et al., Nano. Lett.* **16**, 2426–2431 (2016). **—> Phase Diagram of hydrated phase of V_2O_5**
- *G.S. Gautam, P. Canepa et al., Chem. Commun.* **51**, 13619-13622 (2015). **—> MV Dynamics in V_2O_5**
- *Z. Rong, R. Malik, P. Canepa, G.S. Gautam et al., Chem. Mater.* **27** (17), 6016–6021 (2015). **–> Design rules for MV migration in closed-packed frameworks**
- *M. Liu, …, P. Canepa et al., Evaluation of sulfur spinel compounds for multivalent battery cathode applications, accepted in Energy Environ. Sci.* (2016). **—> HT screening of Sulfide Spinels for MV**
- *P. Canepa, G.S. Gautam, D. C. Hannah et al., submitted to Chem. Rev* ***–> Extensive review of MV intercalation cathodes.***

Anode and electrolytes papers

- *P. Canepa, G.S. Gautam et al., Chem. Mater.* **27** (9), 3317–3325 (2015). **—> Mg Electrolyte deposition at the metal anode.**
- *P. Canepa, G.S. Gautam et al., Energy Environ. Sci.* **8**, 3718-3730 (2015). **—> Phase Diagram of liquid Mg electrolyte**

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