

Role of exchange-correlation functionals on migration barrier predictions in battery materials



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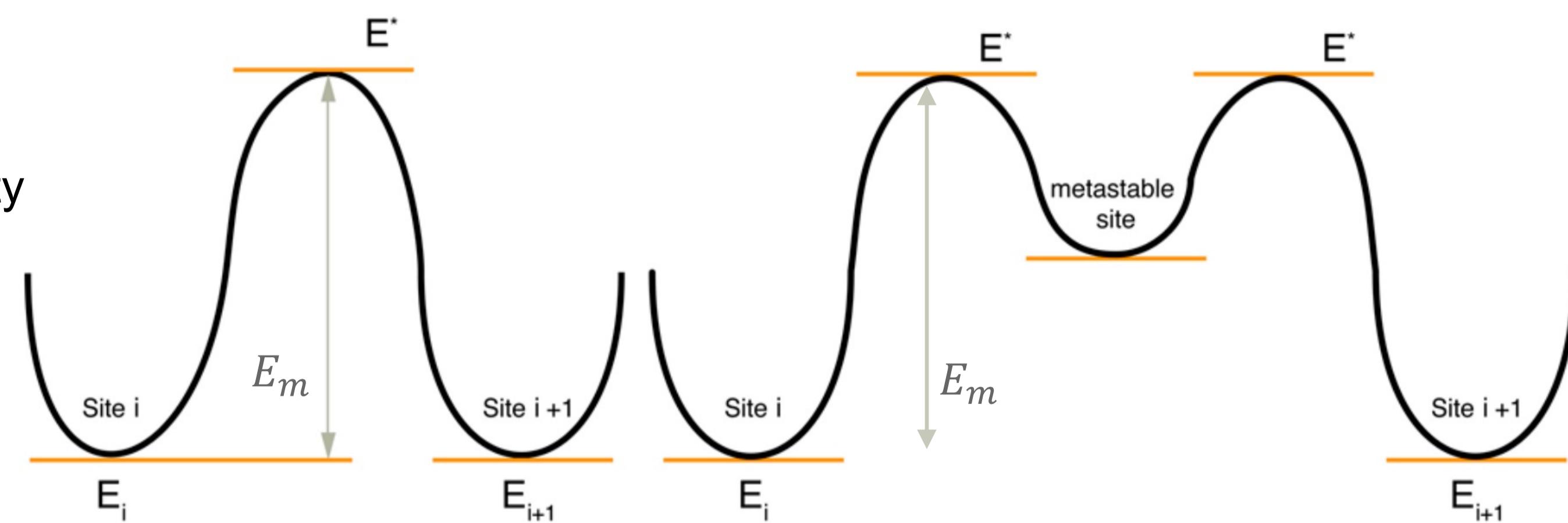
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INTRODUCTION

- Next generation of energy storage technologies require both high energy and power densities
- Critical factor that influences rate (power) performance in intercalation batteries is the diffusivity (D) of electroactive ions within solid host frameworks
 - $D = D_0 \exp\left(-\frac{E_m}{RT}\right)$; E_m is the migration barrier governing ionic diffusion¹
- Theoretical estimates of E_m : density functional theory (DFT) + nudged elastic band (NEB)²
 - How does choice of exchange-correlation (XC) functional in DFT affect E_m ?



METHODS

- All calculations done with Vienna ab initio simulation package (VASP³)
- NEB settings: 7 images, spring force of 5 eV/Å, force converged within $|0.05|$ eV/Å, limited memory Broyden-Fletcher-Goldfarb-Shannon optimizer⁴
- 3 handles that influence E_m explored
 - Generalized gradient approximation (GGA)
 - Perdew-Burke-Ernzerhof⁵
 - Strongly constrained and appropriately normed (SCAN)⁶
 - GGA+U and SCAN+U⁷
 - U value from previous works^{8,9}
 - For electrodes only

Addition of uniform background charge (NE or ne)

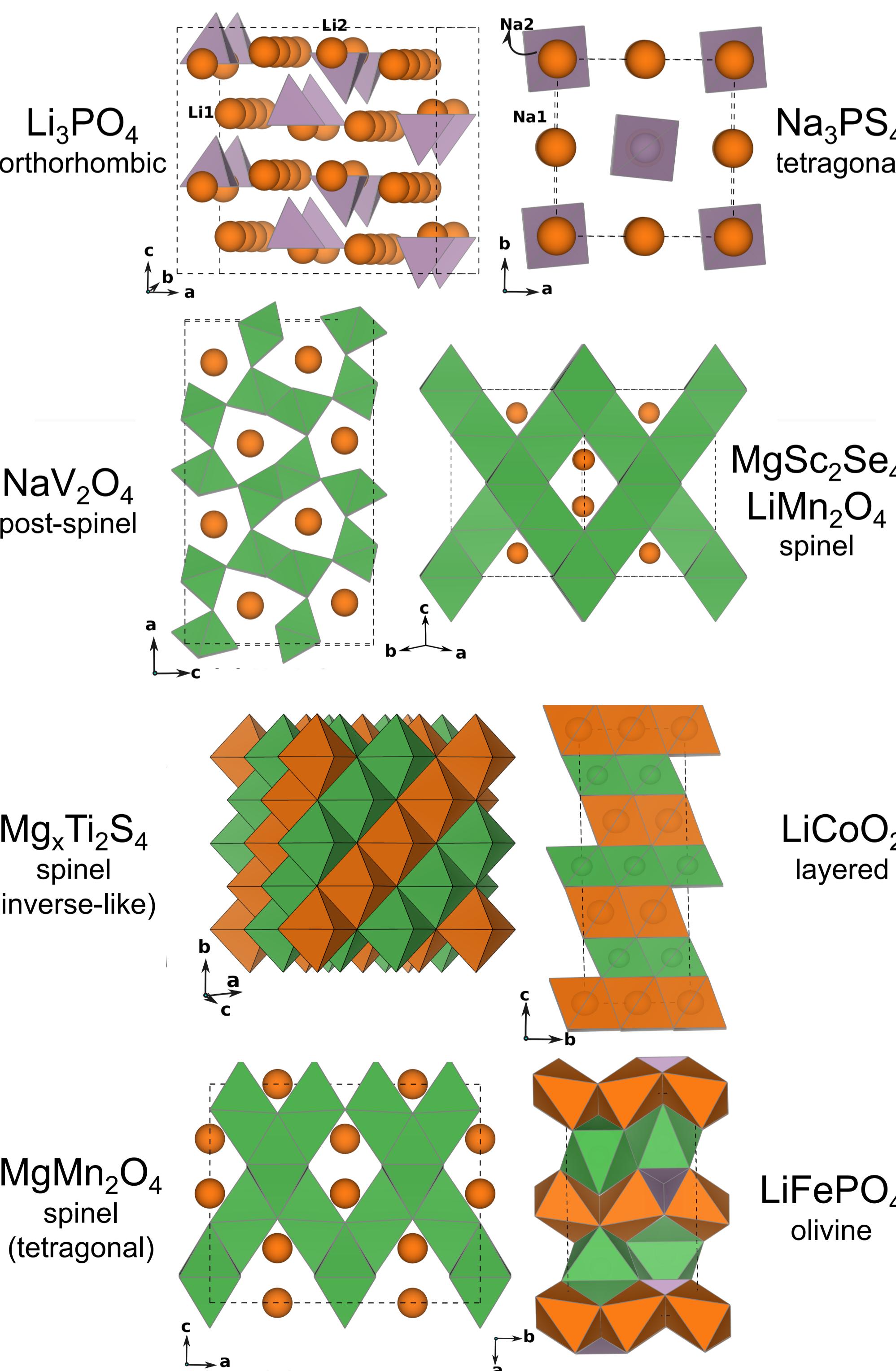
- For solid electrolytes only

Addition of climbing image (CI) approximation

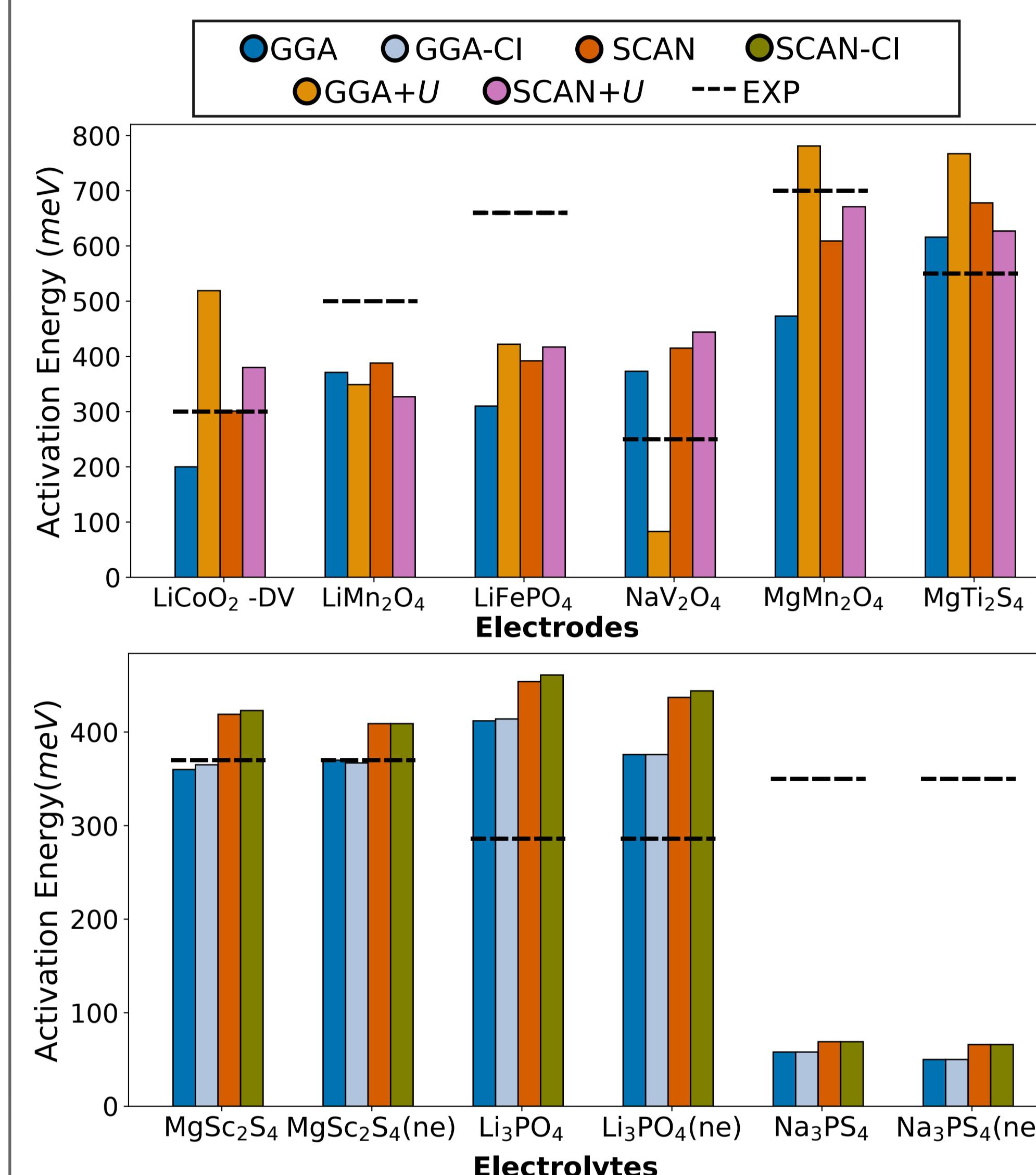
- For solid electrolytes only

SYSTEMS

- 9 distinct systems: 6 electrodes and 3 solid electrolytes
- Choice of system motivated by
 - Experimental data availability
 - Heterogeneity of intercalation ion
 - Diversity of structural frameworks
- All initial structures from inorganic crystal structure database¹⁰



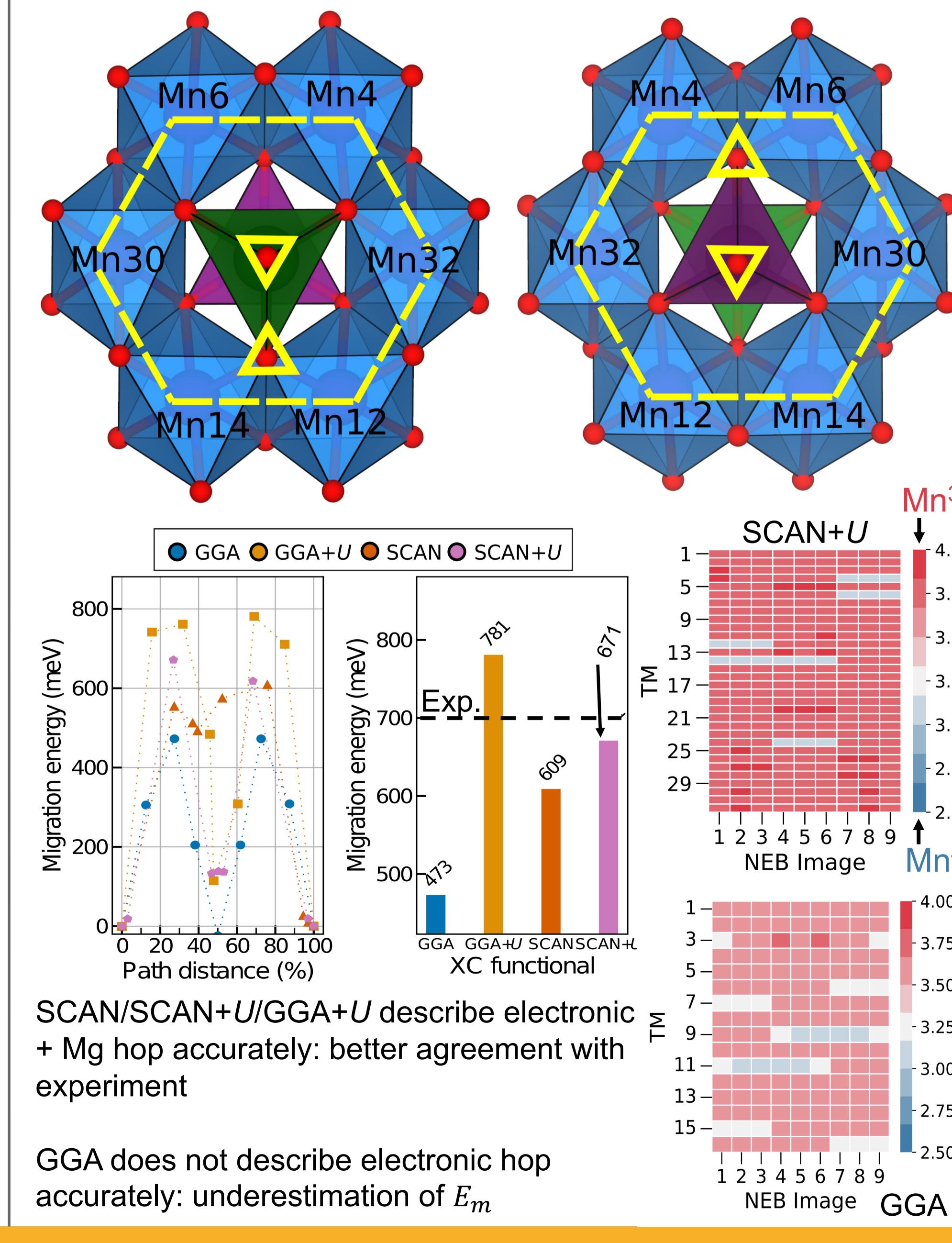
RESULTS



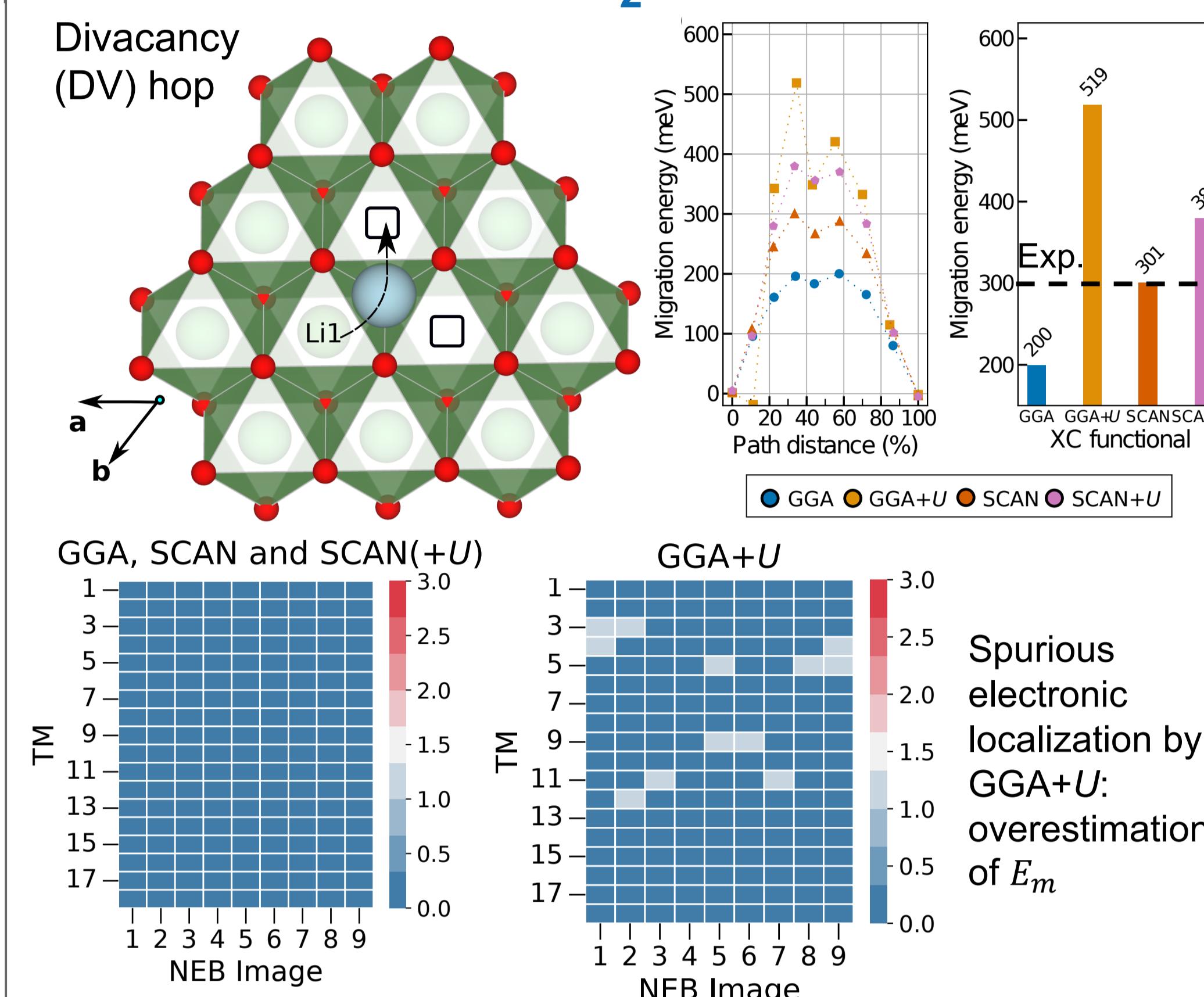
KEY TRENDS

- SCAN has lower mean absolute error (MAE, ~140 meV) compared to other functionals (> 145 meV)
- Addition of NE/ne or CI does not affect E_m in solid electrolytes
- SCAN $E_m >$ GGA E_m
- SCAN+U $E_m <$ GGA+U E_m (except NaV₂O₄)

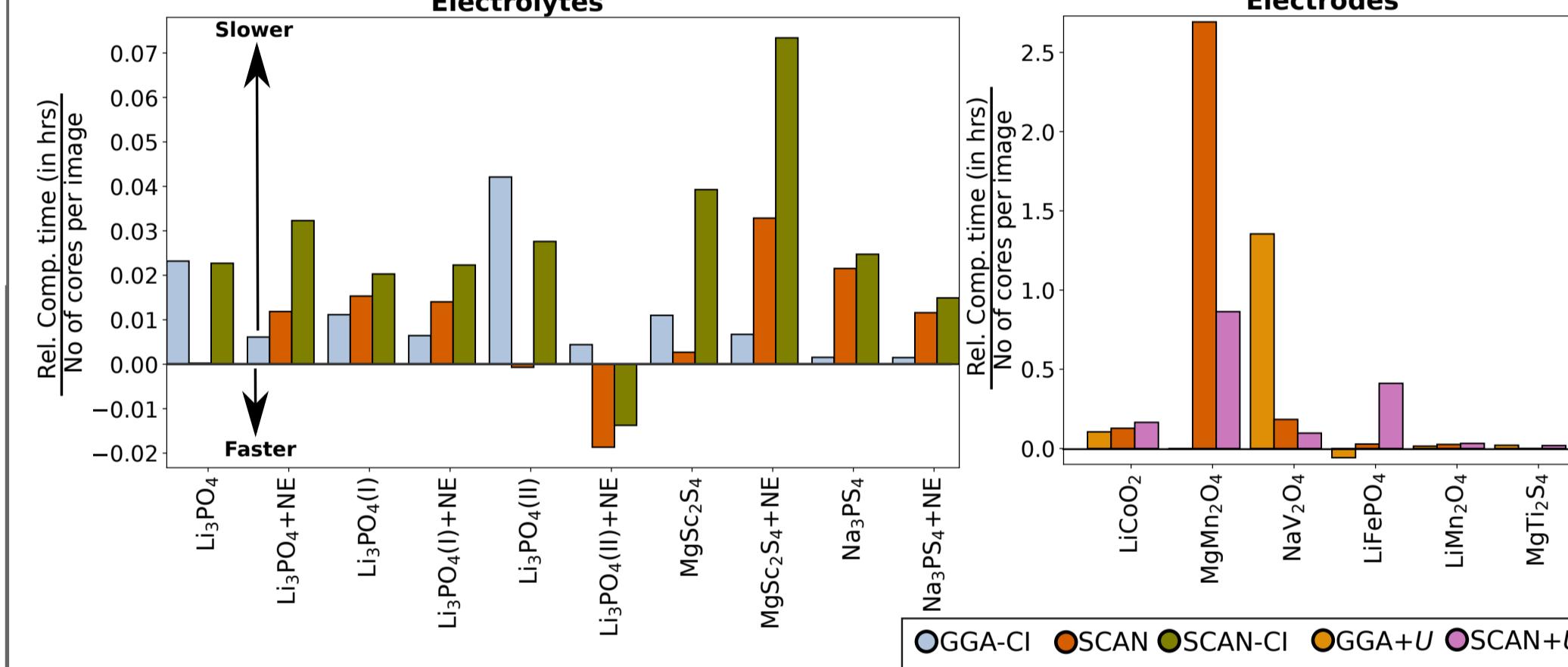
EXAMPLE 1: MgMn₂O₄



EXAMPLE 2: LiCoO₂



COMPUTATIONAL PERFORMANCE



CONCLUSION

Migration barriers are key in determining rate performance of batteries: need accurate computations to predict

We explored accuracy and computational performance of various XC frameworks in 6 electrodes and 3 solid electrolytes

- SCAN has better numerical accuracy than other functionals on average: but notable exceptions exist + convergence difficulties
- Addition of NE/ne or CI does not influence E_m

GGA for "quicker" estimate SCAN for "better" accuracy

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