Intercalation phase diagram of Mg in V_2O_5 from first principles

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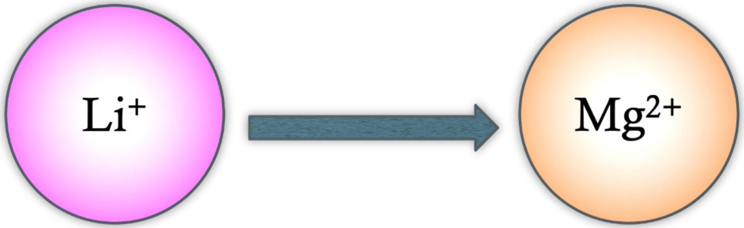
"**The Intercalation phase diagram of Mg in V_2O_5 from first principles**"
(submitted)

V_2O_5: Critical to cathode design of Mg-batteries

Why Mg?

- Next generation electrical devices benefit from high energy density storage systems
- Superior volumetric capacity for Mg metal anode (~3833 mAh/cm^3) vs. Li metal anode (~2046 mAh/cm^3)



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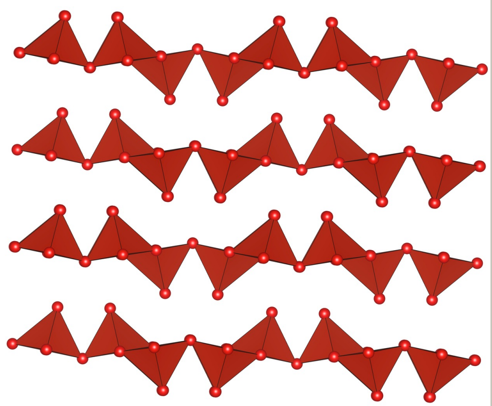
- New chemistry: Cathode design challenge
  - High voltage, high rates, high capacity



Why V_2O_5?

- One of only 3 cathodes to reversibly intercalate Mg
  - Others: Chevrel Mo_3S_4,[1] Layered MoO_3[2]
  - Higher voltage and lower volume change in V_2O_5
- Known Li intercalant

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

How does Mg intercalate into V_2O_5?

Characterize the system through DFT

Ground State hull and Voltage curves

- Benchmark with experiments

↓

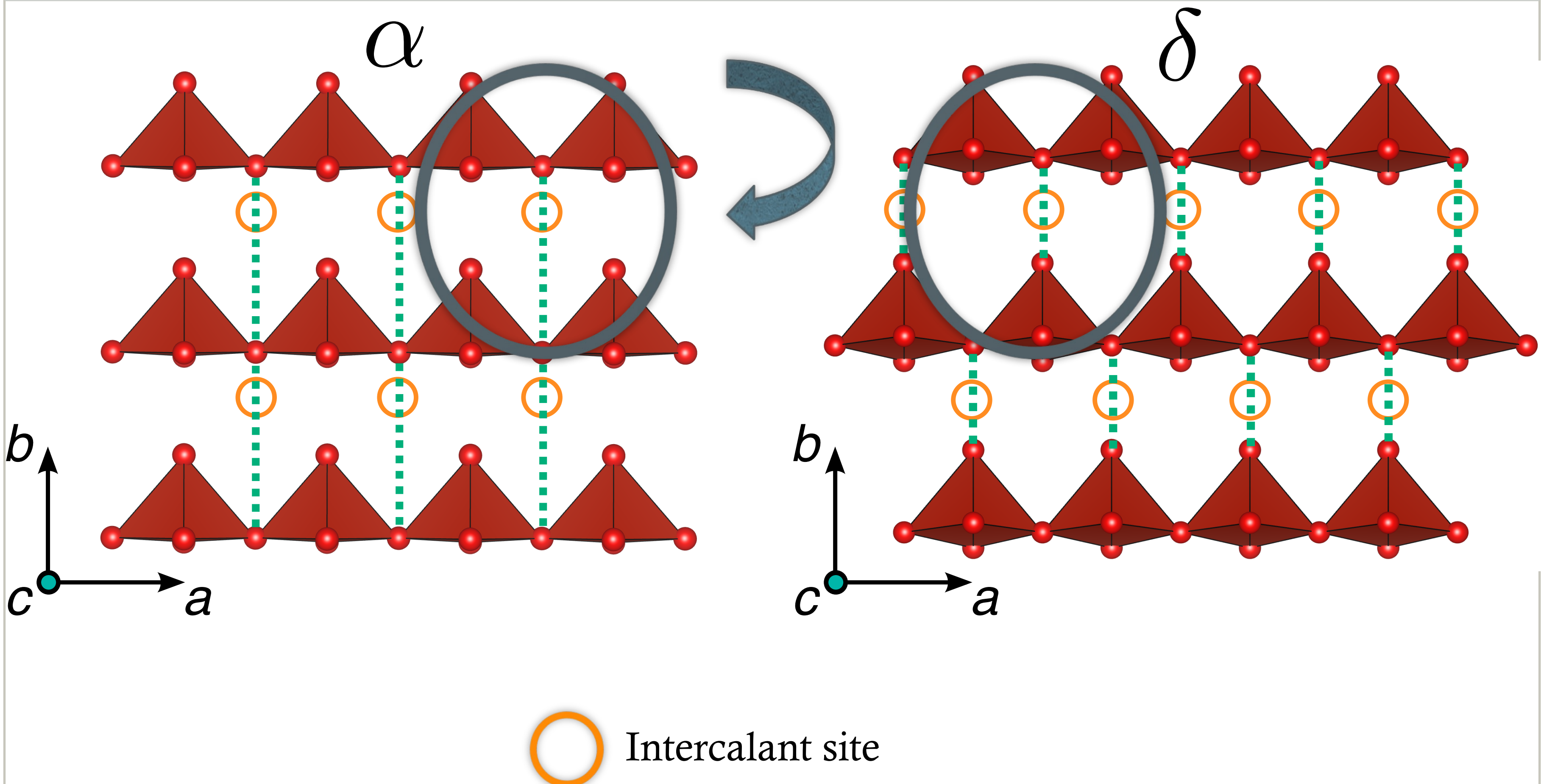
Mg migration barriers

- Determine phase(s) of interest

↓

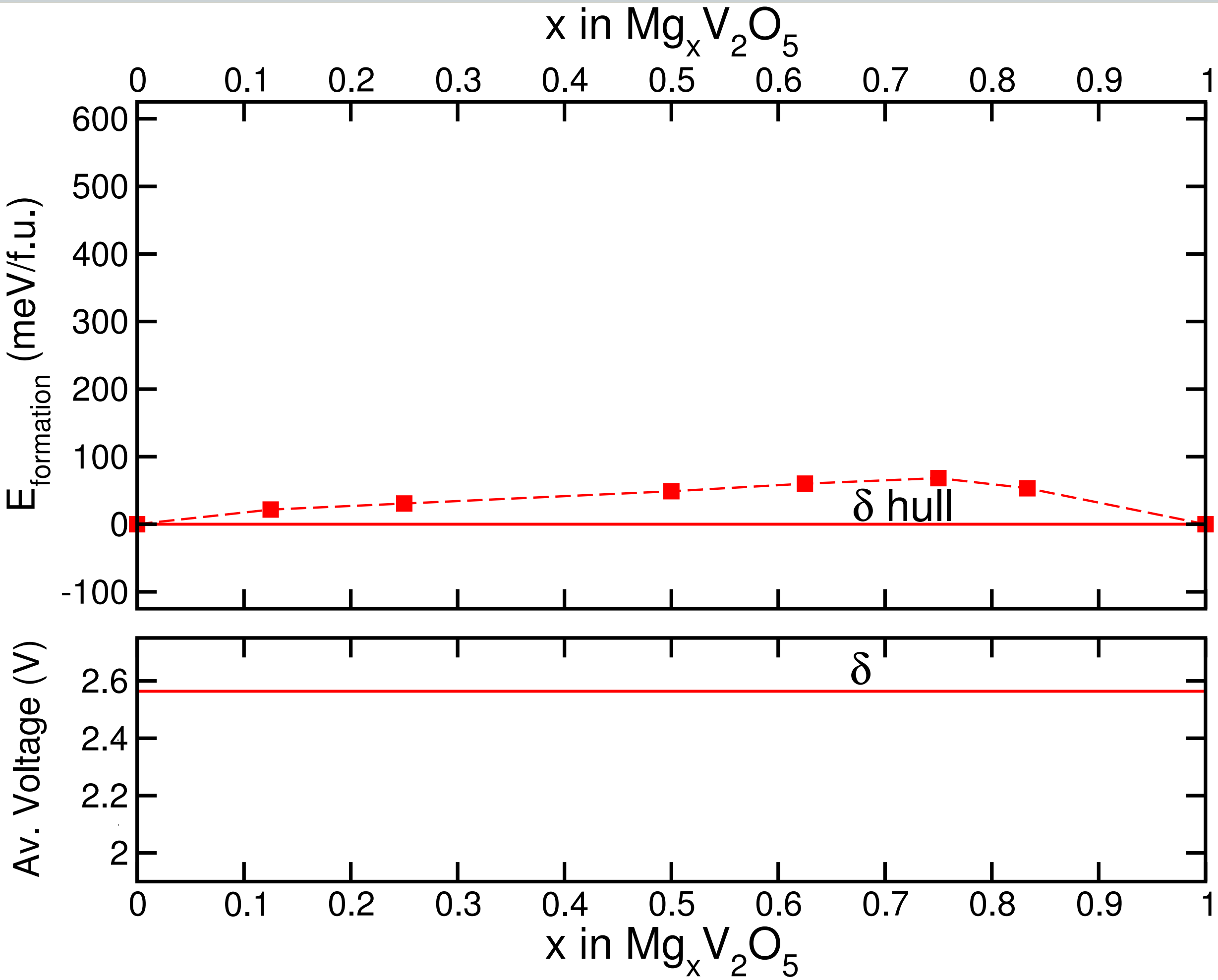
Suggestions to improve performance

Polymorphs of Orthorhombic V_2O_5



Ground State Hull and Voltages

δinserts Mg at a higher voltage than α



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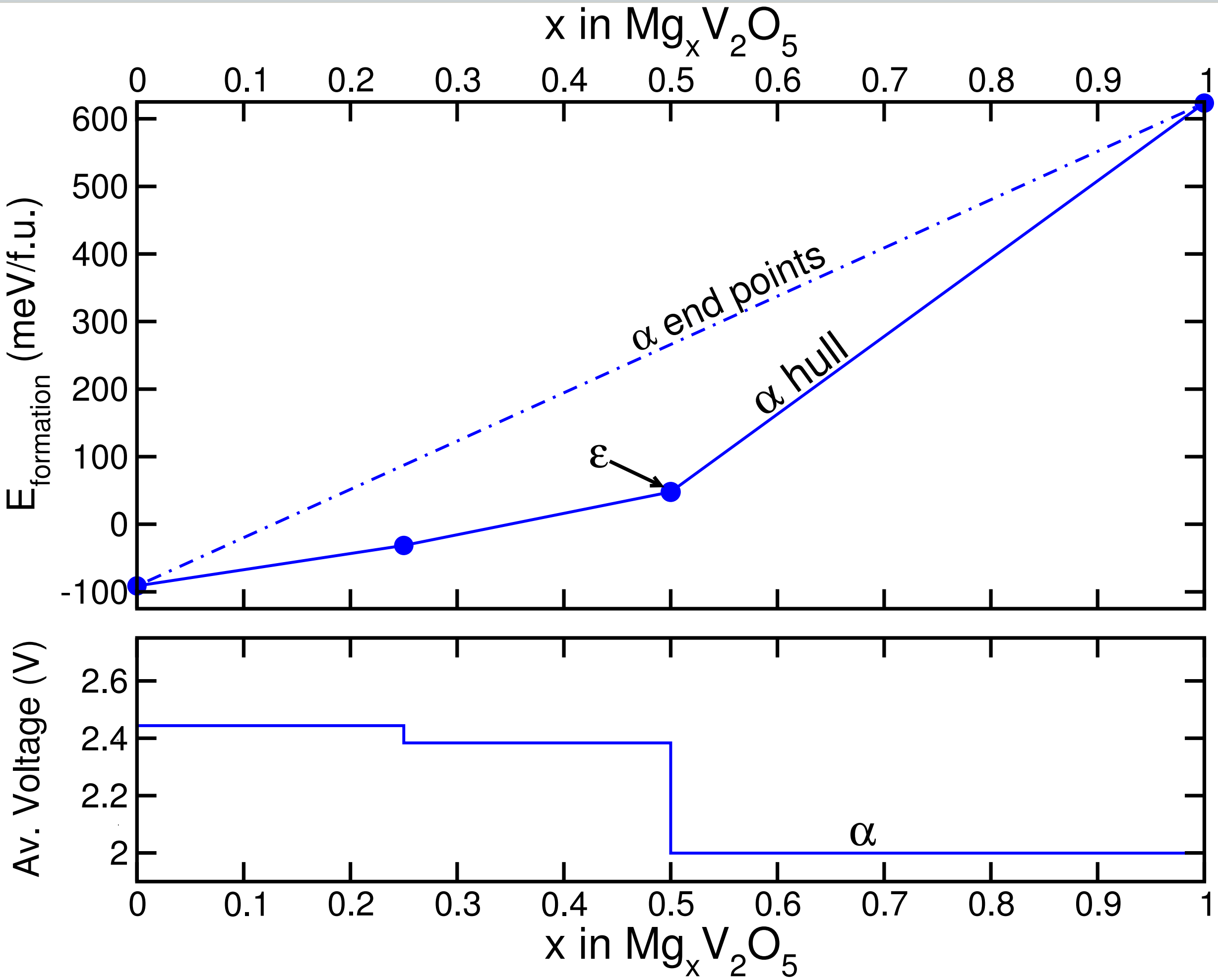

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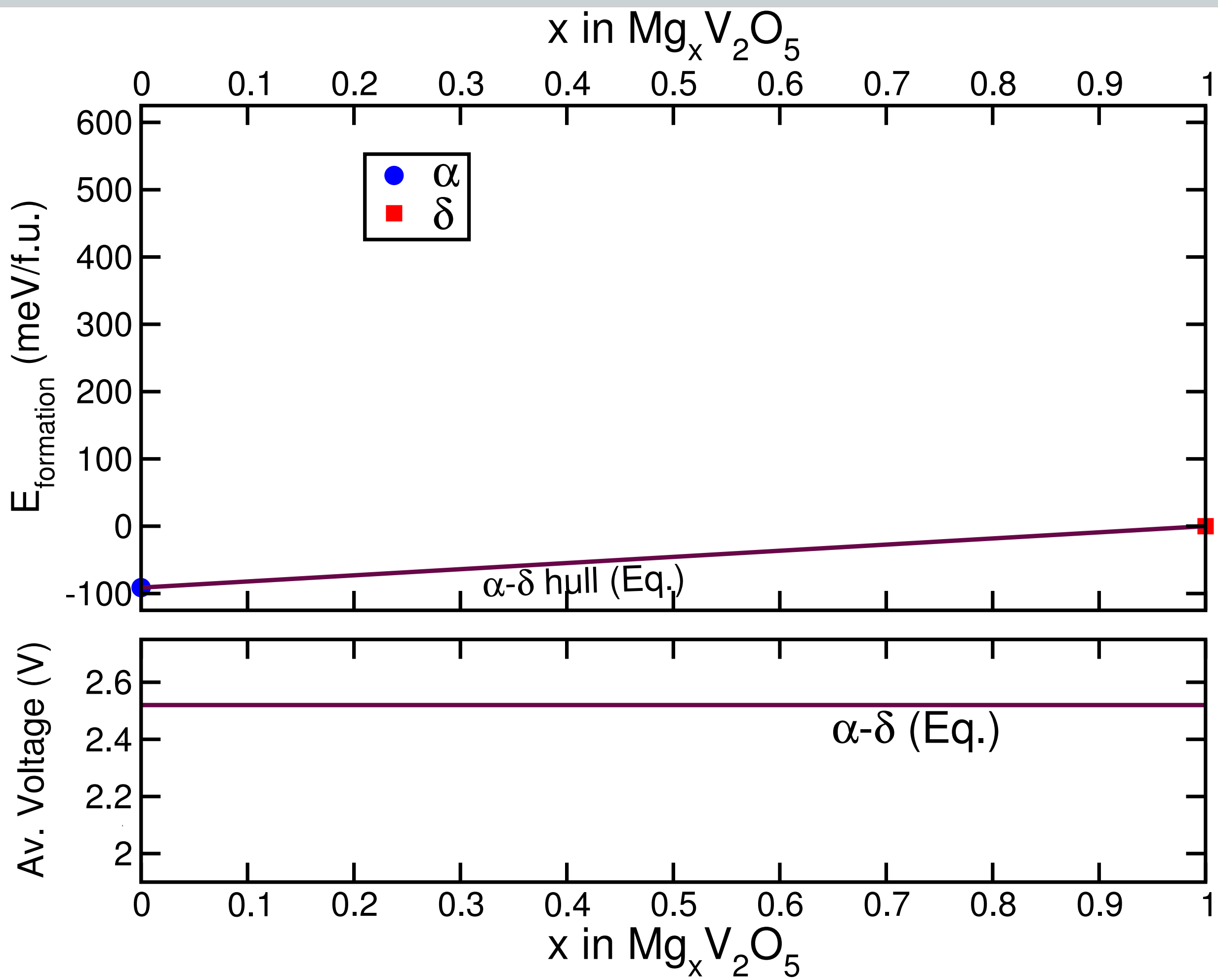

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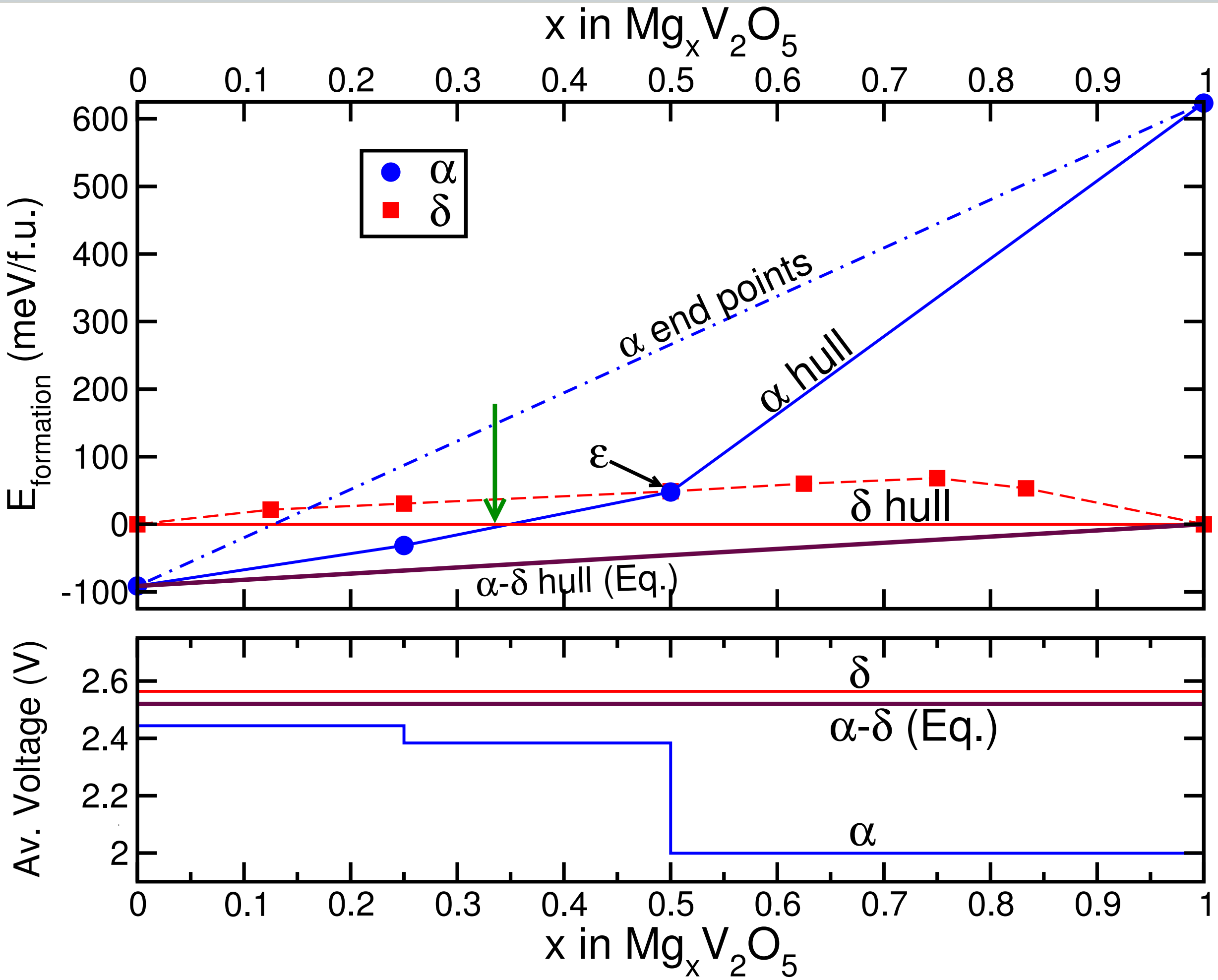
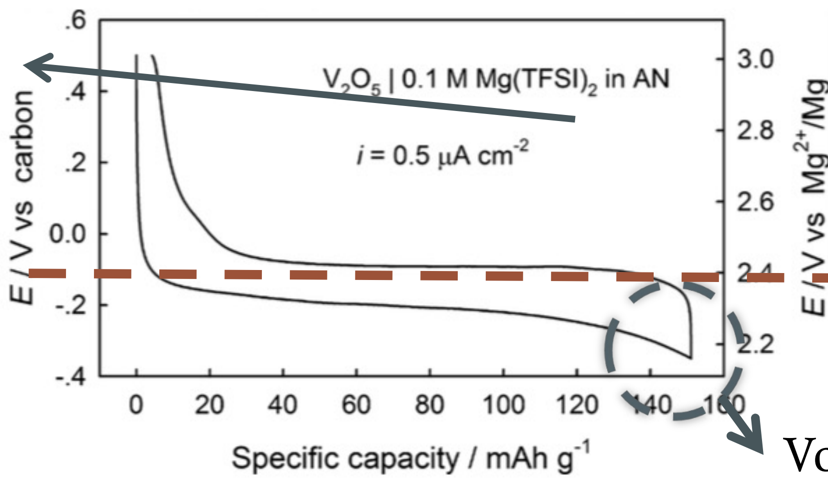


Experimental voltage profile matches α

δ~ 2.56 V
(δ>α)
No V drop

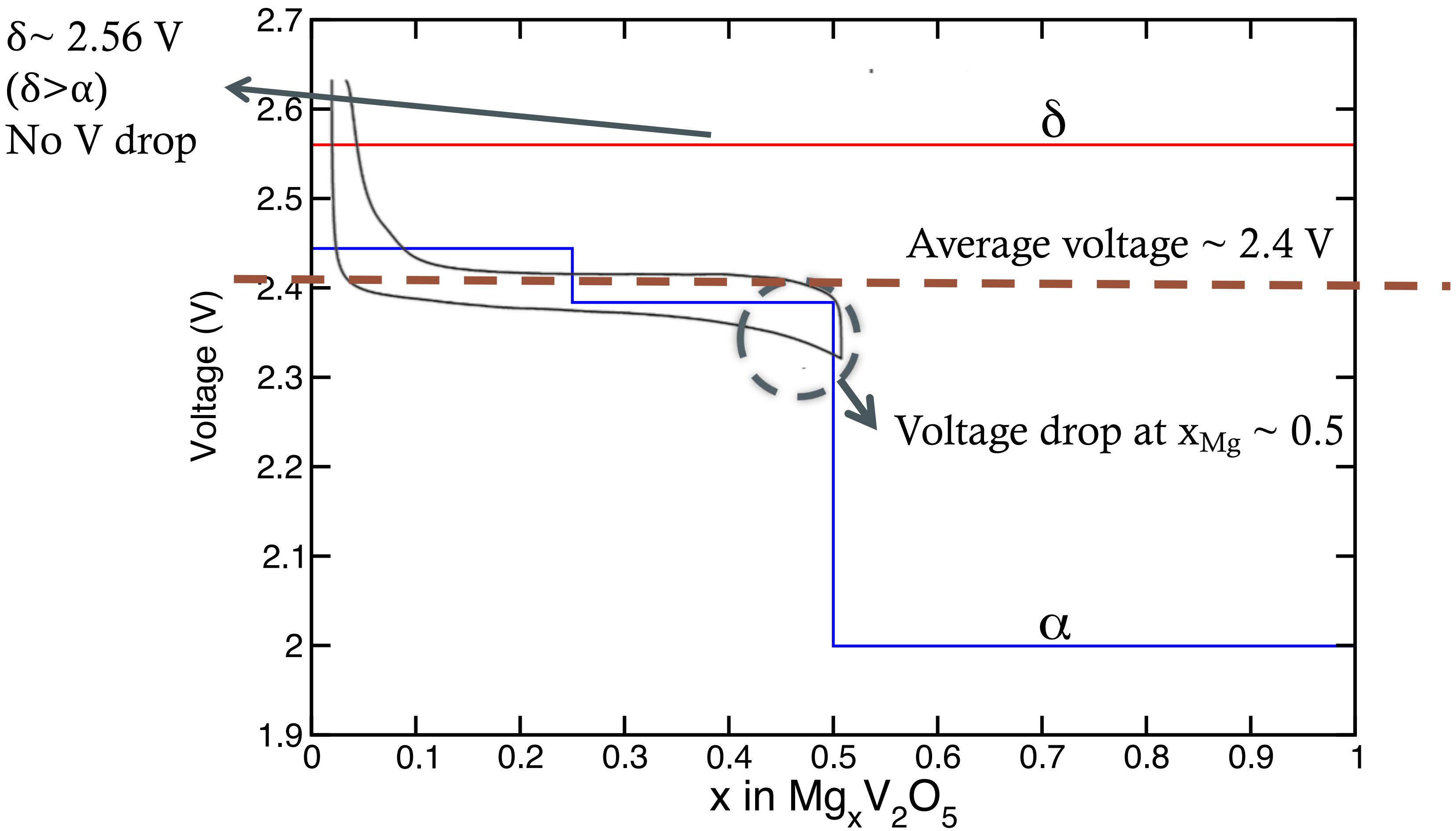


Average voltage ~ 2.35 V

Voltage drop at x_{Mg} ~ 0.5

Experimental voltage curve:
Gershinsky *et al.*, Langmuir, 2013

Experimental voltage profile matches α

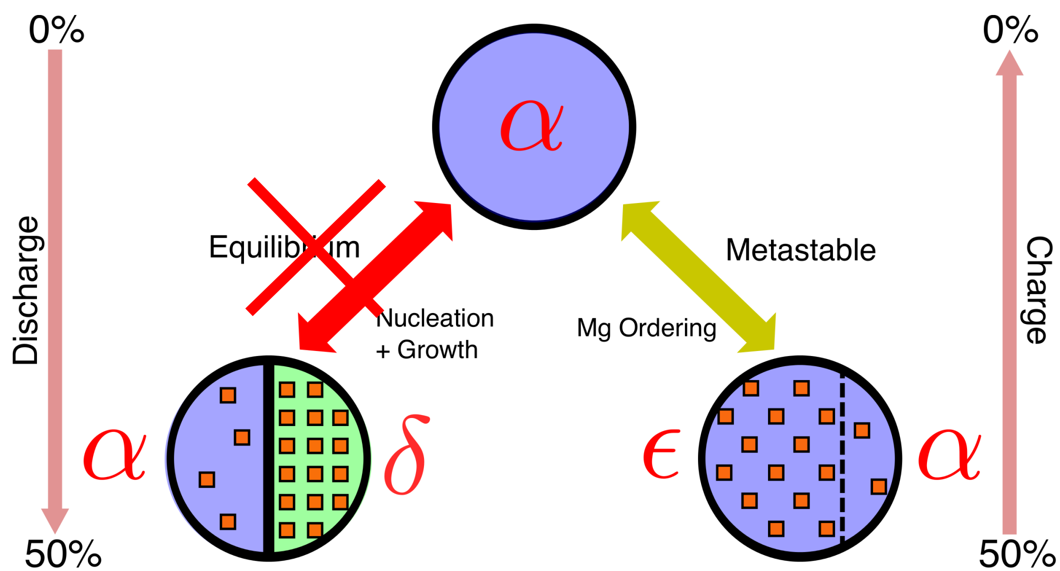


Experimental voltage curve:
Gershinsky *et al.*, Langmuir, 2013

Experiments cycle Mg in α-V_2O_5

When Mg cycling is started in empty (charged) V_2O_5

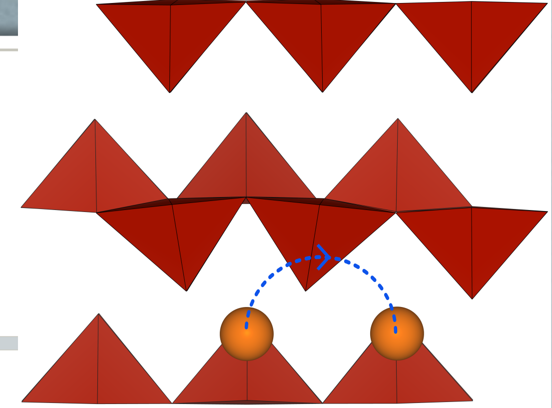
- Experimental voltage profile matches better with α
- α→ δ transformation requires structural rearrangement
- δ-V_2O_5, if accessed, could be metastable upon Mg cycling
  - δ-MgV_2O_5 has been experimentally synthesized[3]

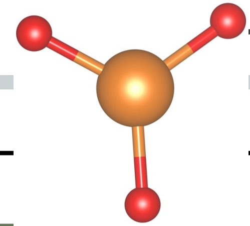


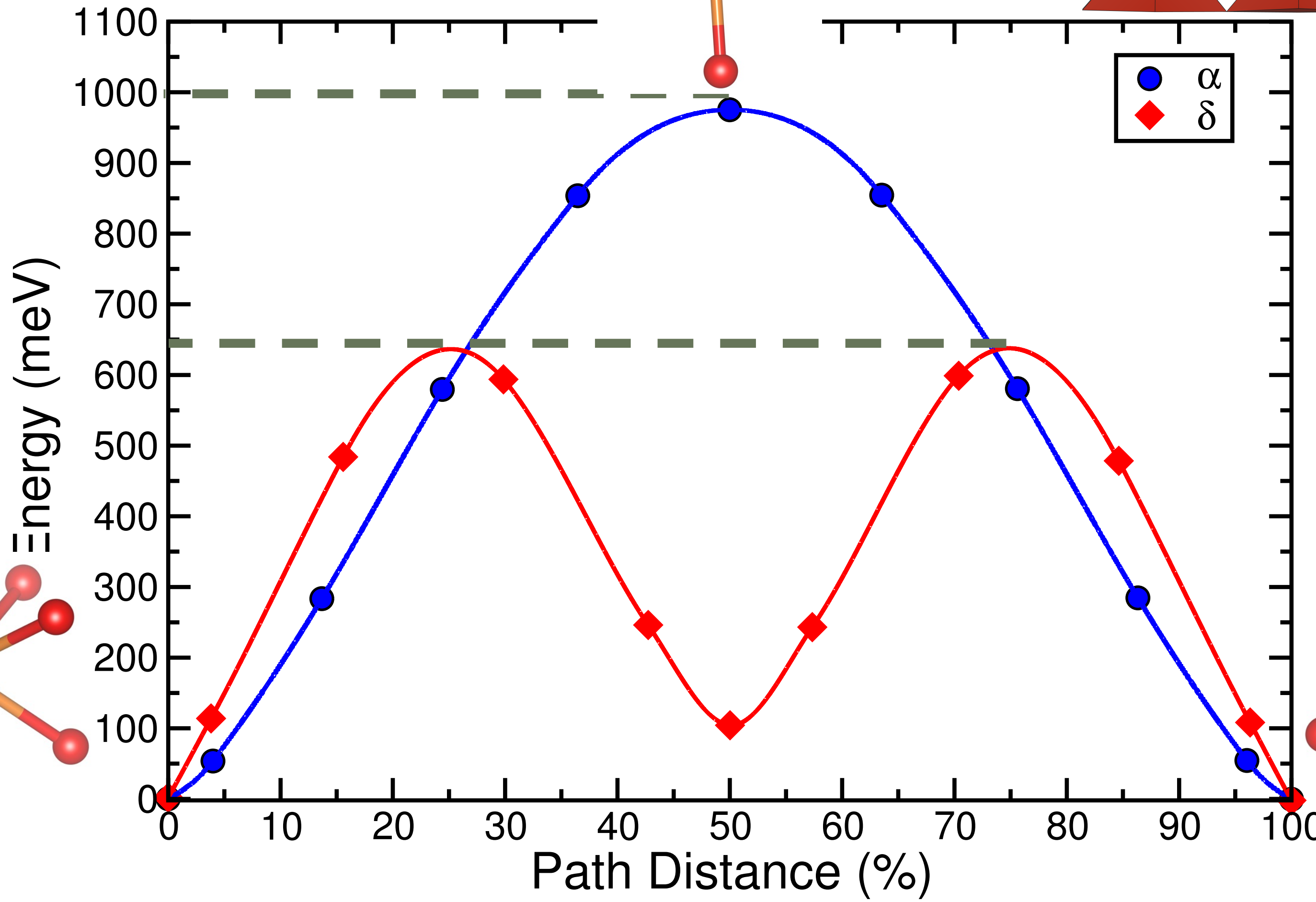
3. Satto *et al.*, J. Solid State Chem., 1998

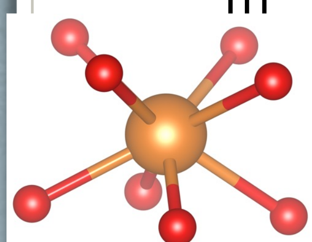
Mg Migration barrier

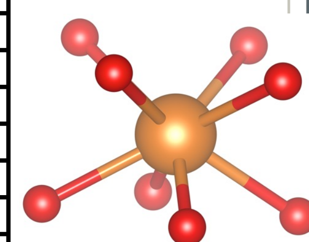
δis a better diffuser than α











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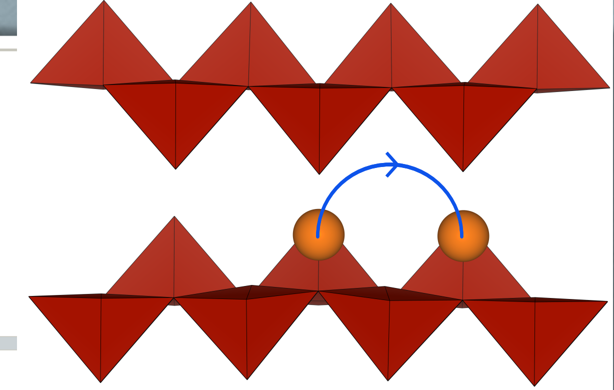
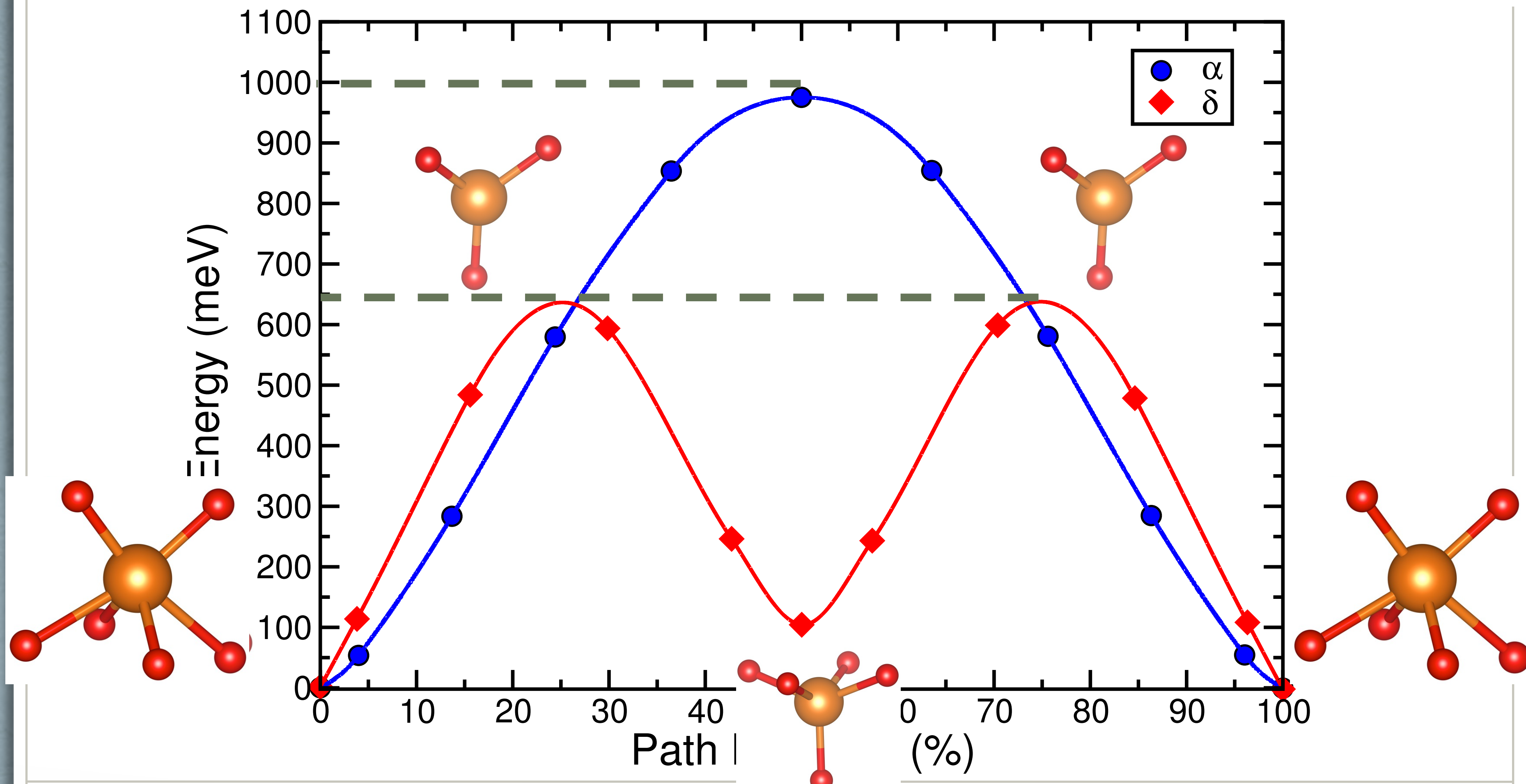
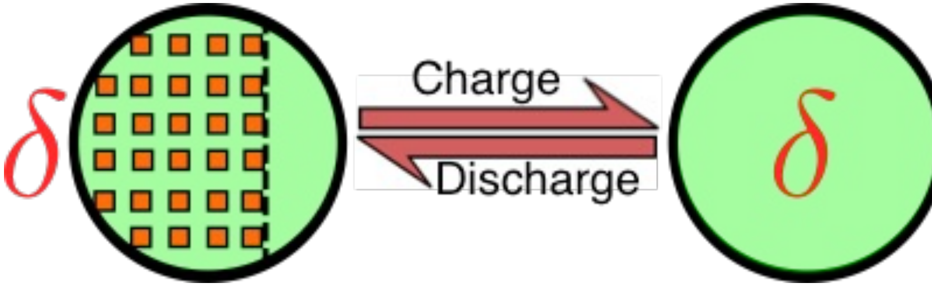




Conclusions

Mg cycling in δis better than α

- Mg cycling when begun in empty (charged) V_2O_5 stays in α
  - Voltage profile matches with experiments
- δis better than α
  - Lower Mg migration barrier(s)
  - Higher Mg insertion voltage



Mg cycling when begun in full (discharged) V_2O_5 could stay in δ

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