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

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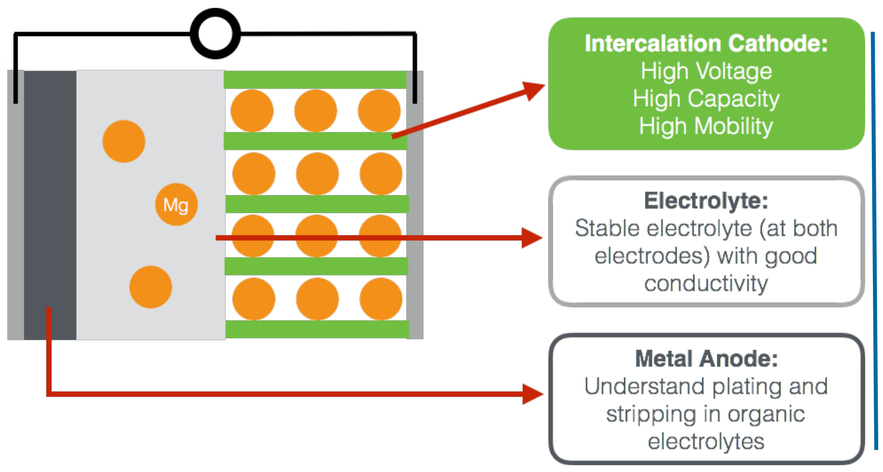
How does Mg intercalate into V_2O_5?

- ✓ Next generation of electric devices will benefit from higher energy density storage systems
- ✓ New chemistry: new challenges, one of which is finding cathodes that can reversibly intercalate multi-valent (MV) ions at high voltage, high capacity and high rates
- ✓ V_2O_5 is critical for designing multi-valent cathodes



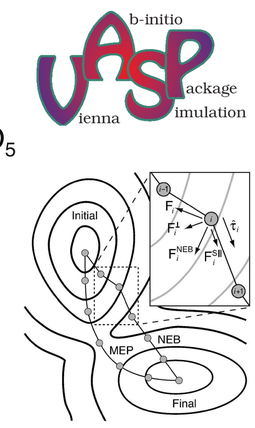
Methods

Density Functional Theory (DFT)

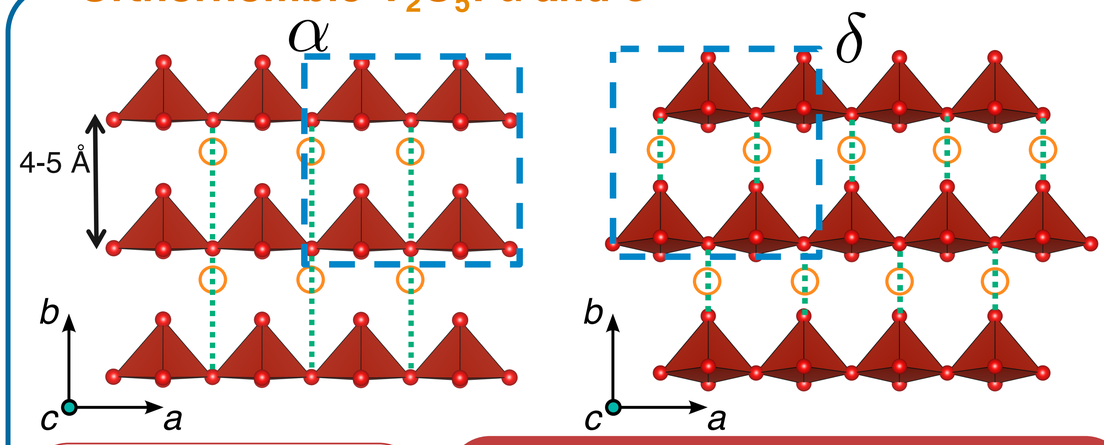
- Resolve structures
  - H_2O positions in Xerogel-V_2O_5
- 0 K phase diagrams
- Voltages

Nudged Elastic Band (NEB)

- Activation barriers for ionic diffusion[1]
- DFT-based NEB



Orthorhombic-V_2O_5: α and δ

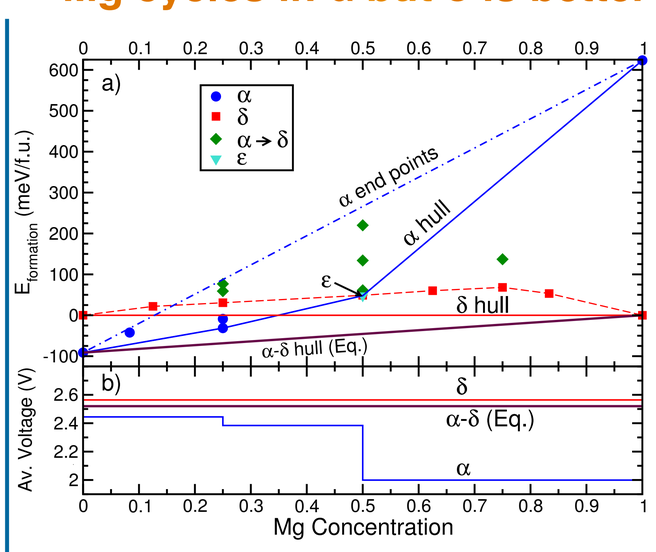


- ✓ Layer stacking difference between α and δ
- ✓ Difference in Mg (MV) Coordination: 8 in α and 6 in δ

How does Mg intercalation compare in α and δ?

- Benchmark experimental voltage curves with theoretically predicted curves
- Estimate activation barrier for Mg diffusion in both polymorphs

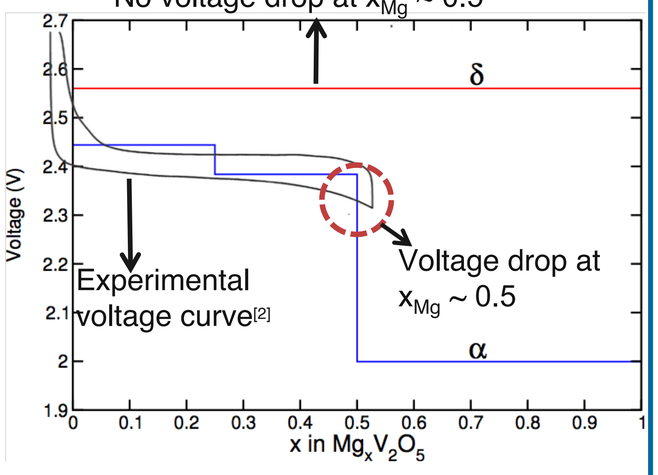
Mg cycles in α *but* δ is better



DFT-prediction:
2-phase behavior between empty α and magnesiated δ

δ ~ 2.56 V > α

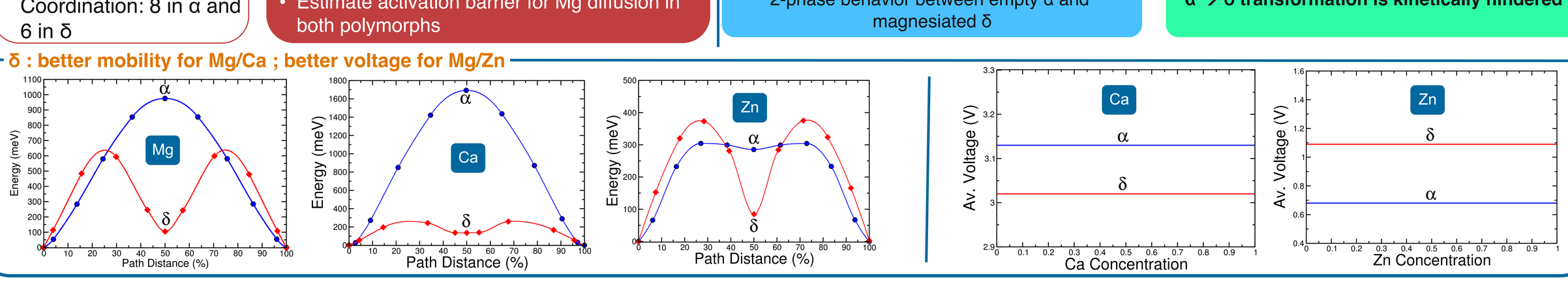
No voltage drop at x_{Mg} ~ 0.5



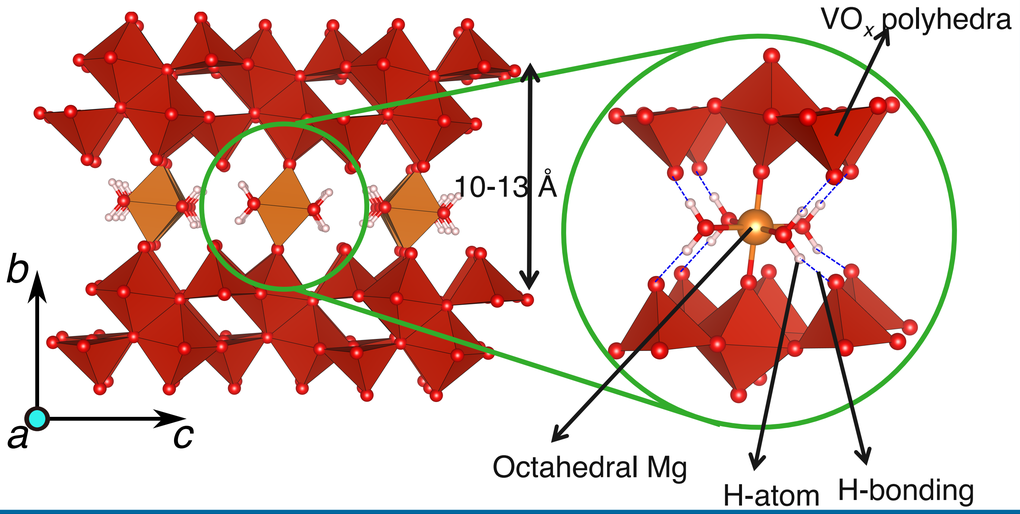
Experimental voltage curve matches prediction for α

Experiments: Mg cycles in α
α → δ transformation is kinetically hindered

δ : better mobility for Mg/Ca ; better voltage for Mg/Zn



Xerogel-V_2O_5: hydrated structure



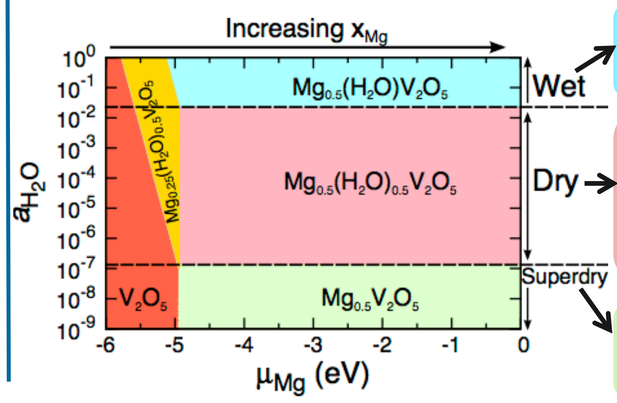
H_2O co-intercalates with Mg^{2+} in wet electrolytes

Does H_2O stay in Xerogel or shuttle with Mg^{2+}?

- Use grand-potential phase diagrams

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

Gibbs energy (DFT) | Water content in electrolyte | Voltage



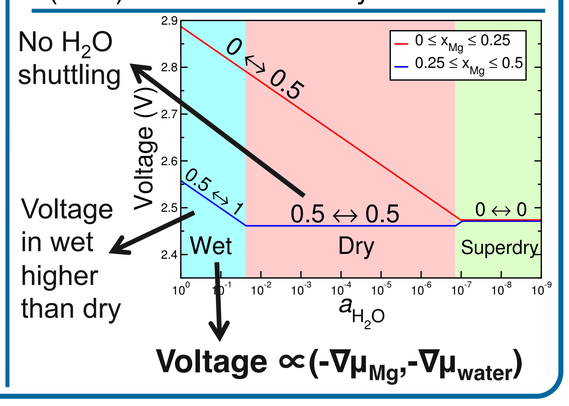
H_2O content change with x_{Mg}: **H_2O shuttles**

H_2O content constant at high x_{Mg}: **H_2O does not shuttle at high x_{Mg}**

H_2O exits Xerogel: **H_2O does not shuttle**

No H_2O shuttling

Voltage in wet higher than dry



Voltage ∝ $(-\nabla\mu_{Mg}, -\nabla\mu_{water})$

Key Take-Away

- ✓ A potential way to improve energy density over Li-ion is to use MV-chemistry
- ✓ Finding cathode materials that can cycle MV-ions is a significant challenge
- ✓ Orthorhombic V_2O_5 holds promise since δ is predicted to be better than α
- ✓ Solvent (H_2O) co-intercalation can have a significant impact on the voltage and phase behavior of an electrode, while mitigating sluggish (Mg^{2+}) mobility

Relevant publications:

1. G. Sai Gautam, *et al.*, "The Intercalation phase diagram of Mg in V_2O_5 from first principles", **Chem. Mater., 2015, *27*(10), 3733-3742**
2. G. Sai Gautam, *et al.*, "First-principles evaluation of multi-valent cation insertion into orthorhombic V_2O_5", **Chem. Commun., 2015, *51*, 13619-13622**
3. 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)

References:

1. D. Sheppard et al., J. Chem. Phys., 2008, 128, 134106
2. G. Gershinsky et al., Langmuir, 2013, 29, 10964-10972

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