First-principles study of V_2O_5 polymorphs as Mg (and multi-valent) cathode materials

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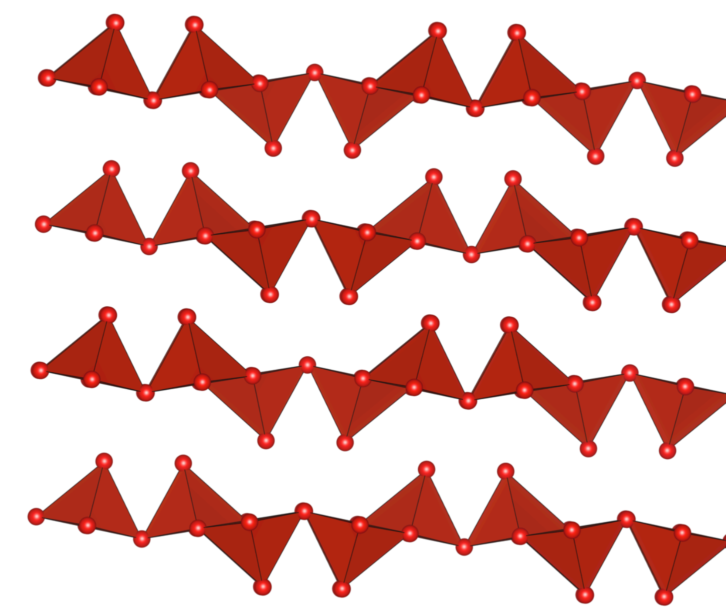
V_2O_5: Critical to cathode design of Mg-batteries

- Why Mg (or Multi-valent)?
  - Next generation of electric devices will benefit from higher energy density storage systems
  - Superior volumetric capacity for Mg metal as anode (~3833 mAh/cm^3) vs. Li metal (~2046) or Li in graphite (~800)
- New chemistry: Cathode design challenge
  - High Voltage, High Capac[illegible]obility



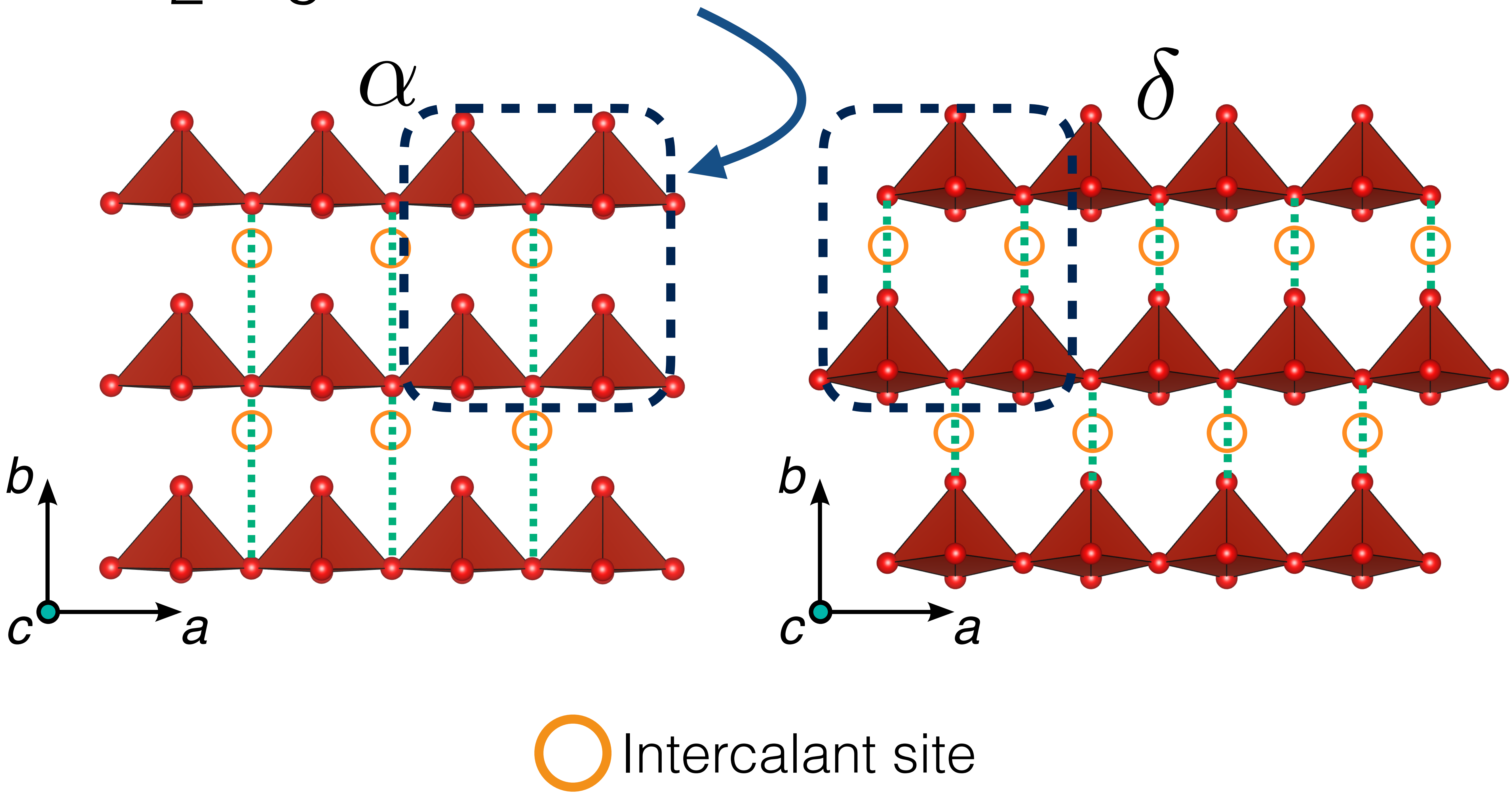
- Why V_2O_5?
  - One of only 3 cathodes to reversibly intercalate Mg
    - Higher voltage than Chevrel Mo_3S_4 [1] and lower volume change than layered MoO_3 [2]
  - Known Li-intercalant ; Orthorhombic and Xerogel

1. Aurbach *et al.*, Nature, 2000
2. Gershinsky *et al.*, Langmuir, 2013

Orthorhombic V_2O_5

α and δ

Polymorphs of orthorhombic V_2O_5



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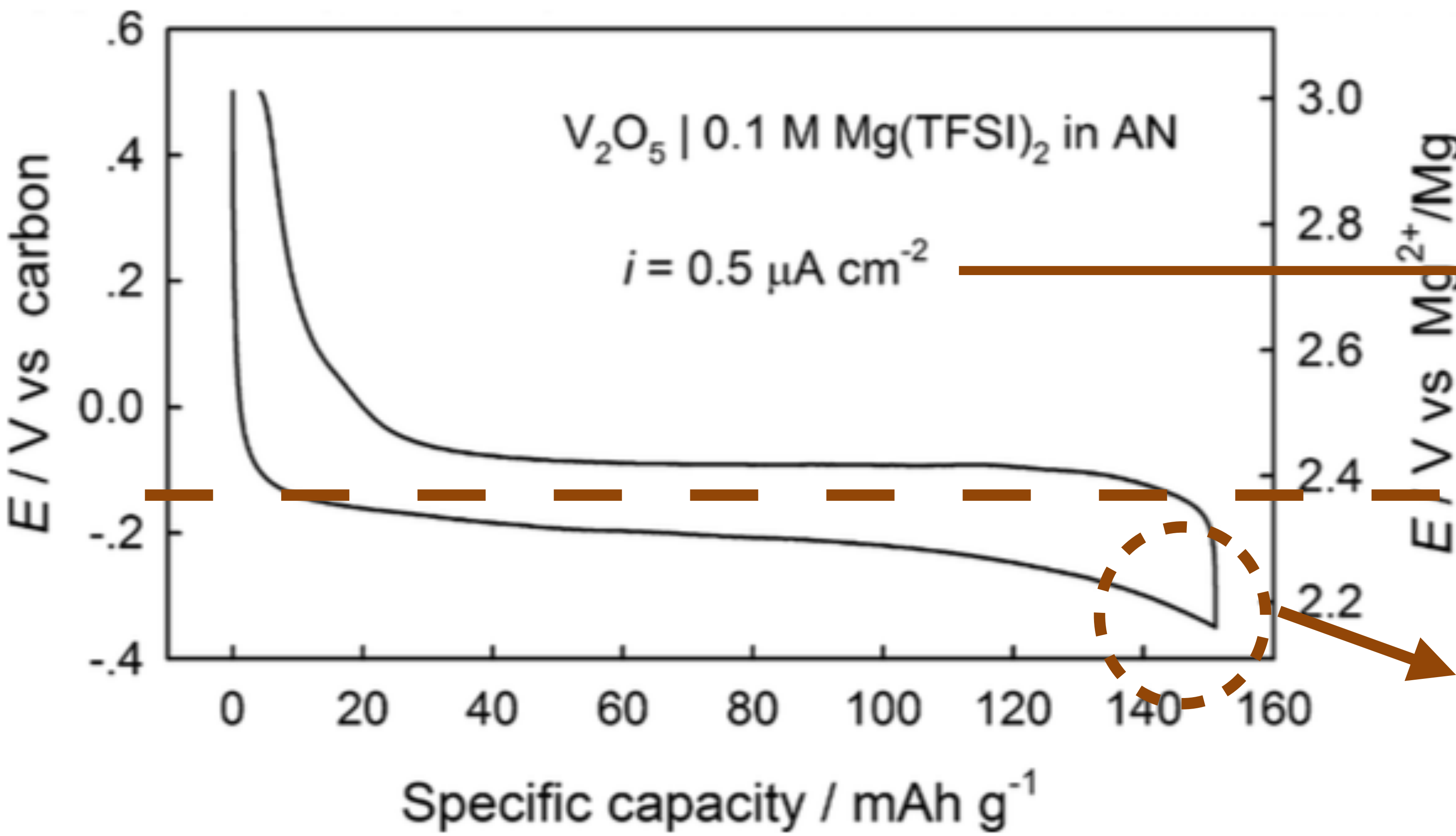
Typical experimental voltage profile for Mg insertion into V_2O_5



Mg cycled with empty V_2O_5

~ Slow rates

Average voltage ~2.35 V

Voltage drop at x_{Mg}~0.5

Can we benchmark the experimental voltage curves with theoretical predictions?

- Need to calculate the "ground state hull" for Mg insertion into V_2O_5 (with DFT)

Image from Gershinsky *et al.*, Langmuir 2013

Ground state hull and voltages

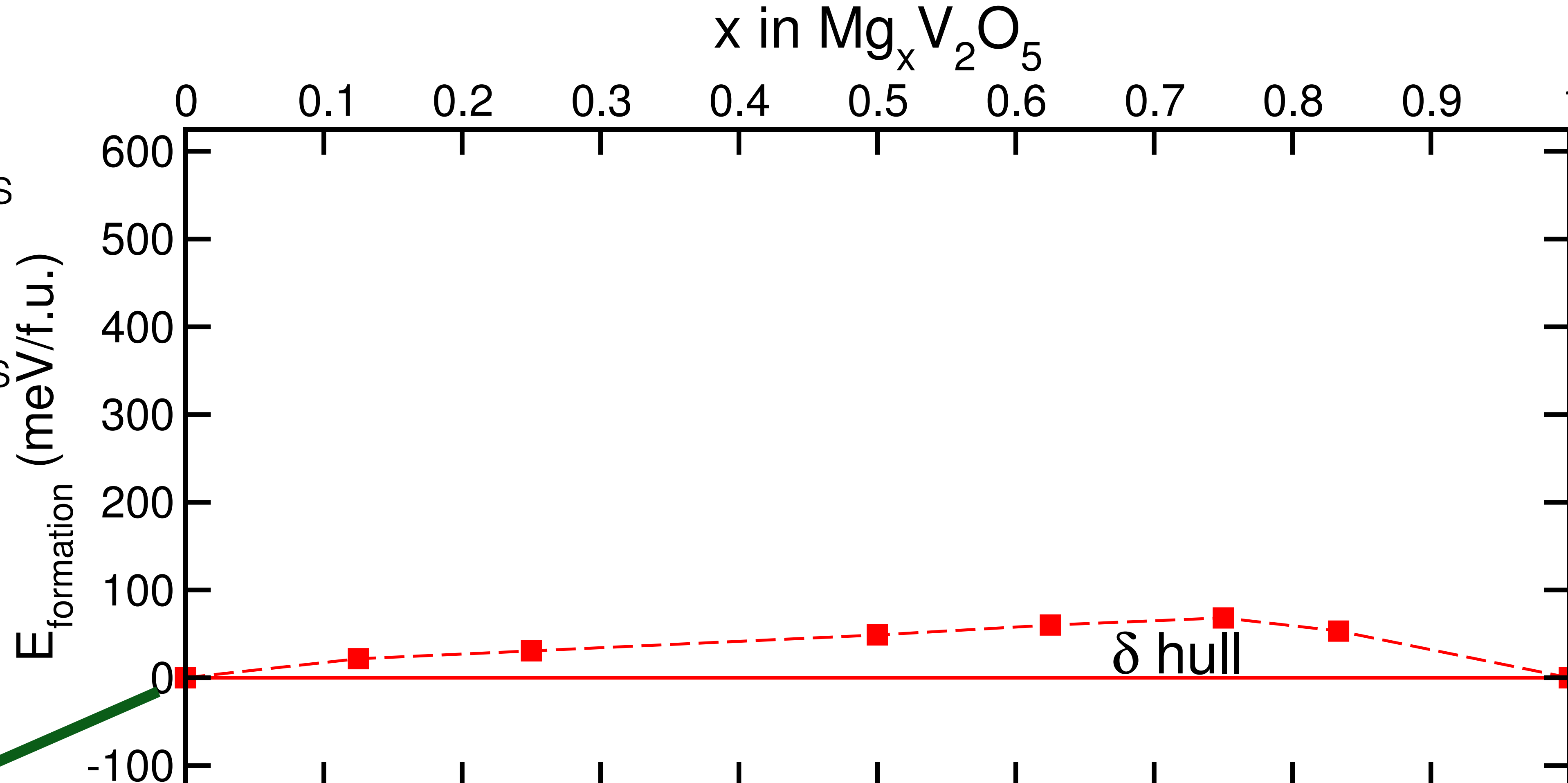
α- V_2O_5 should phase separate with δ-V_2O_5

Topatactic δ:
2-phase

Topatactic α:
Intermediates

Topatactic α:
Intermediates

Low Mg: α
High Mg: δ



Magnesiated
α-V_2O_5

Empty
δ-V_2O_5

Empty
α-V_2O_5

Magnesiated
δ-V_2O_5

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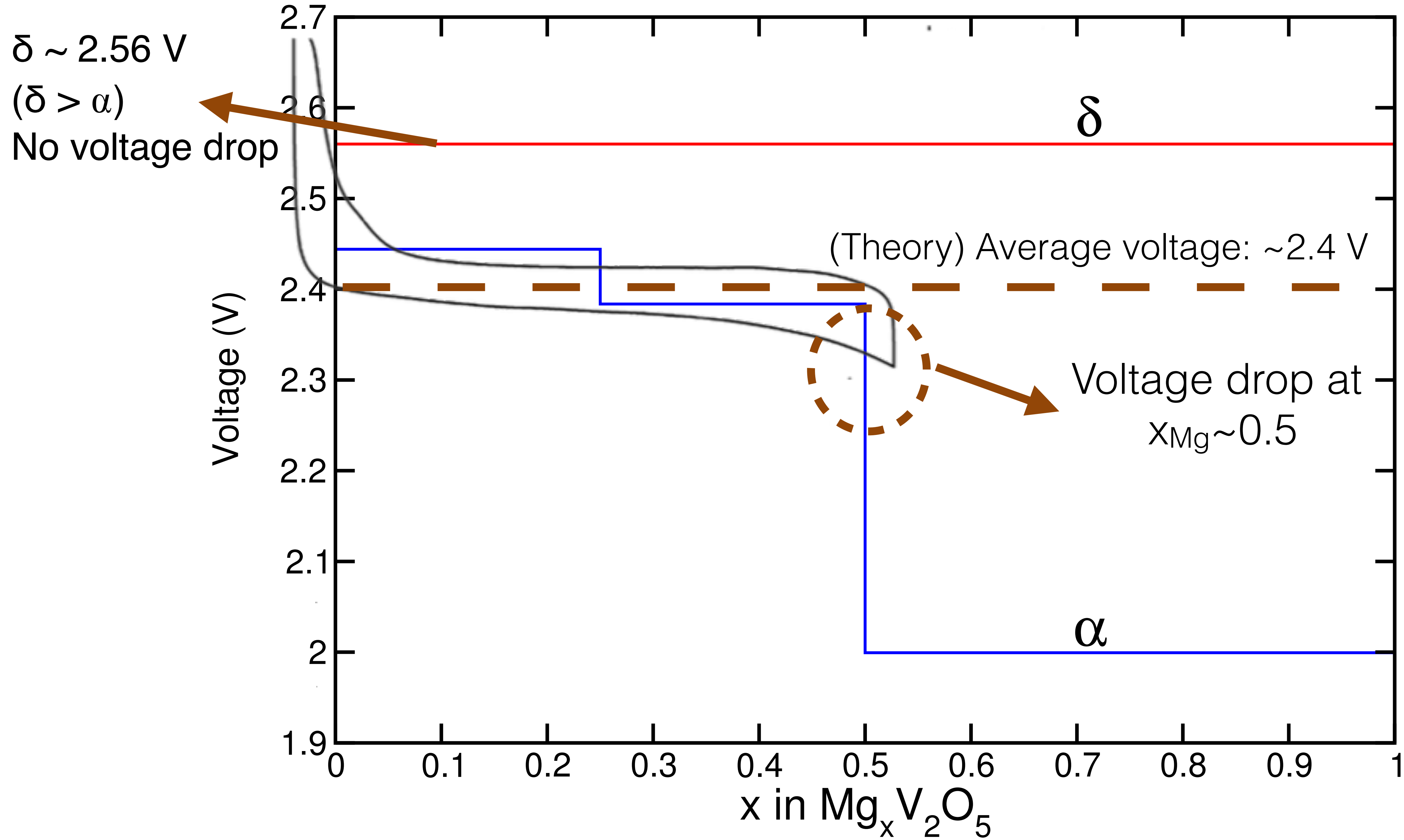
Experimental voltage curve matches α voltage profile



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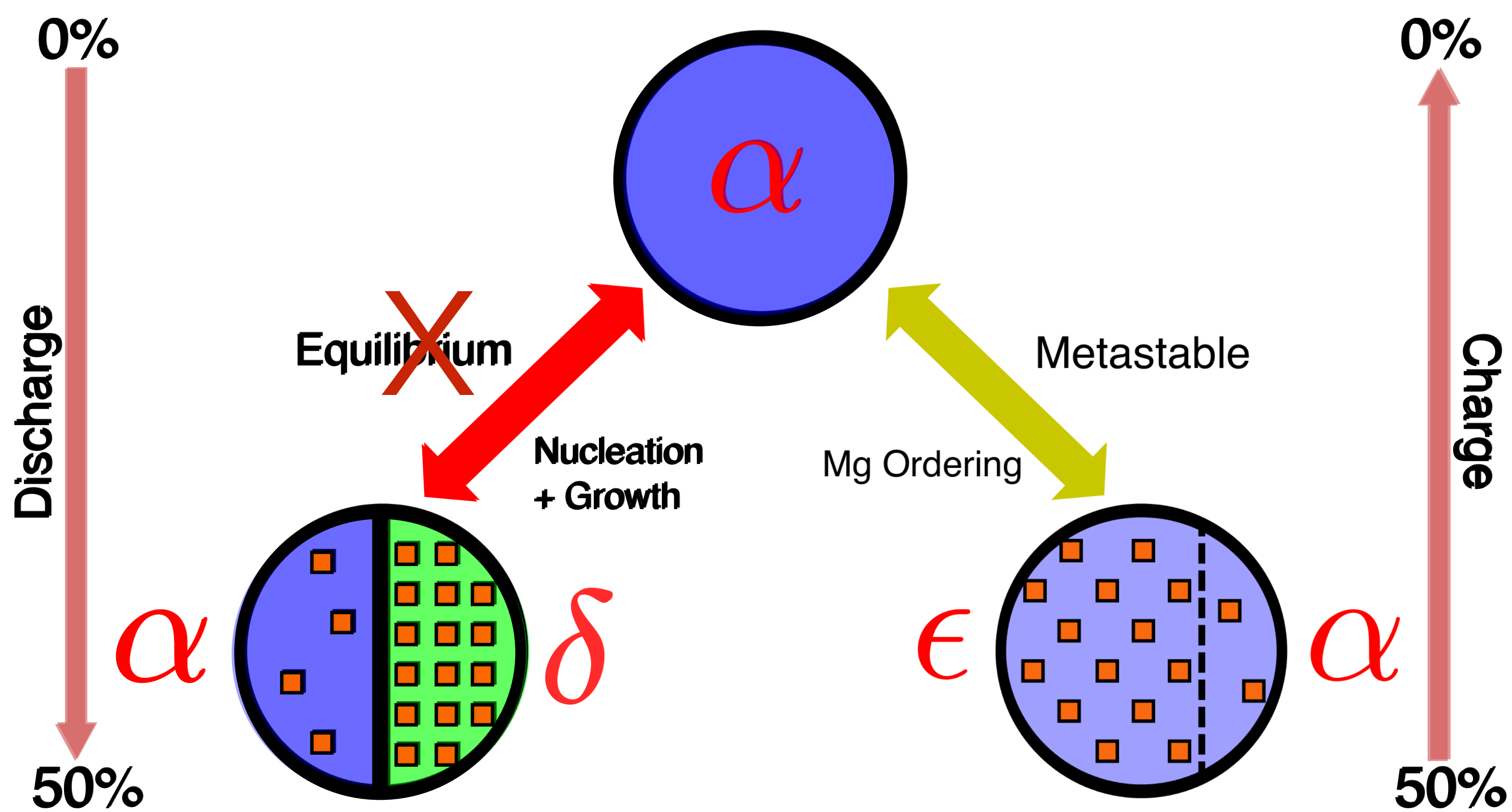
Experiments cycle Mg in α-V_2O_5

When Mg cycling is started 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

- Requires structural arrangement

What about Mg mobilities in α and δ?

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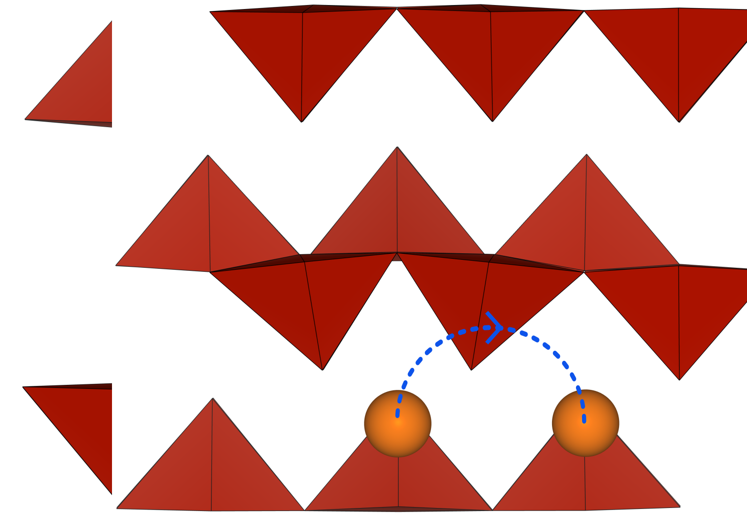
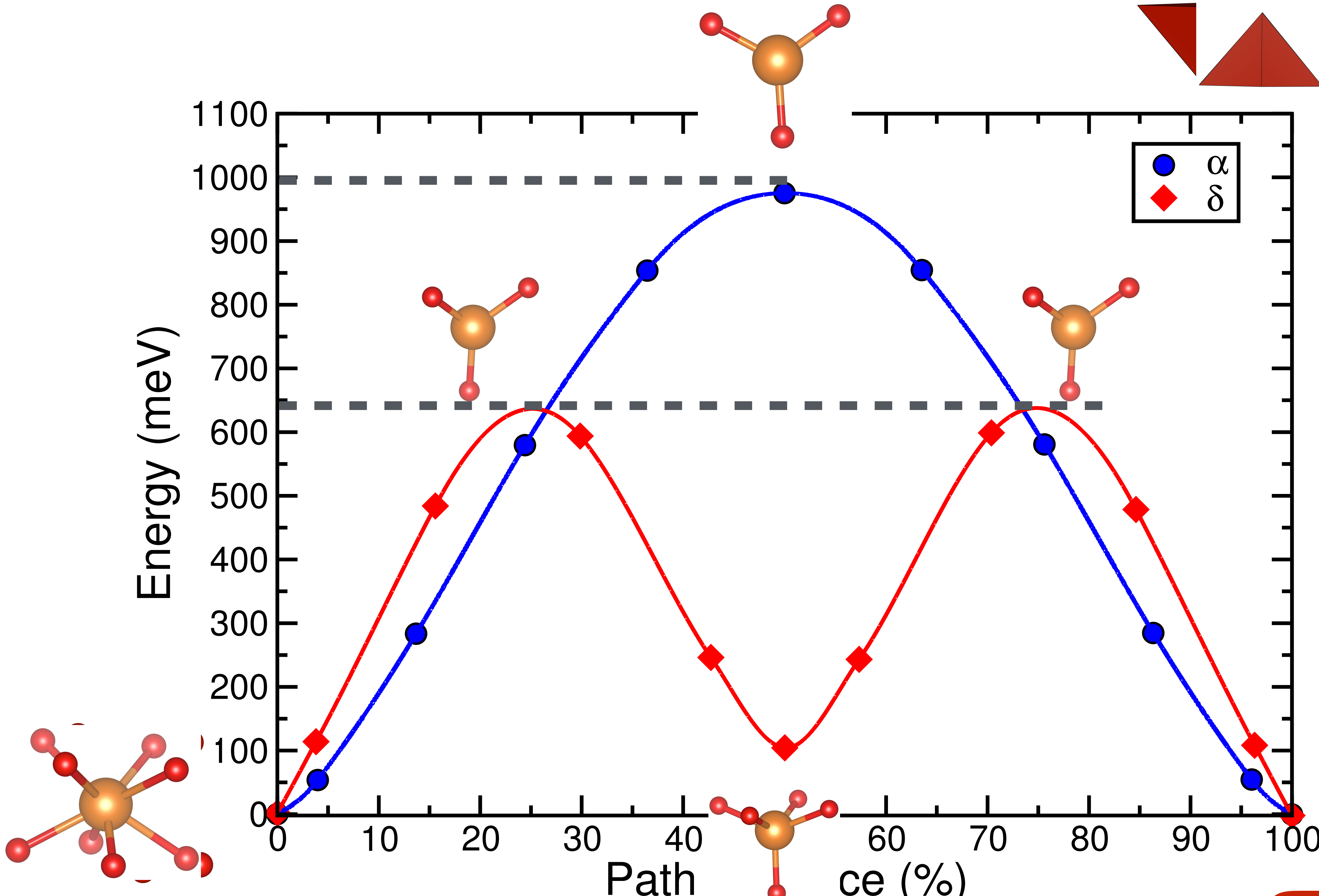
Mg migration barriers
δ is better than α





Can Mg-cycling be done on δ?

- May be, if begun in δ-MgV_2O_5

δ for other MV systems?

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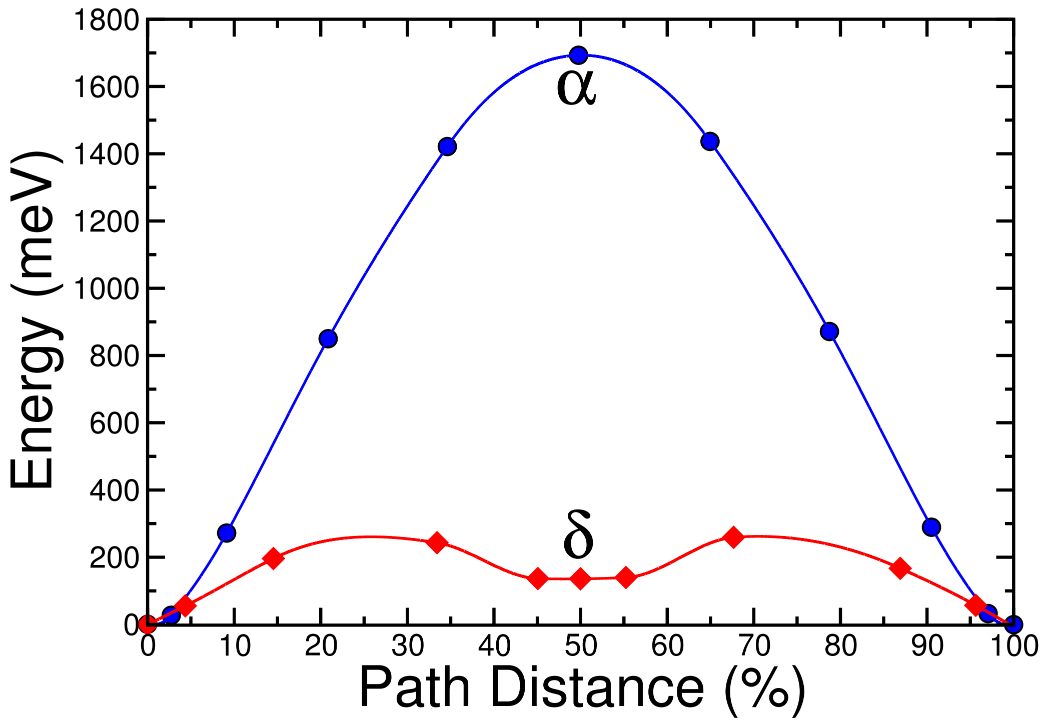
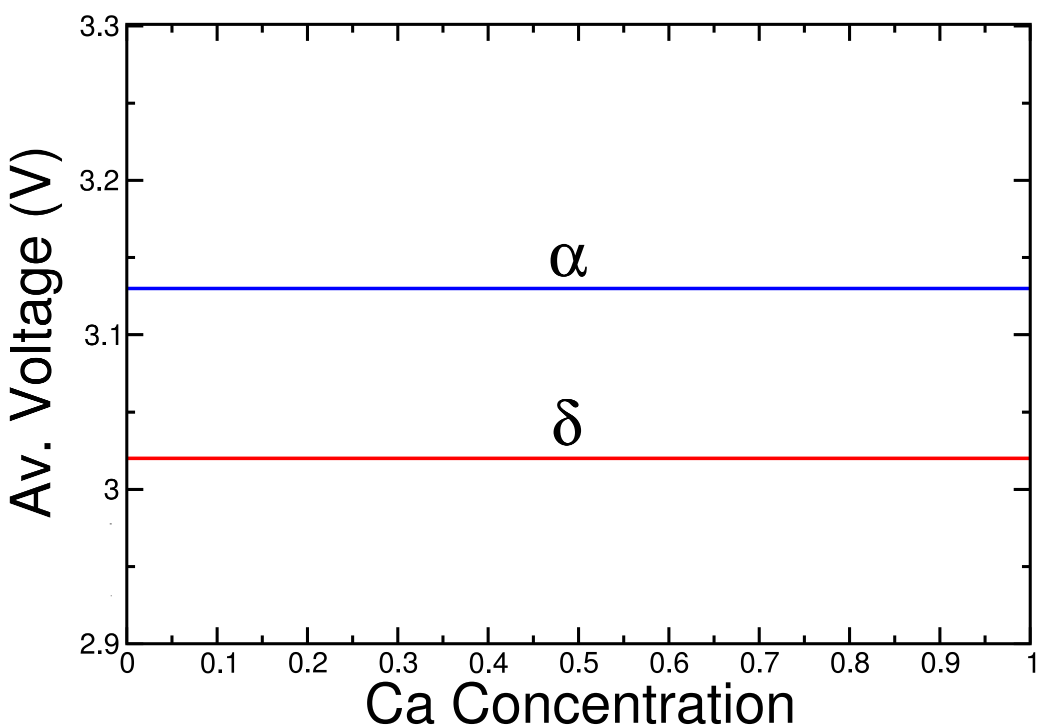
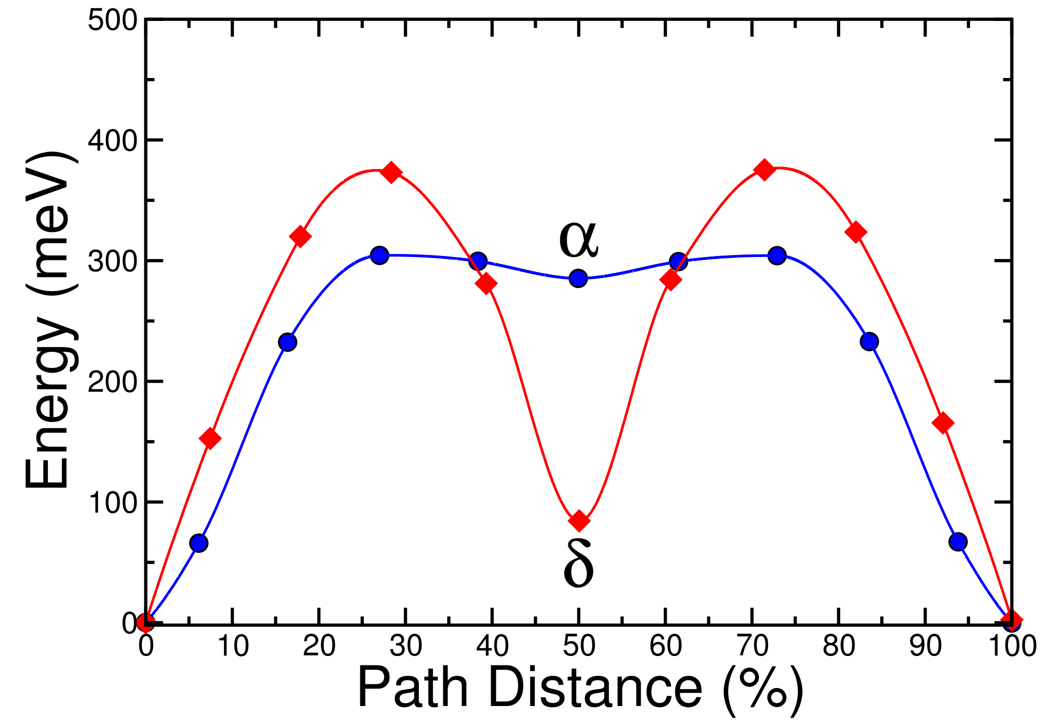
δ is better for other MV systems also

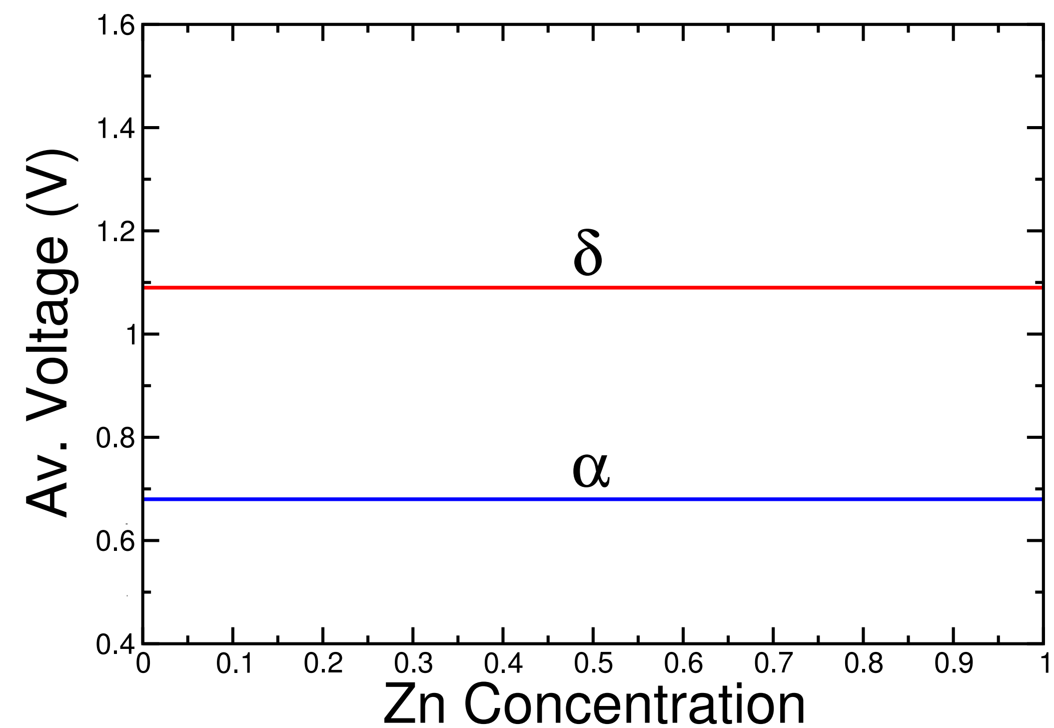
Ca^{2+}: δ *better mobility* than α





Zn^{2+}: δ **better voltage** than α





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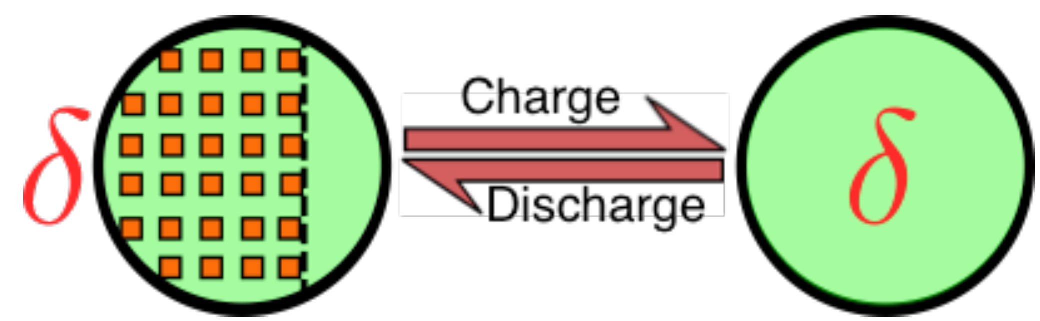
Summary: Orthorhombic V_2O_5

- Mg cycling when begun in empty (charged)-V_2O_5 stays in α
  - ✦ Voltage profile match with experiments
- δ is better than α
  - ✦ Better migration barriers for Mg^{2+}, Ca^{2+}
  - ✦ Better voltages for Mg^{2+}, Zn^{2+}



- Mg cycling could be done on δ
  - ✦ Since $\alpha \rightarrow \delta$ transformation is hindered

Impact of increased layer spacing and/or co-intercalation?

- Case of Mg in **Xerogel-V_2O_5**

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Xerogel V_2O_5

Solvent co-intercalation

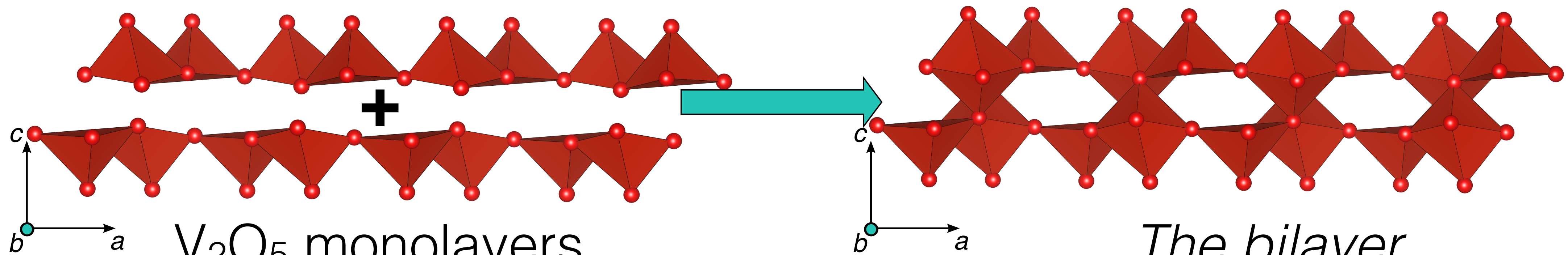
What is Xerogel-V_2O_5?

Does H_2O “shuttle” with Mg?

Hydrated version of V_2O_5

Possesses a “bilayer” structure

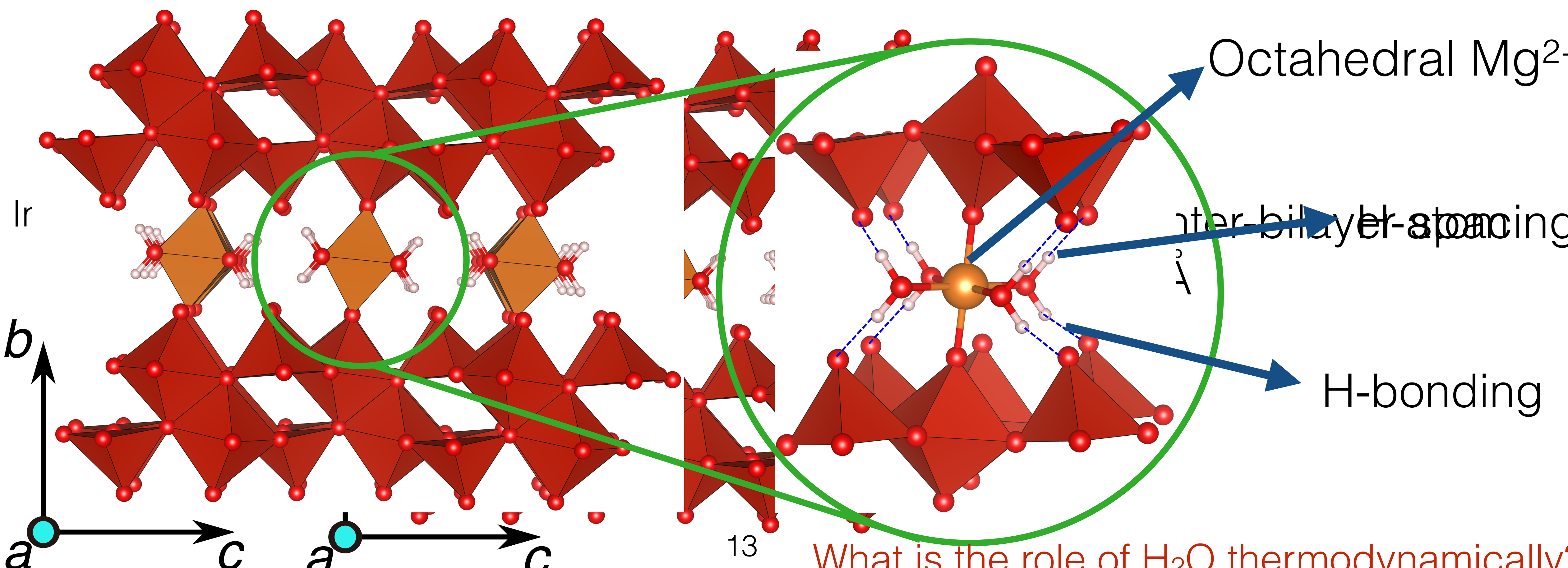
$$\text{Xerogel} \xrightarrow[-H_2O]{573\ \text{K}} \text{Orthorhombic}$$



V_2O_5 monolayers

The bilayer

H_2O + Ir



What is the role of H_2O thermodynamically?

Methods detour: how do we calculate grand-potential phase diagrams?

Grand-potential phase diagrams are used to study open systems

$$\Phi = G_{\mathrm{MgV_2O_5}} - n_{\mathrm{H_2O}} . \mu_{\mathrm{H_2O}}$$

Grand-potential (Φ)
Governing thermodynamic potential
Minimize this to get stable phases

Gibbs energy (*G*)
Xerogel Mg-V_2O_5 with H_2O
Computed with DFT

Number of moles of H_2O (*n*)
In a given Xerogel structure

Chemical potential of H_2O (μ)
External to the Xerogel (electrolyte)
Can be expressed in activities

$$\mu_{\mathrm{H_2O}} = \mu^0_{\mathrm{H_2O}} - RT \ln a_{\mathrm{H_2O}}$$

Computed with DFT (Vapor)
Corrected with experimental values

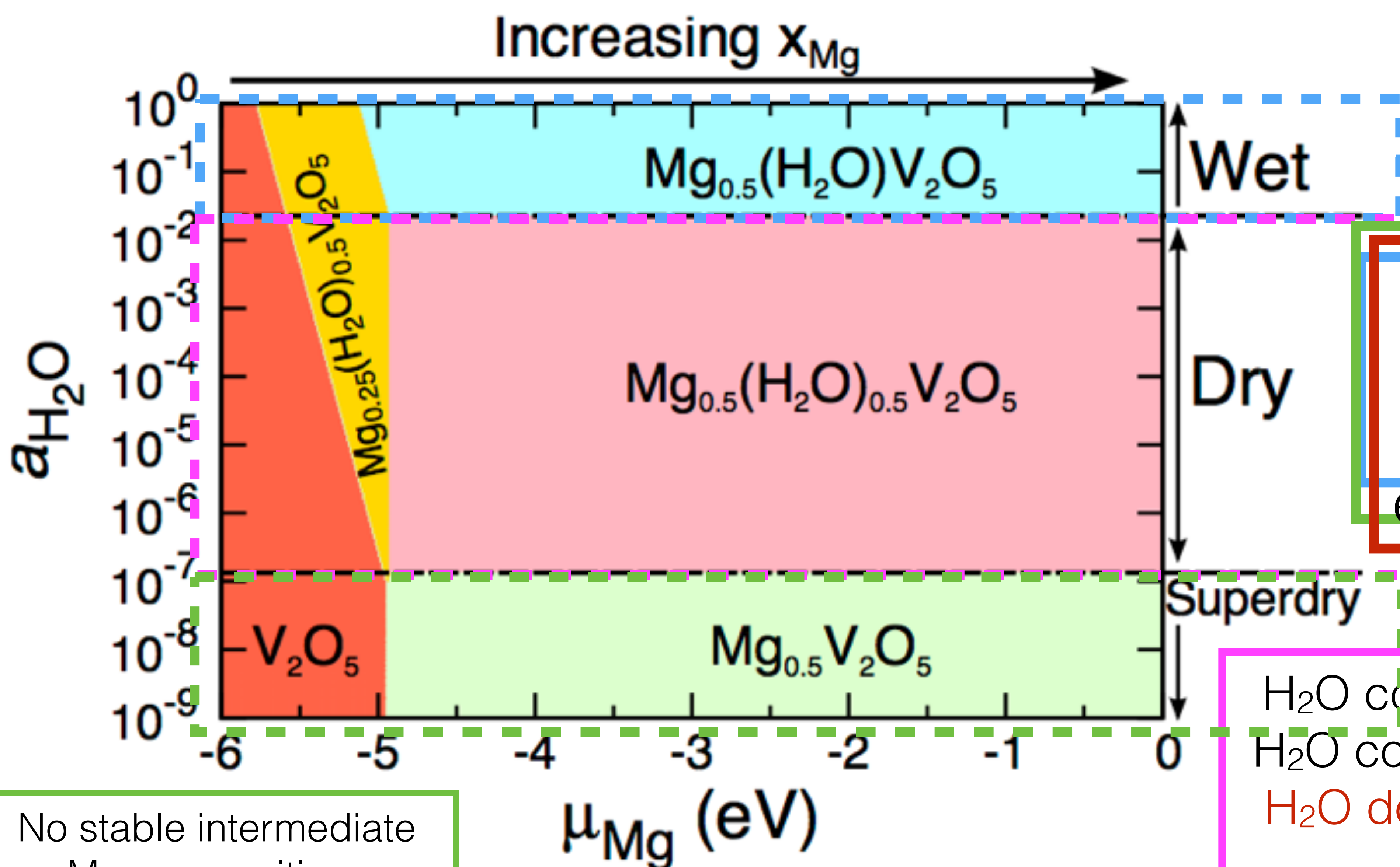
Set manually based on wet, dry and superdry conditions

Grand-potential phase diagram

Electrolyte-dependent H_2O shuttling

$$\Phi = G_{\mathrm{MgV_2O_5}} - \boxed{n_{\mathrm{H_2O}} \cdot \mu_{\mathrm{H_2O}}} - \boxed{x_{\mathrm{Mg}} \cdot \mu_{\mathrm{Mg}}}$$

Activity **Voltage**



All H_2O exits from the Xerogel structure

Water+Mg co-intercalation depends on electrolyte conditions

H_2O content changes with Mg content

No H_2O shuttling with Mg

H_2O shuttles with Mg

No stable intermediate Mg compositions

H_2O content changes at low x_{Mg}
H_2O content constant at high x_{Mg}
H_2O does not shuttle with Mg at high x_{Mg}

G. Sai Gautam *et al.*, "Role of H_2O in intercalation electrodes: the case of Mg in nano-crystalline Xerogel-V_2O_5", **Nano Lett.** (accepted)

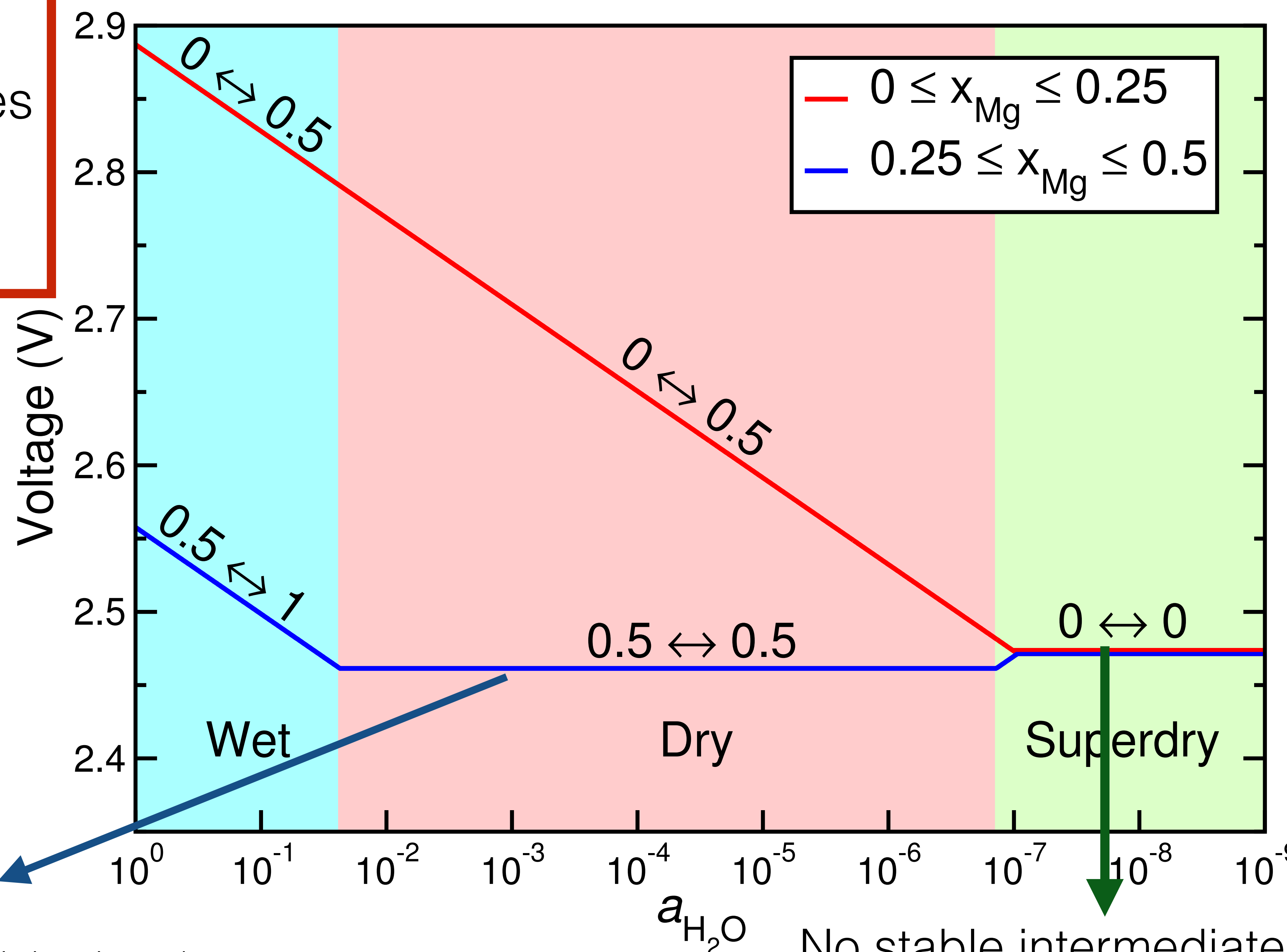
Voltage curves

Electrolyte-dependent voltages could be important

Normally, V $\propto(-\nabla\mu_{Mg})$

When H_2O co-intercalates with Mg,
Voltage $\propto(-\nabla\mu_{Mg},-\nabla\mu_{H_2O})$

Voltage in wet > dry



No water shuttling with Mg

No stable intermediate Mg compositions

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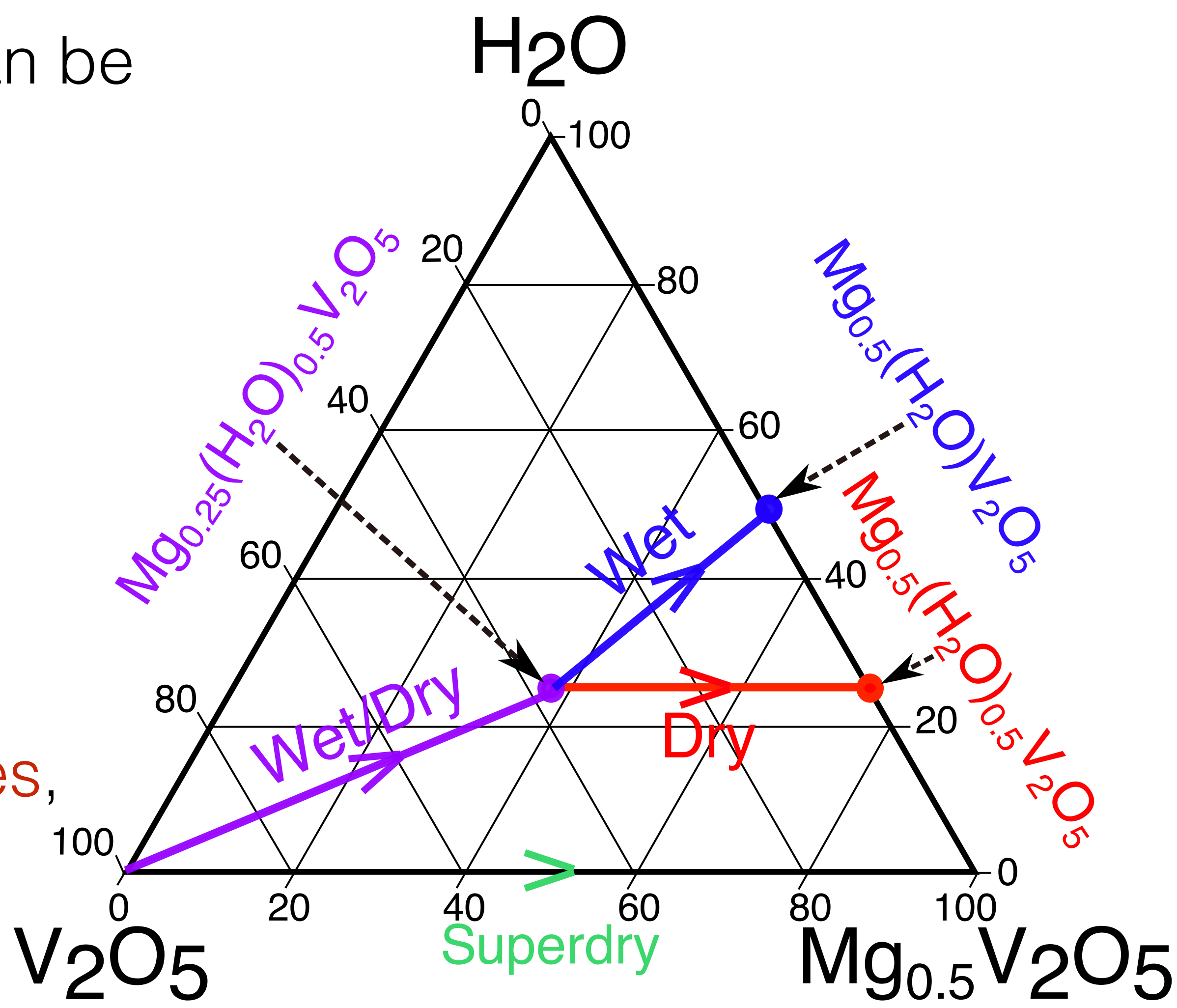
Summary: Xerogel-V_2O_5

- Solvent co-intercalation can impact an electrode's performance
- Sluggish mobility of Mg in oxide frameworks can be partly overcome through water co-intercalation
    - Electrostatic shielding by H_2O molecules
- Water co-intercalation depends on electrolytic conditions
    - Full (wet) → Part (dry) → None (superdry)
- Voltages can become dependent on electrolytes, leading to important consequences
    - Because of solvent co-intercalation
- Work can be extended to other solvent co-intercalation systems



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Conclusions

- A potential way to improve the energy density of modern secondary batteries is to use a MV chemistry
- New chemistry leads to new challenges: the chief being cathode search

- Orthorhombic V_2O_5 holds promise for MV systems, with δ predicted to have superior performance than α
- Solvent co-intercalation can mitigate sluggish MV mobility, with consequent impacts on the voltages and phase behavior as illustrated by the Mg-Xerogel V_2O_5 system

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