The effect of the exchange-correlation functionals on migration barrier estimation in battery materials

Contributory Talk

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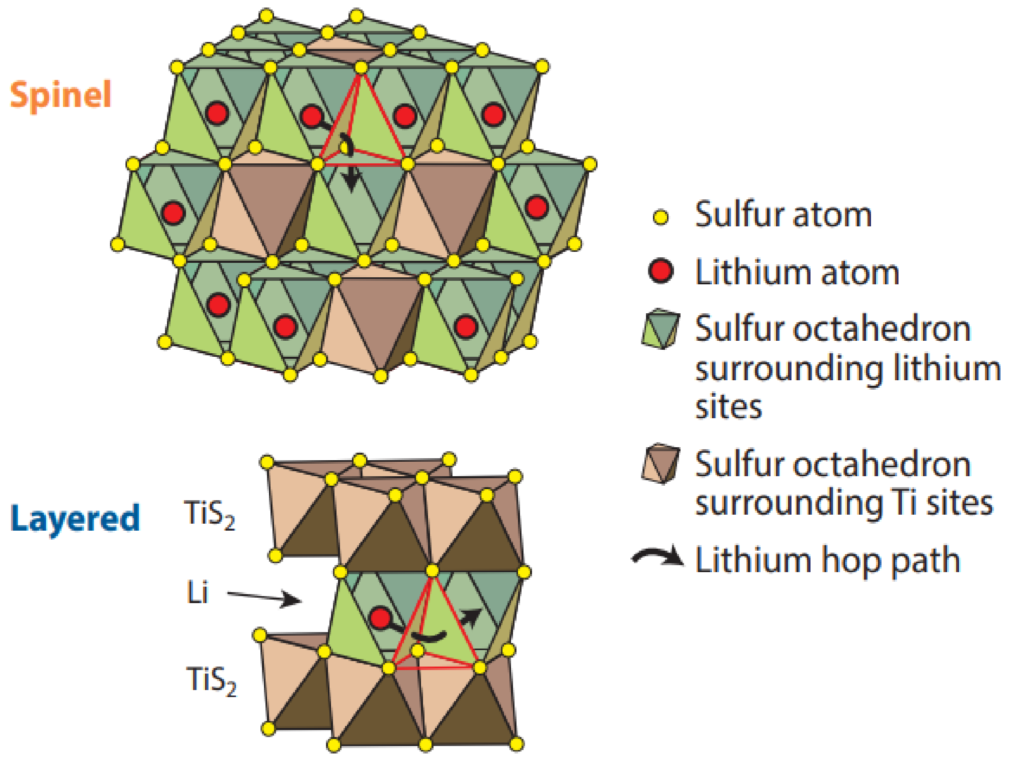
Rate performance of batteries is critical

- Better charging rates play a critical role in the application of Li and beyond-Li-ion battery technologies
- Intercalation systems: energy barrier to the diffusing ions in the host lattice primarily dictate the overall rate performance of the battery

$$D = D_0 exp(\frac{-E_m}{RT})$$

Activation Energy for Migration

Diffusivity

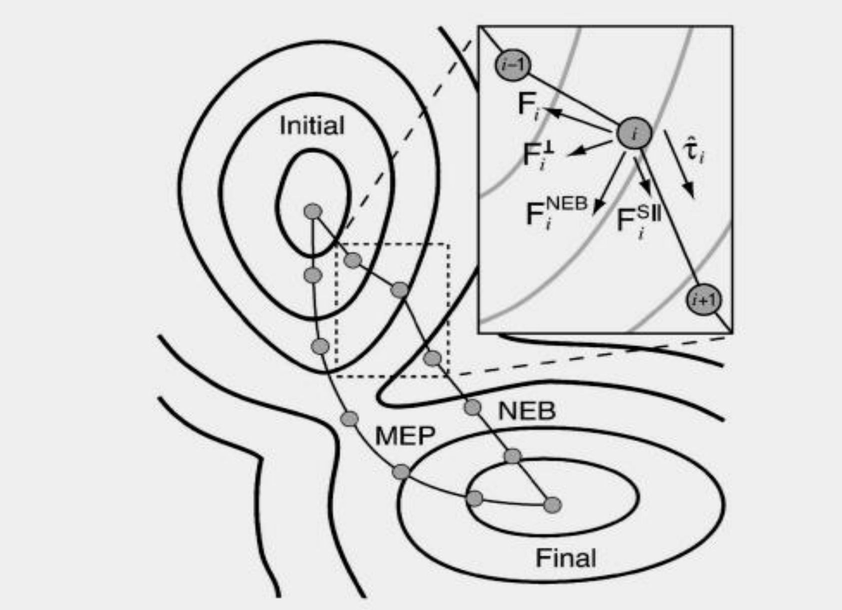


- Experimentally the energy barrier can be estimated using techniques such as variable temperature impedance spectroscopy and nuclear magnetic resonance

- **How accurate are theoretical/computational predictions of migration barriers (E_m) against available experimental data?**

Van der Ven, Anton, et al. *Annual Review of Materials Research* 48 (2018): 27-55.

Computational metrics for barrier estimation: 3 handles



- Nudged elastic band **(NEB)**[1] calculations are useful to estimate migration barriers computationally
- Typically uses 4-20 images to mimic an elastic band, and in turn estimate $\mathbf{E_m}$ and the minimum energy path **(MEP)**
- Parallel component (springs) of the force ensures equal spacing of the images
- In climbing image **(CI)**, spring forces on the image with highest energy is removed

NEB used in conjecture with Density Functional Theory(DFT)[2,3]

↓

Exchange correlational (XC) functional

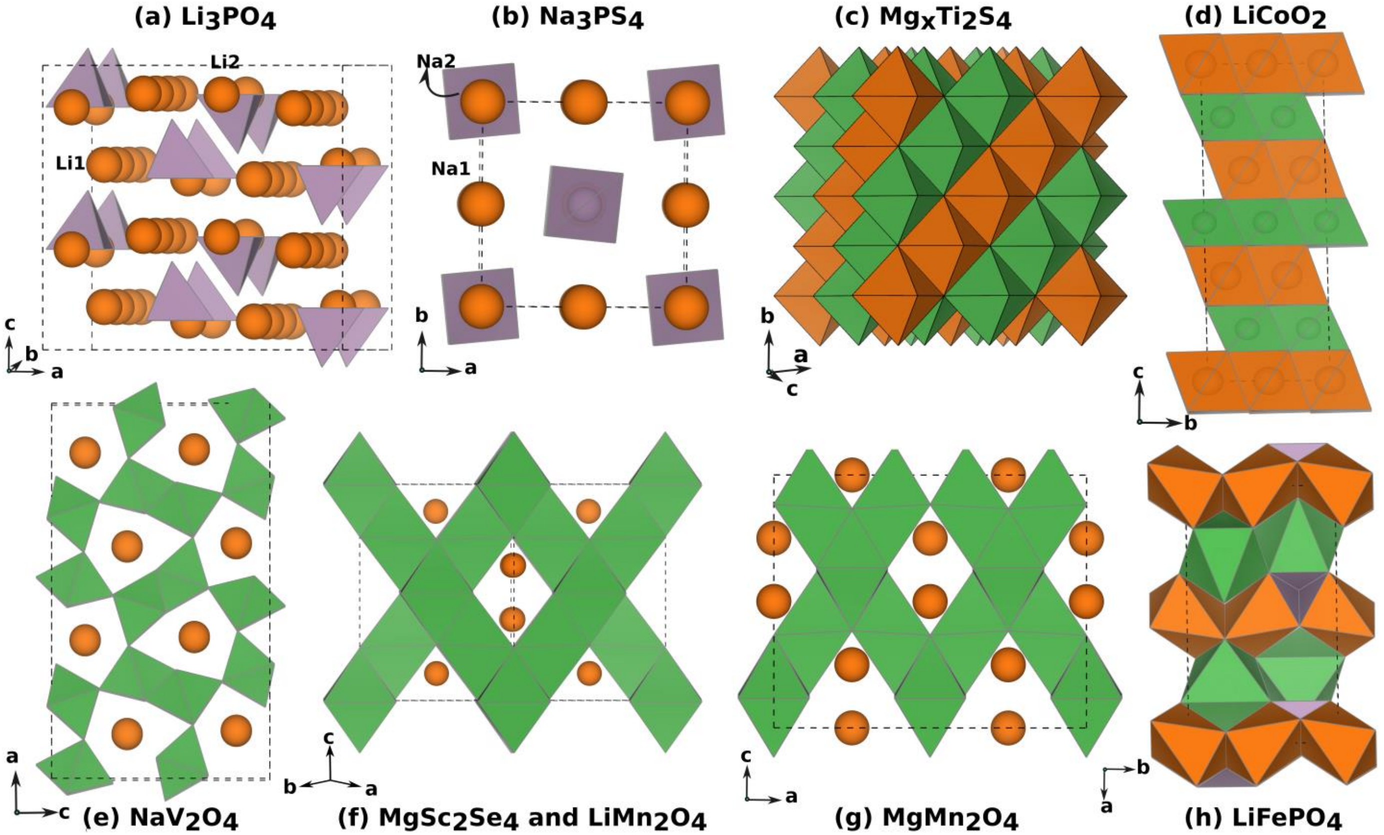
→ **XC choice**
  - **Strongly constrained and appropriately normed (SCAN)[5]**
  - **Generalized gradient approximation (GGA)[4]**
  - **DFT + Hubbard(*U*)[6]**

→ **Addition of uniform background charge (NELECT)**

→ **Addition of CI approximation**

1. Sheppard et al.J. Chem. Phys. 128, 134106 (2008)
2. Kohn, W. & Sham, L. J. Phys. review 140, A1133 (1965).
3. Hohenberg et al. Phys. review 136, B864 (1964).
4. Perdew, J. P et al. Phys. review letters 77, 3865 (1996).
5. Sun, J. et al.Nat. chemistry 8, 831–836 (2016).
6. Anisimov, V. et al. Phys. Rev. B 44, 943 (1991).

9 distinct systems considered



6 Electrodes

- $LiCoO_2$
- $Mg_xTi_2S_4$
- $LiFePO_4$
- $MgMn_2O_4$
- $LiMn_2O_4$
- NaV_2O_4

3 Electrolytes

- Li_3PO_4
- Na_3PS_4
- $MgSc_2Se_4$

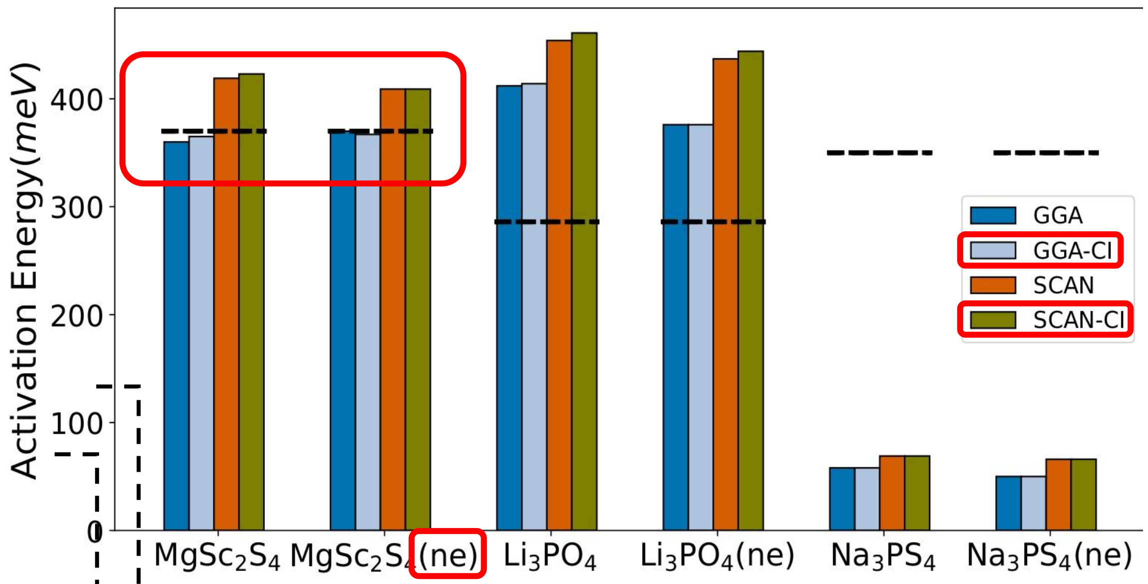
Availability of experimental data

Heterogeneity of intercalation ion

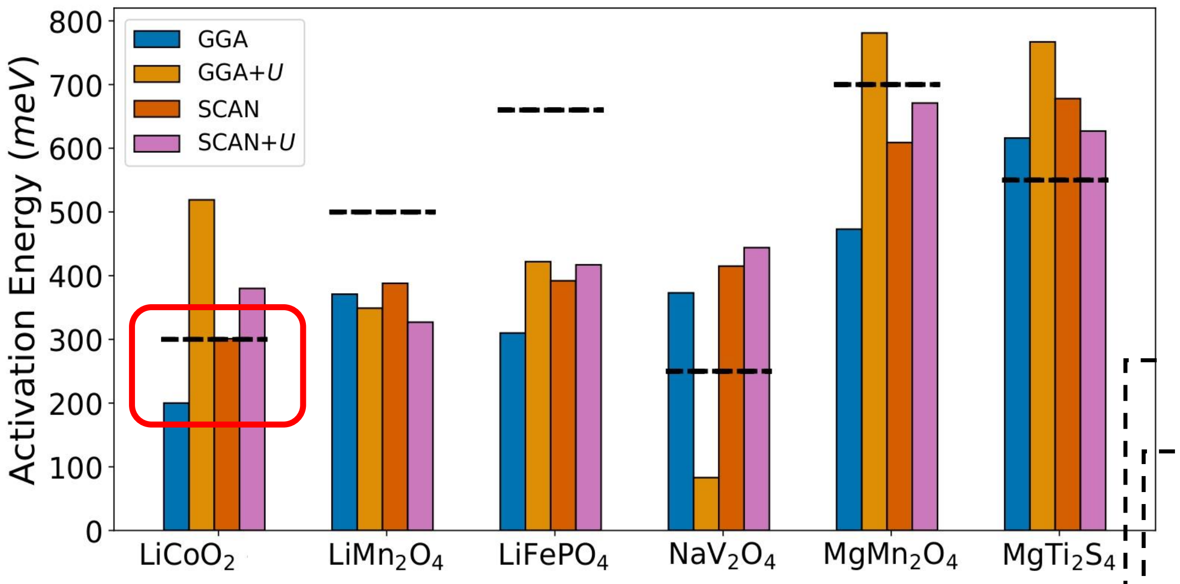
Diversity of structural frameworks

SCAN exhibits better numerical accuracy

Electrolytes



Electrodes



Addition of NELECT or CI does not affect E_m

E_m from SCAN > E_m from GGA

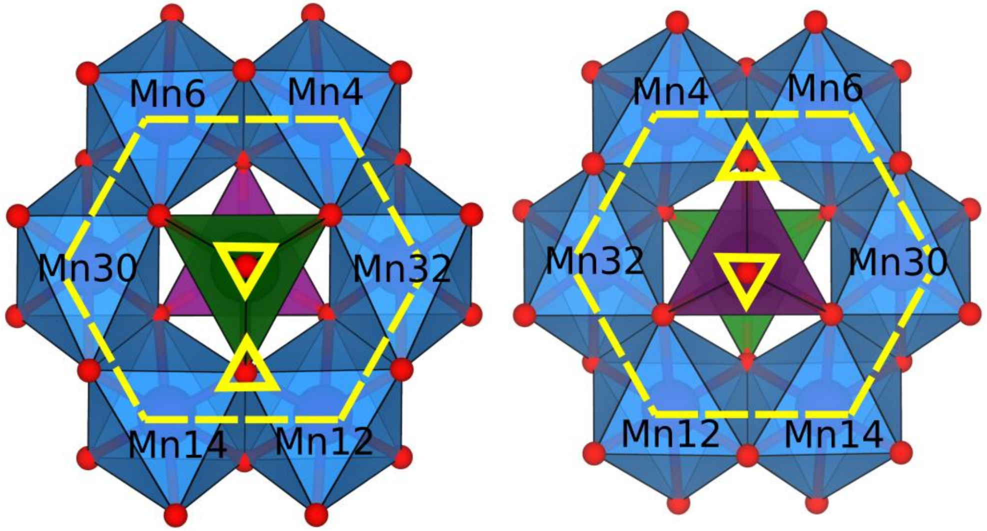
E_m from SCAN+*U* < E_m from GGA+*U*

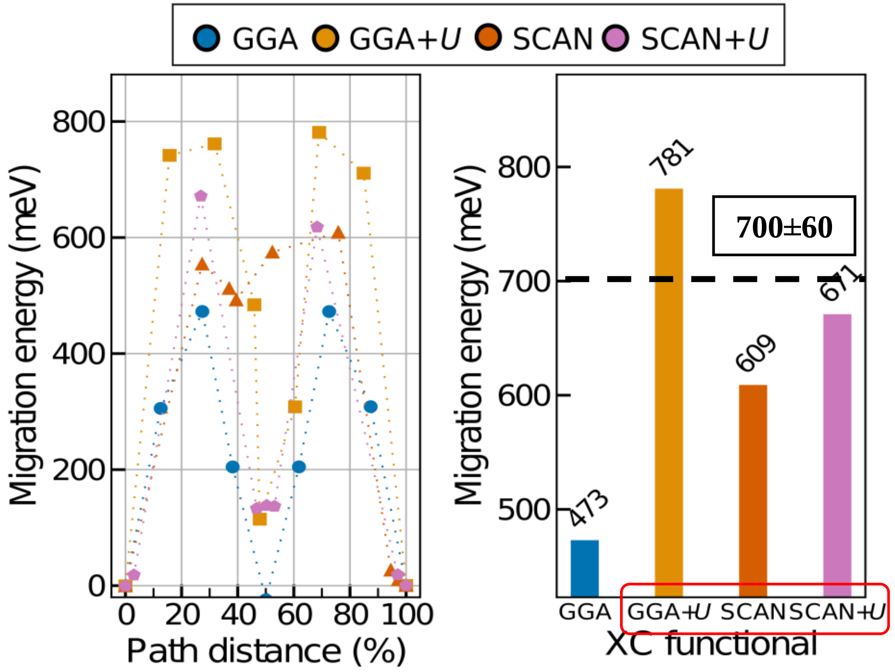
E_m from SCAN > E_m from GGA

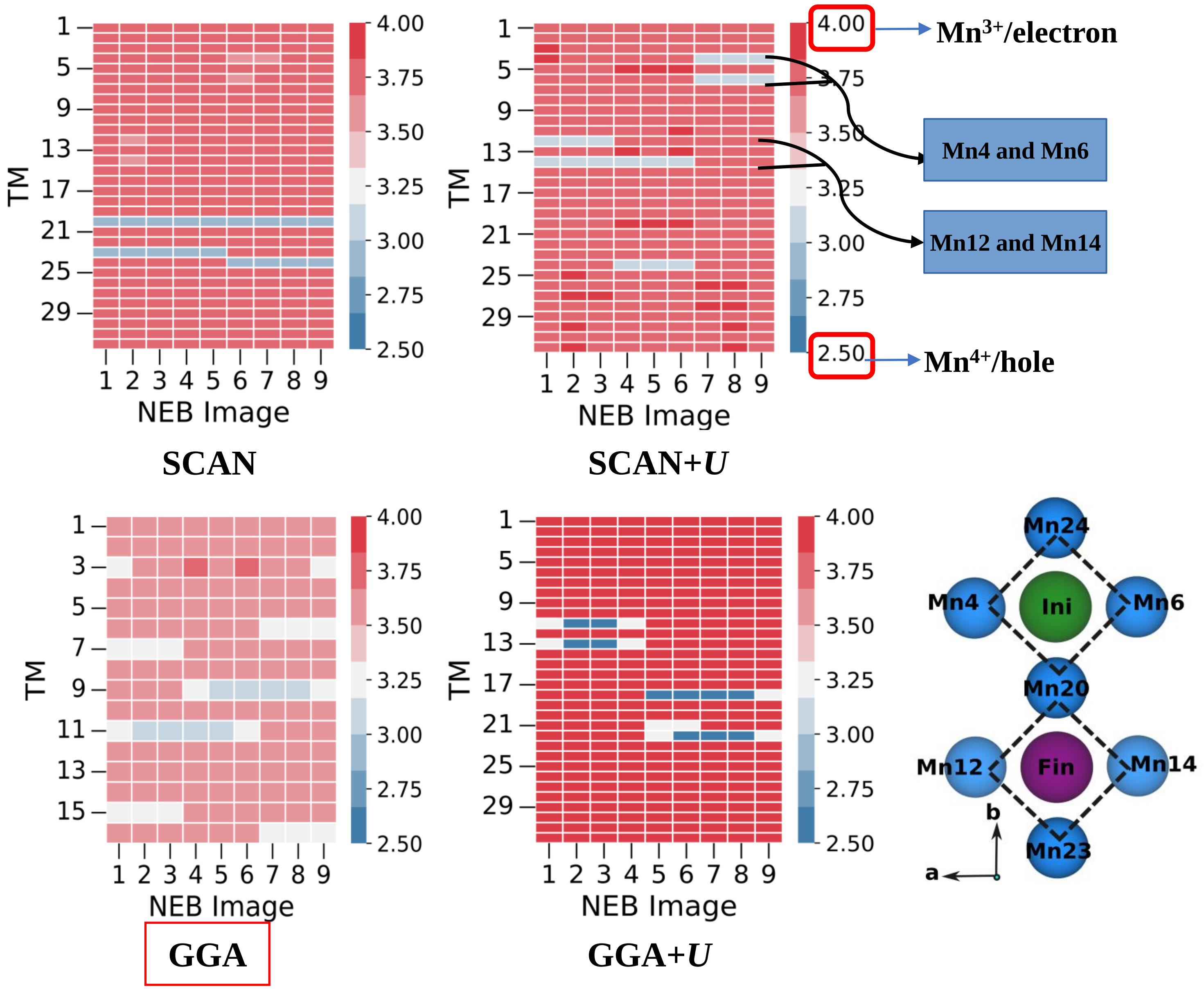
- GGA and SCAN can give lower and upper bounds to experimental E_m prediction
- SCAN has lower mean absolute error (MAE = 140 meV) compared to other functionals (>145 meV)

Let’s examine a few select materials

Spinel-$MgMn_2O_4$: GGA underestimates significantly

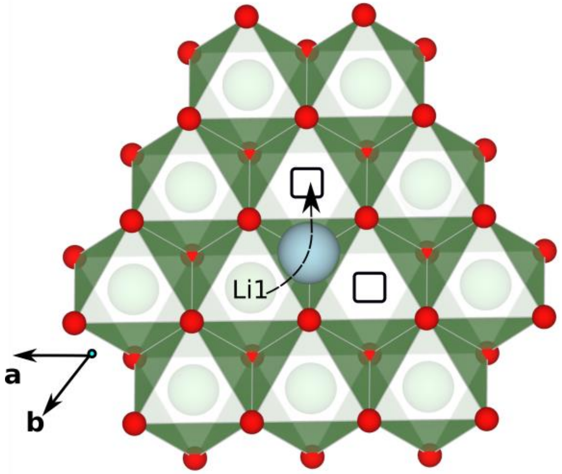




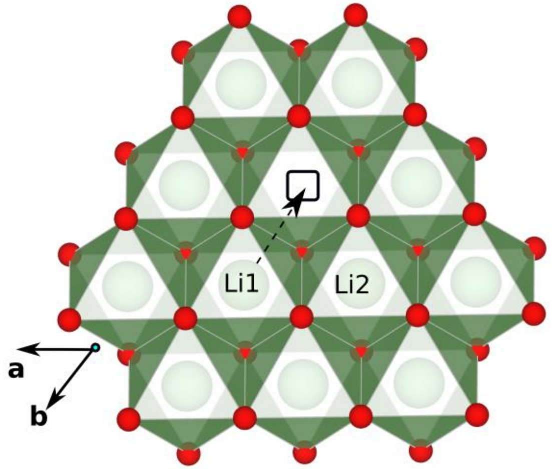


Layered-$LiCoO_2$: GGA+*U* overestimates significantly

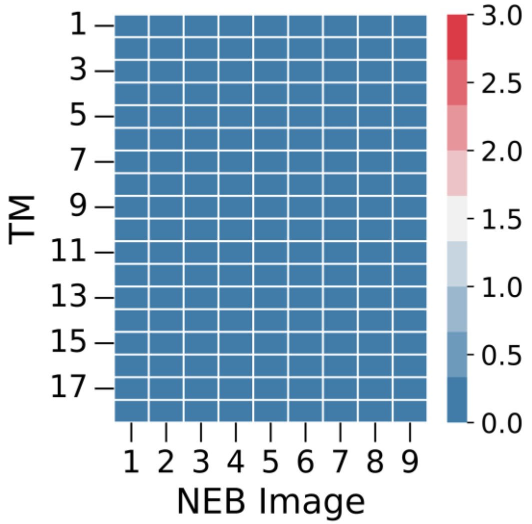
Tetrahedral site hop(TSH)



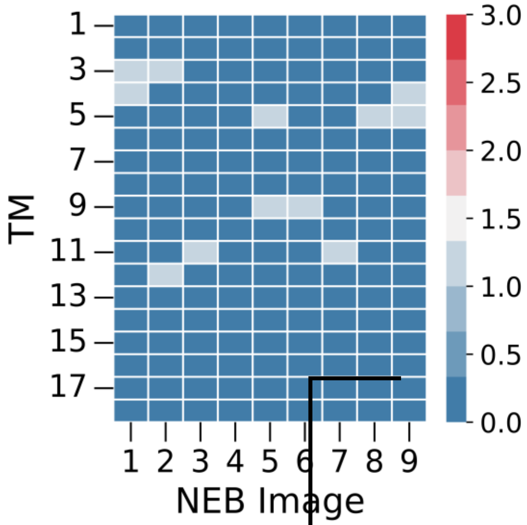
Oxygen dumbbell hop(ODH)



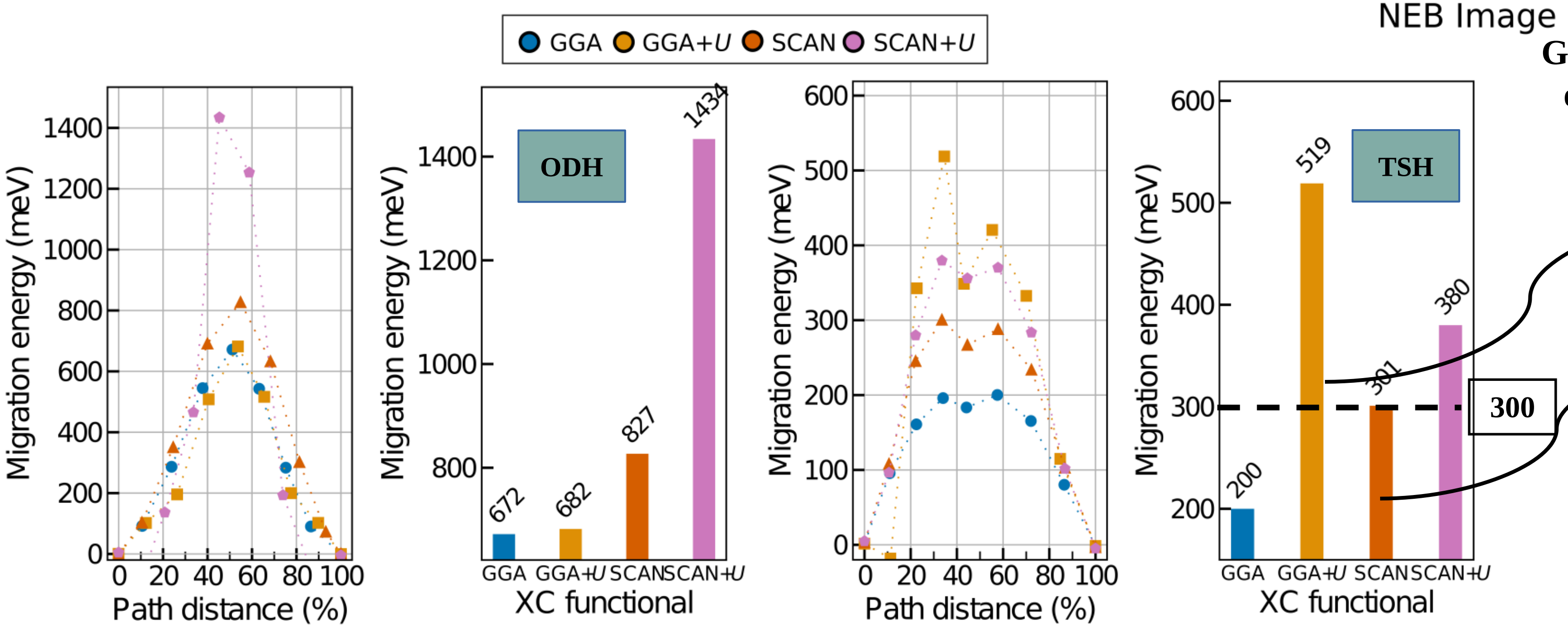
Other Functionals



GGA+*U*



GGA+*U* does not capture electron delocalization



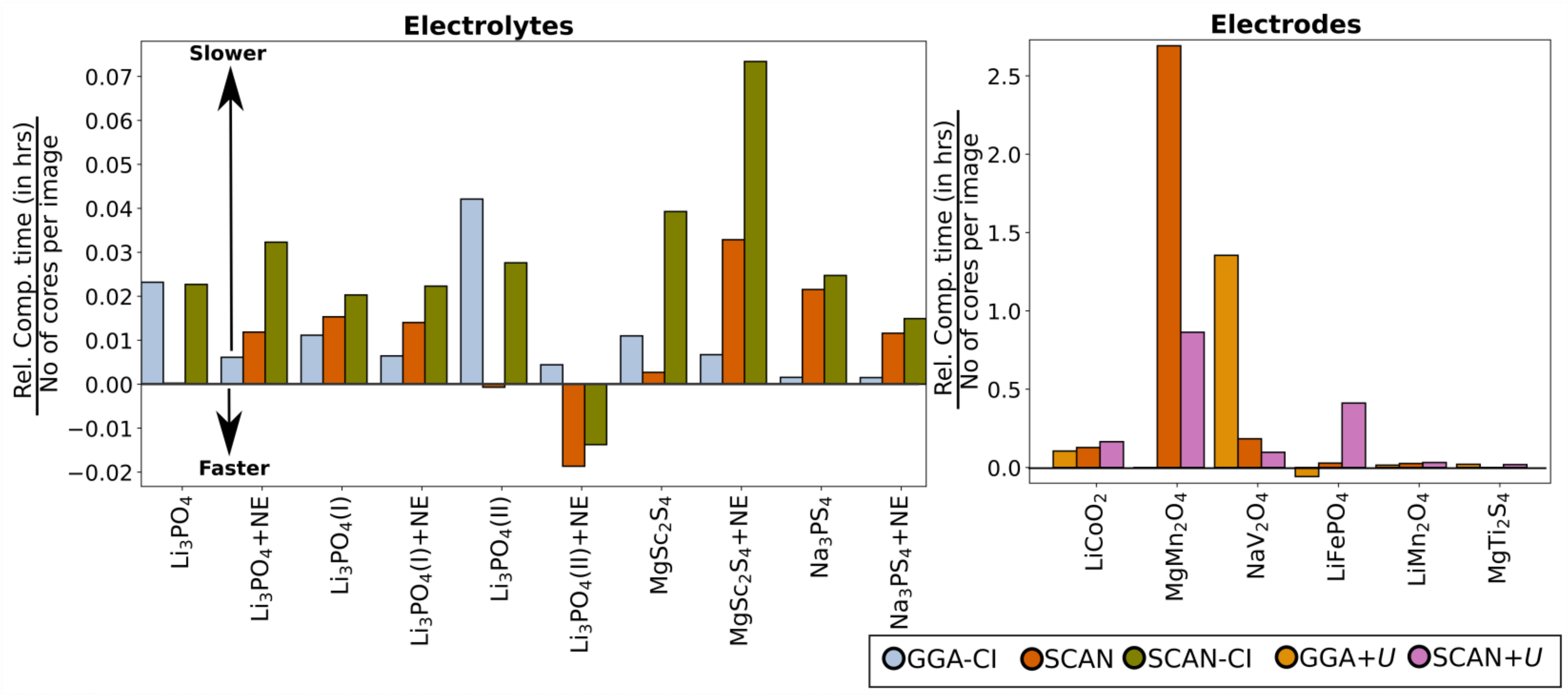
GGA+*U* overestimates by 73%

SCAN is identical to experimental barrier

Computational cost: is SCAN-NEB worth it?

- SCAN has better numerical accuracy when compared to other XC functionals
- SCAN (and SCAN+*U*) captures the underlying electronic structure well

But is SCAN worth pursuing? → **Need to look at the computational time**



- Computational time reduces by 75% in the case of GGA/GGA+*U* vs. SCAN
- SCAN is typically faster than SCAN+*U*
- Convergence difficulties encountered in the case of SCAN/SCAN+*U*

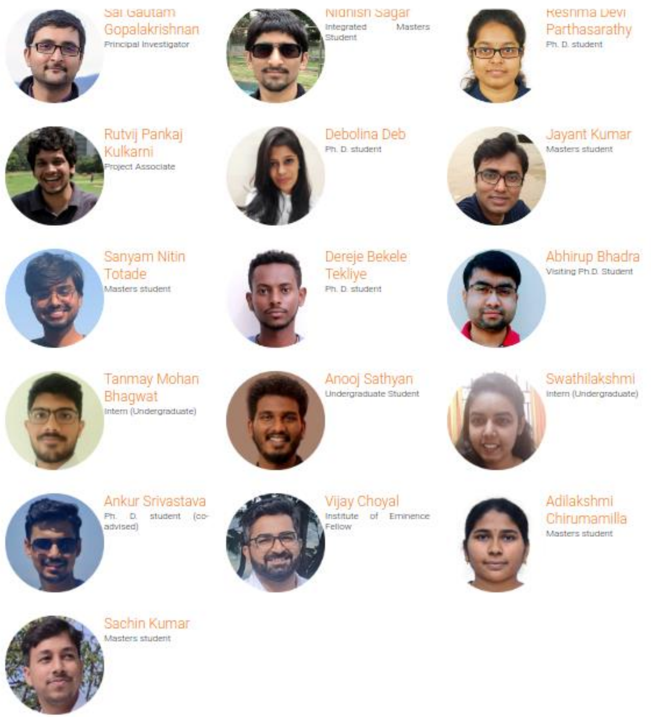
GGA for "Quick" estimation of E_m

SCAN for "higher" numerical accuracy

Conclusions and Acknowledgments

- Migration barriers are key in governing rate performance of batteries: need accurate computations to predict
- SCAN has a better numerical accuracy than GGA/GGA+*U*/SCAN+*U*, but is computationally expensive and exhibits convergence difficulties
- The addition of **NELECT** and **CI** to the functionals doesn't affect E_m significantly in solid electrolytes

Simulations And Informatics of MATerials Group



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R. Devi, B. Singh, P. Canepa, and G. Sai Gautam, **"Effect of exchange-correlation functionals on the estimation of migration barriers in battery materials"**, *under review*

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