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

Contributory Talk

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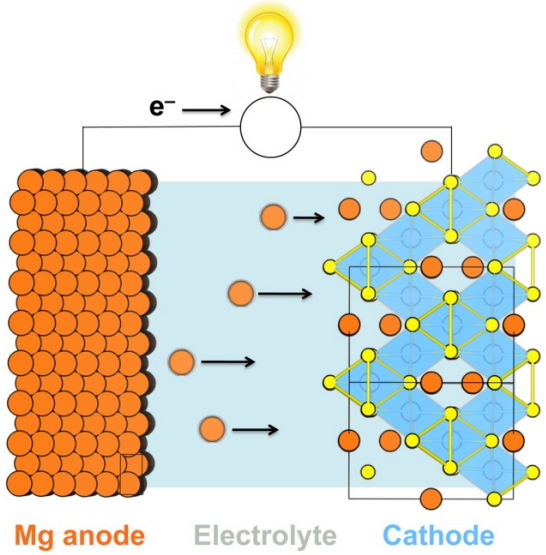
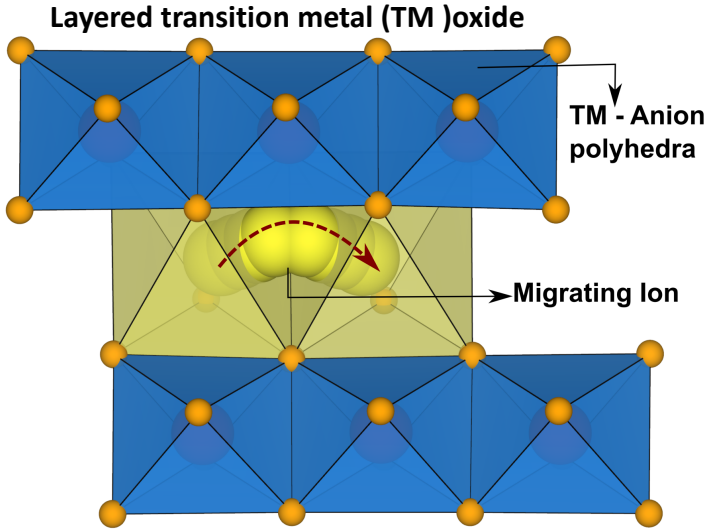
A battery's rate performance is very critical



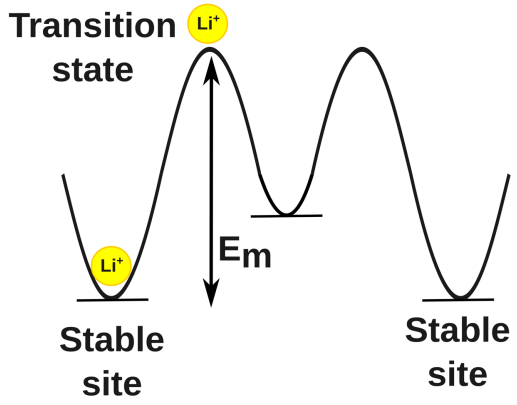
- Good ion transport in solid electrolytes and electrodes is a vital pre-requisite for the deployment of Li and beyond Li-ion batteries
- In intercalation electrodes and electrolytes ionic diffusivity within the bulk influence the rate performance

$$D = D_0 \exp\left(\frac{-E_m}{K_B T}\right)$$

D : Ionic diffusivity
D_0 : Diffusivity pre-factor
E_m : Migration barrier
K_B : Boltzmann constant
T : Temperature



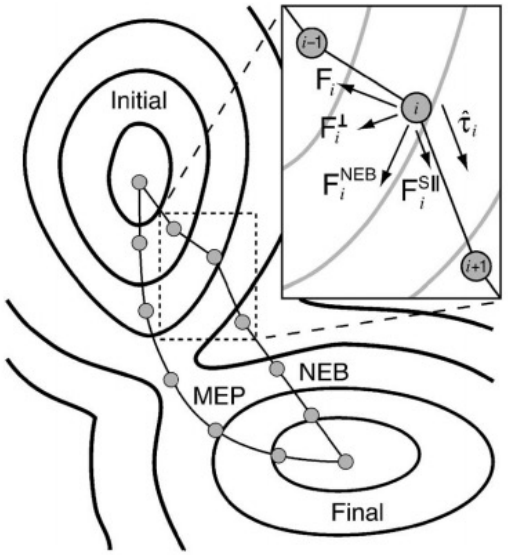
- Experimentally E_m is estimated using techniques like variable temperature impedance spectroscopy and nuclear magnetic resonance
- Computationally E_m is estimated using ab initio molecular dynamics and **nudged elastic band (NEB)** techniques



How accurately can we predict E_m computationally?

1.Canepa et al., Chem. Rev. 117, 4287-4341 (2017)

3 handles and 9 distinct systems considered



- **NEB**[1] calculations directly evaluate E_m
- Estimates the saddle point by optimising the perpendicular component of the force
- In climbing image **(CI)**, spring forces on the image with highest energy is removed

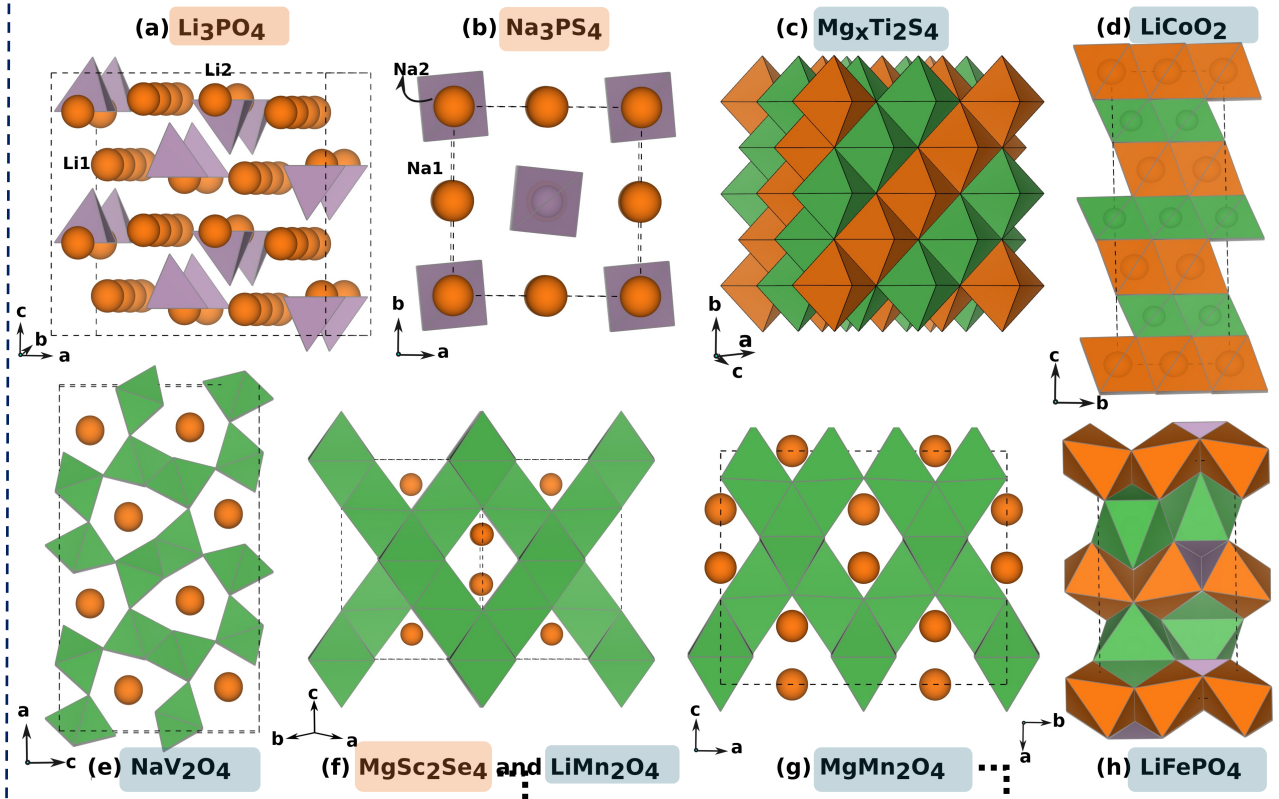
NEB used in conjunction with Density Functional Theory(DFT)[2,3]

Exchange correlational (XC) functional

1. Strongly constrained and appropriately normed (SCAN) [4]
2. Generalized gradient approximation (GGA) [5]
3. DFT + Hubbard(*U*) [6]

Addition of uniform background charge (NELECT)

Addition of CI approximation



3 electrolytes

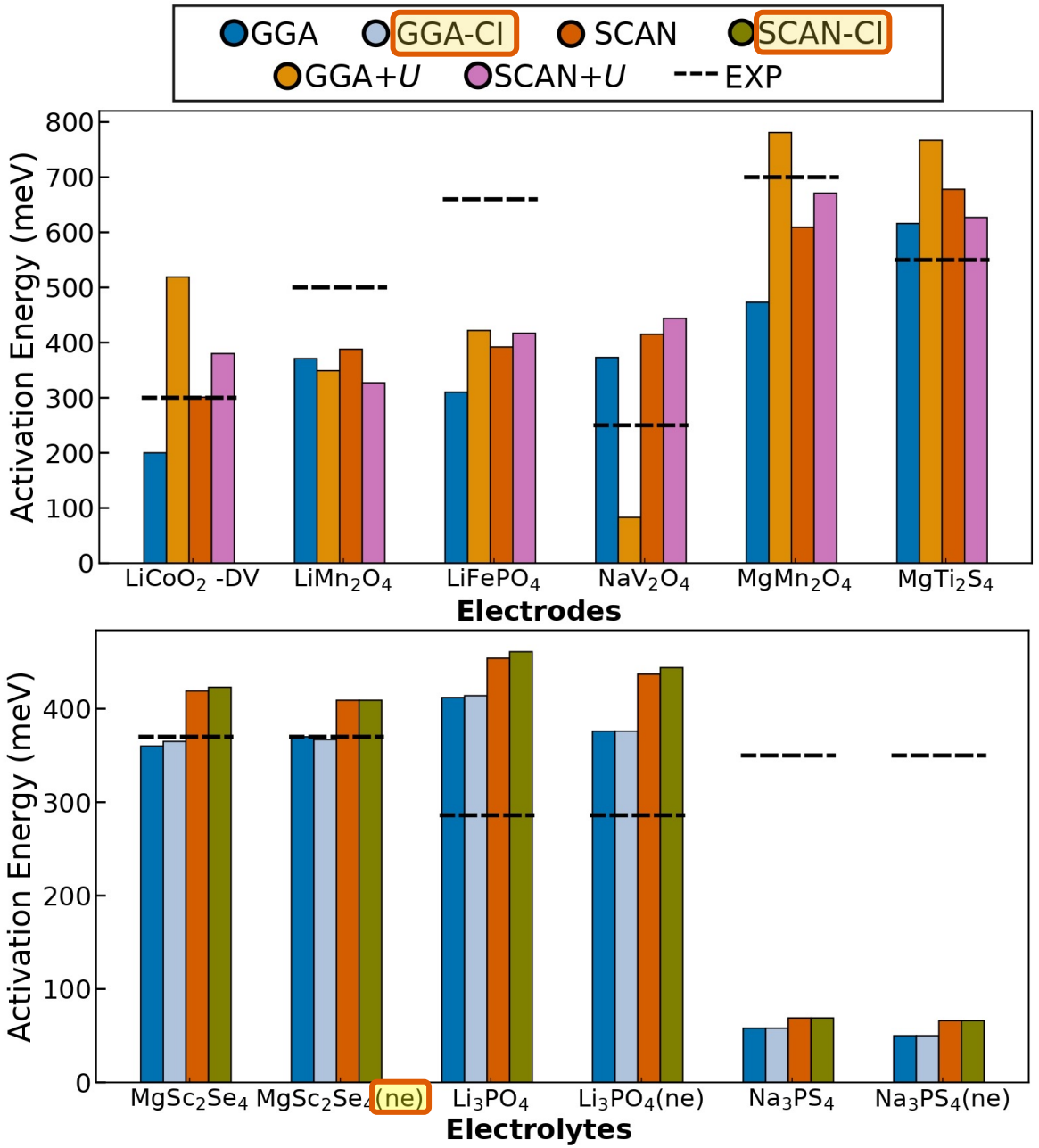
6 electrodes

Why these systems?

- Heterogeneity of intercalation ion
- Diversity of structural frameworks
- Availability of experimental data

1. Sheppard et al., Chem. Phys. 128, 134106 (2008)
2. Kohn & Sham, Phys. Rev. 140, A1133 (1965)
3. Hohenberg et al., Phys. Rev. 136, B864 (1964)
4. Sun et al., Phys. Rev. Lett. 115, 036402 (2015)
5. Perdew et al., Phys. Rev. Lett. 77, 3865 (1996)
6. Anisimov et al., Phys. Rev. B 44, 943 (1991)

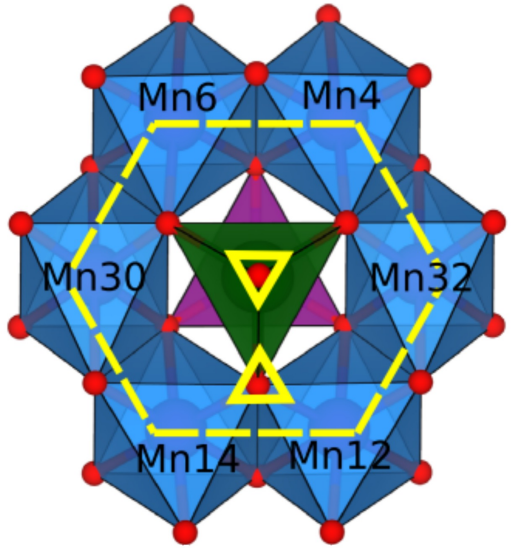
SCAN exhibits better numerical accuracy on average

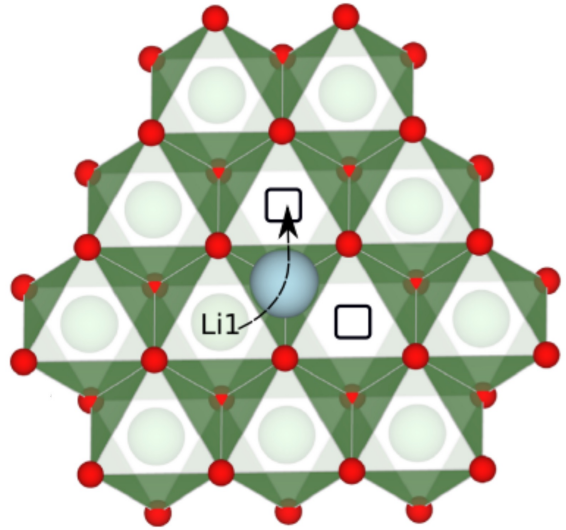


- Addition of NELECT or CI does not affect E_m
- E_m from SCAN > E_m from GGA
- E_m from SCAN+*U* < GGA+*U*

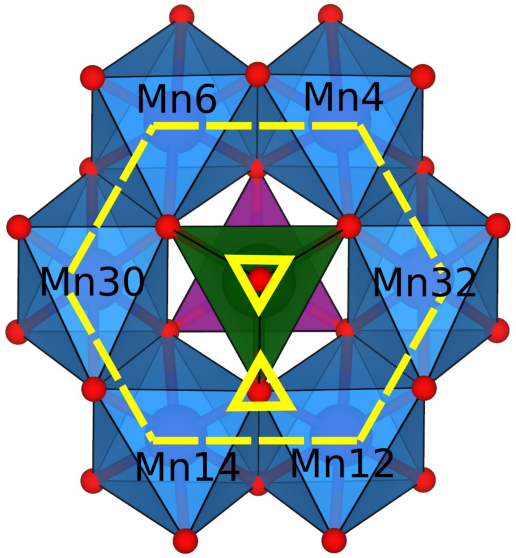
SCAN has lower mean absolute error (MAE = 140 meV) compared to other functionals (>145 meV)

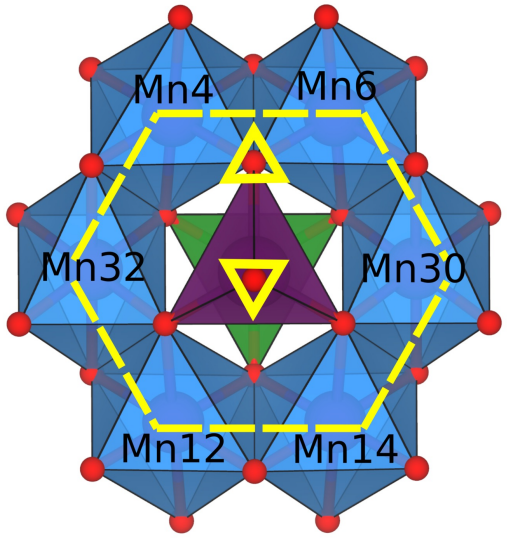
Two Systems to highlight the trends and anomalies

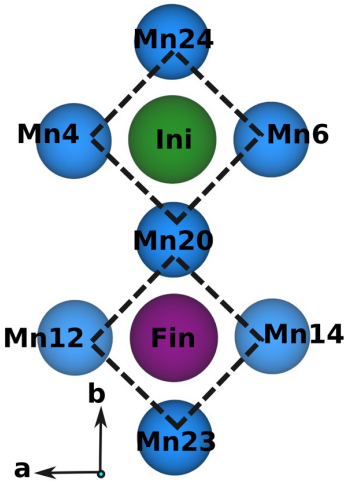


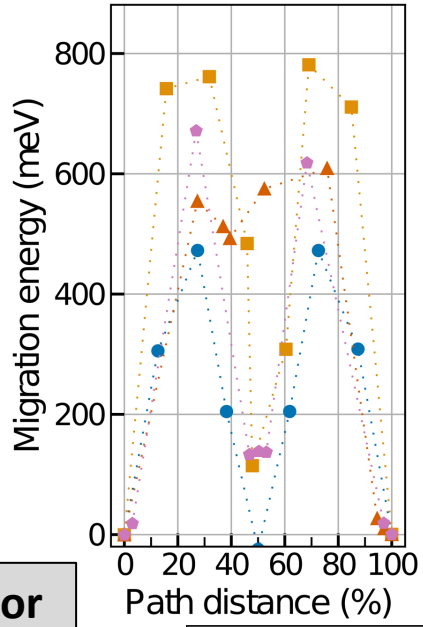


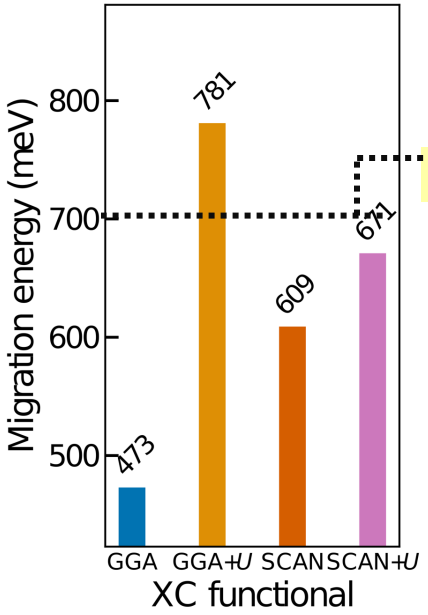
Spinel-$MgMn_2O_4$: GGA underestimates significantly









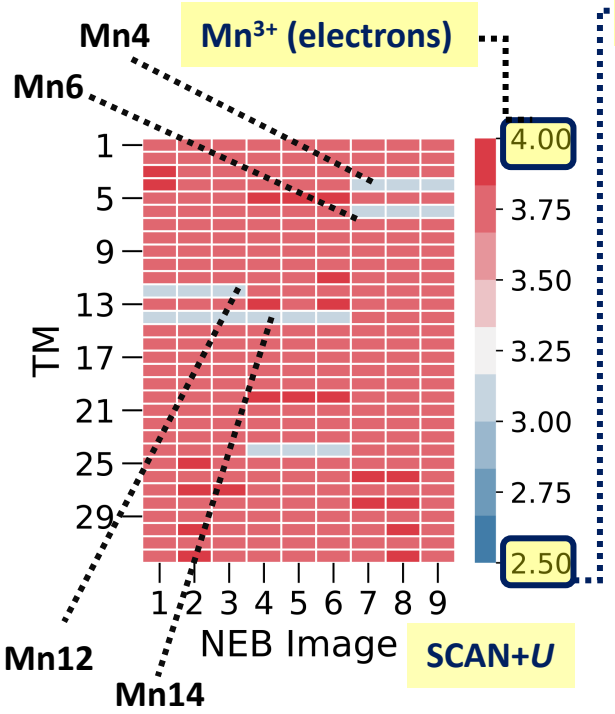


700 ± 60 meV

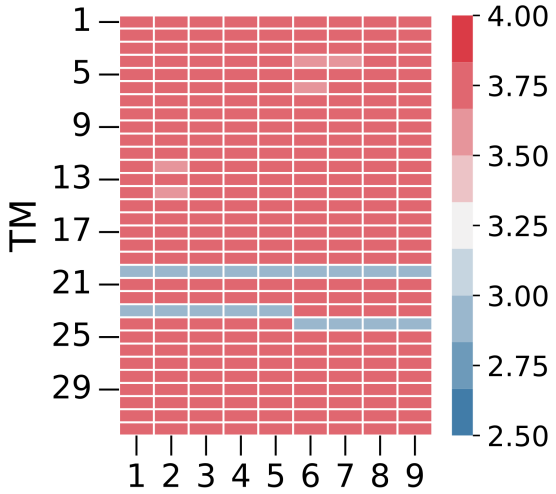
Mn^{3+} (electrons)

Mn^{4+} (holes)

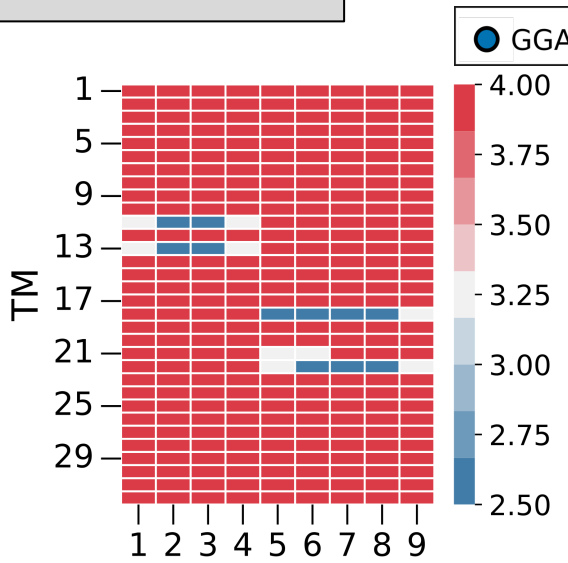
$MgMn_2O_4$ is a semiconductor



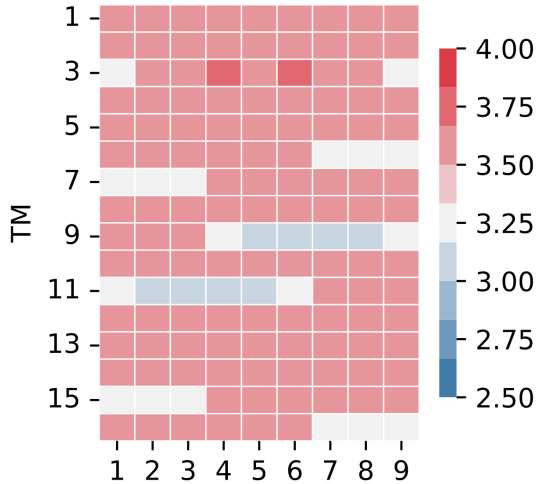
SCAN+*U*



SCAN

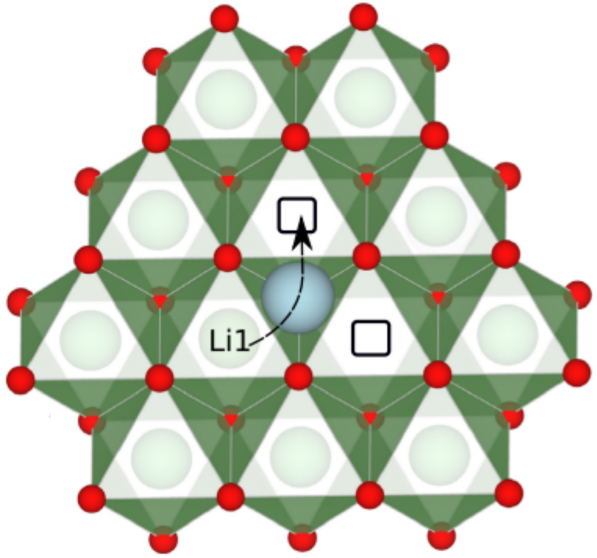


GGA+*U*



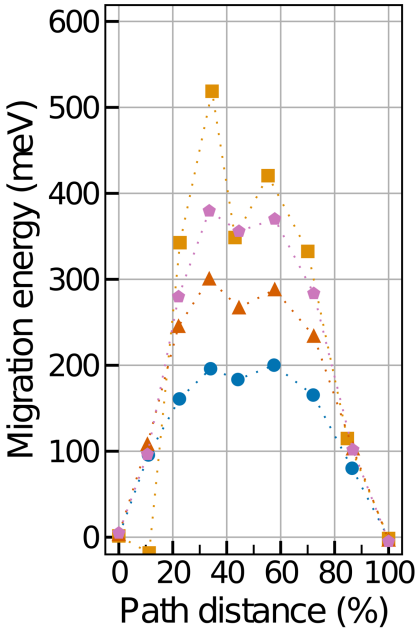
GGA

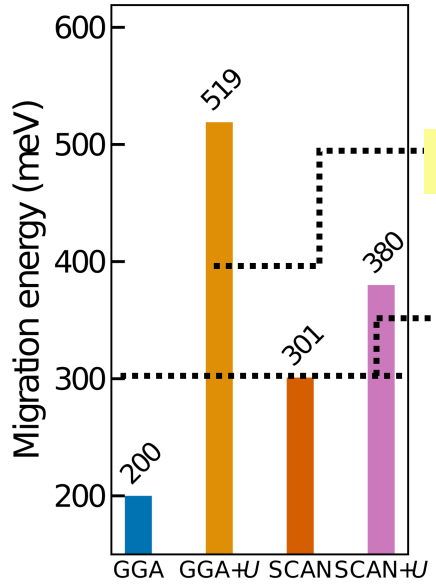
Layered-$LiCoO_2$: GGA+*U* overestimates significantly



Tetrahedral site hop (TSH)

$LiCoO_2$ is metallic for most of the Li compositions

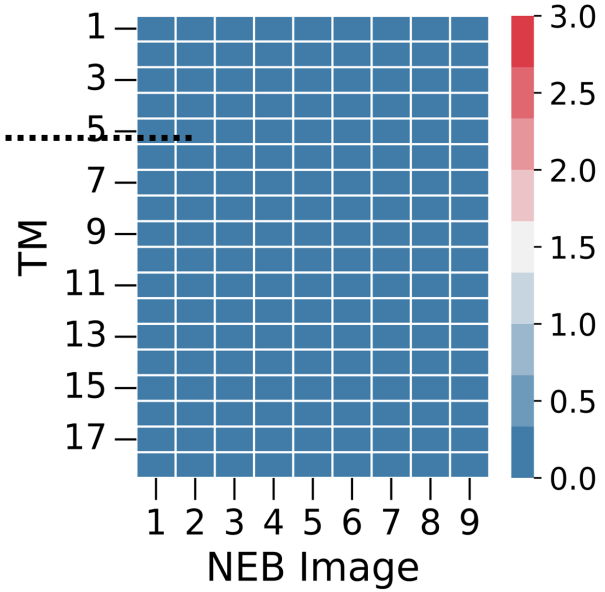


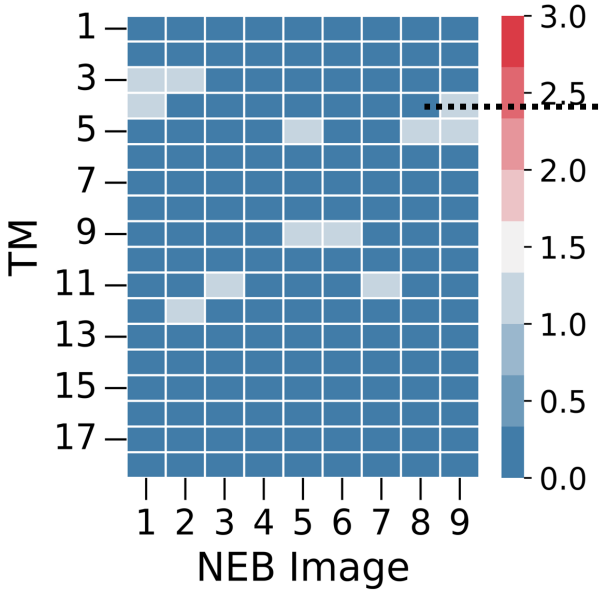


Overestimation by GGA+*U*

300 meV

Other functionals



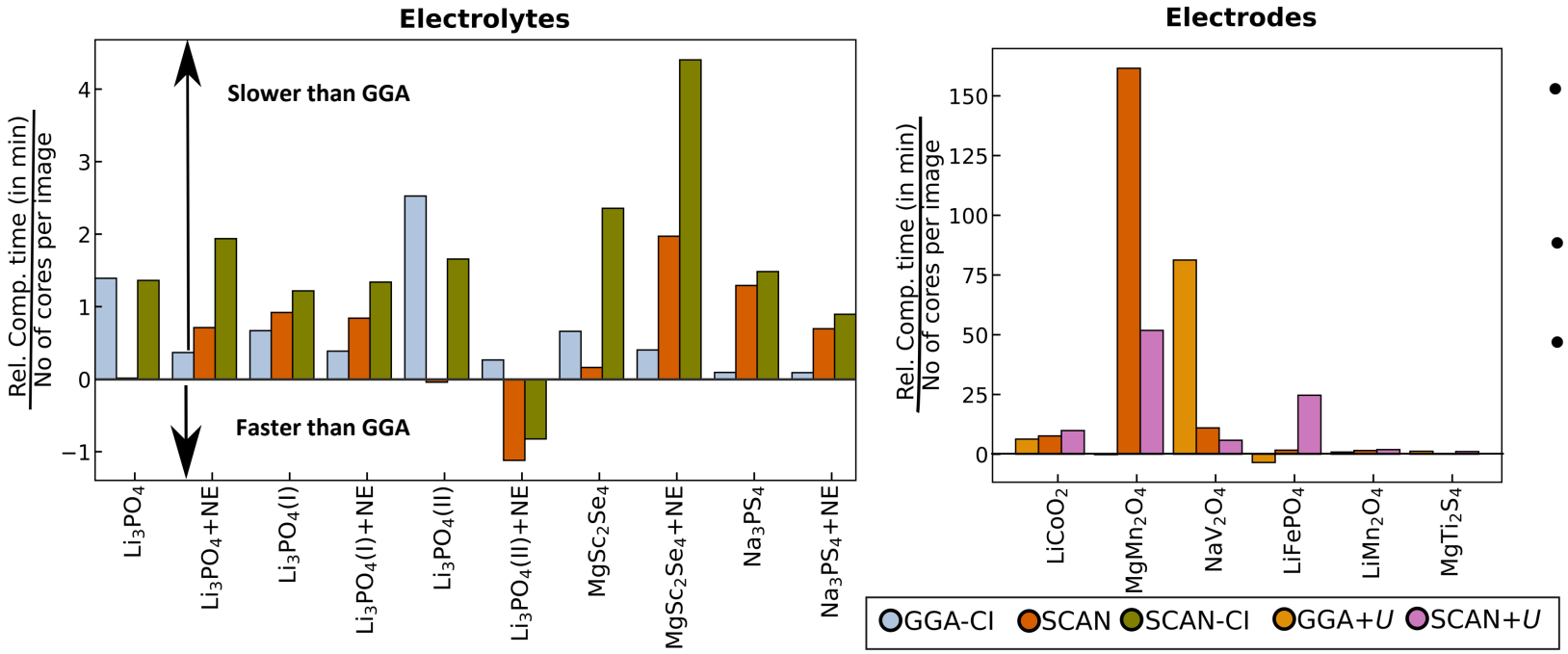


GGA+*U* shows spurious localization of electrons

Computational cost: Is SCAN-NEB worth it?

- SCAN has better numerical accuracy on average 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

SCAN for "better" accuracy

Major takeaways

- Accurate computational prediction of E_m is important as it governs the rate performance of the batteries
- SCAN has a better numerical accuracy on average than GGA/GGA+*U*/SCAN+*U*, but is computationally expensive and exhibits convergence difficulties
  - GGA can provide good qualitative trends
- The addition of **NELECT** and **CI** to the functionals doesn't affect E_m significantly in solid electrolytes

npj computational materials
www.nature.com/npjcompumats

Devi et al., npj Comput. Mater. *8*, 160 (2022)

ARTICLE OPEN

Check for updates

Effect of exchange-correlation functionals on the estimation of migration barriers in battery materials

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