

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



SAI GAUTAM GOPALAKRISHNAN<sup>1</sup>, RESHMA DEVI<sup>1</sup>, BALTEJ SINGH<sup>2</sup>, PIEREMANUELE CANEPA<sup>2,3</sup>

<sup>1</sup>Department of Materials Engineering, Indian Institute of Science, Bengaluru 560012, India

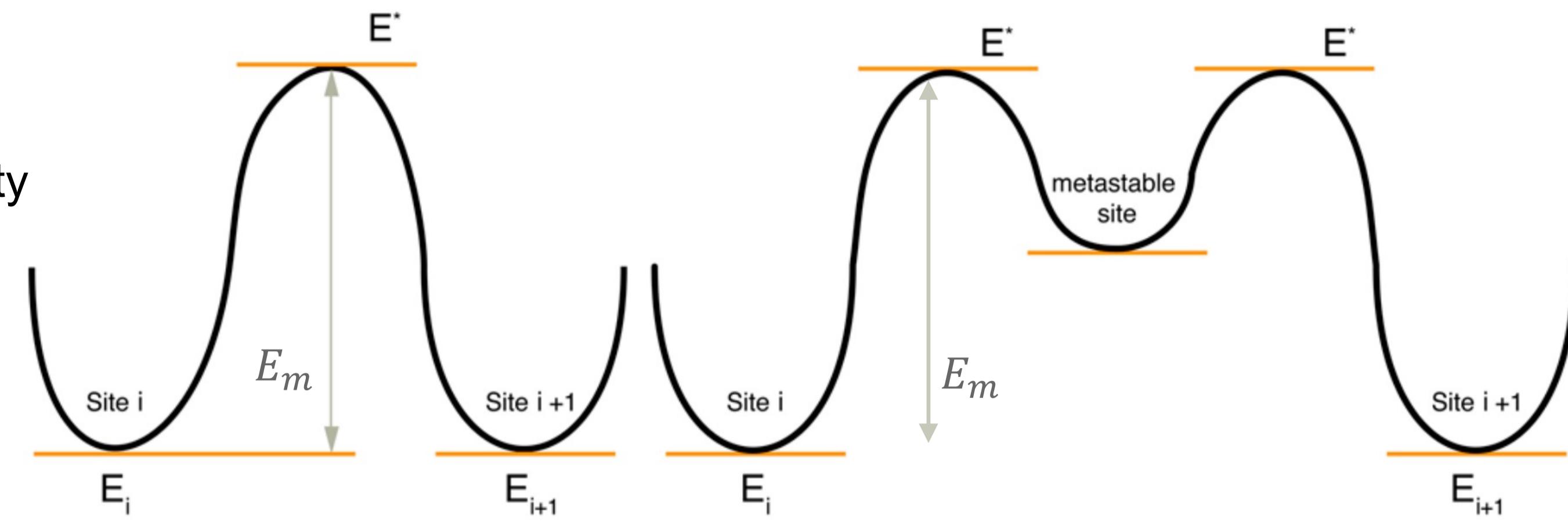
<sup>2</sup>Department of Materials Science and Engineering, National University of Singapore, Singapore 117575

<sup>3</sup>Department of Chemical and Biomolecular Engineering, National University of Singapore, Singapore 117575

sai.gautamg@iisc.ac.in  
<https://sai-mat-group.github.io>

## 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 diffusion<sup>1</sup>
- Theoretical estimates of  $E_m$ : density functional theory (DFT) + nudged elastic band (NEB)<sup>2</sup>
  - How does choice of exchange-correlation (XC) functional in DFT affect  $E_m$ ?



## METHODS

- All calculations done with Vienna ab initio simulation package (VASP<sup>3</sup>)
- NEB settings: 7 images, spring force of 5 eV/Å, force converged within  $|0.05|$  eV/Å, limited memory Broyden-Fletcher-Goldfarb-Shannon optimizer<sup>4</sup>
- 3 handles that influence  $E_m$  explored
  - Generalized gradient approximation (GGA)
    - Perdew-Burke-Ernzerhof<sup>5</sup>
  - Strongly constrained and appropriately normed (SCAN)<sup>6</sup>
  - GGA+U and SCAN+U<sup>7</sup>
    - $U$  value from previous works<sup>8,9</sup>
    - For electrodes only

Addition of uniform background charge (NE or ne)
 

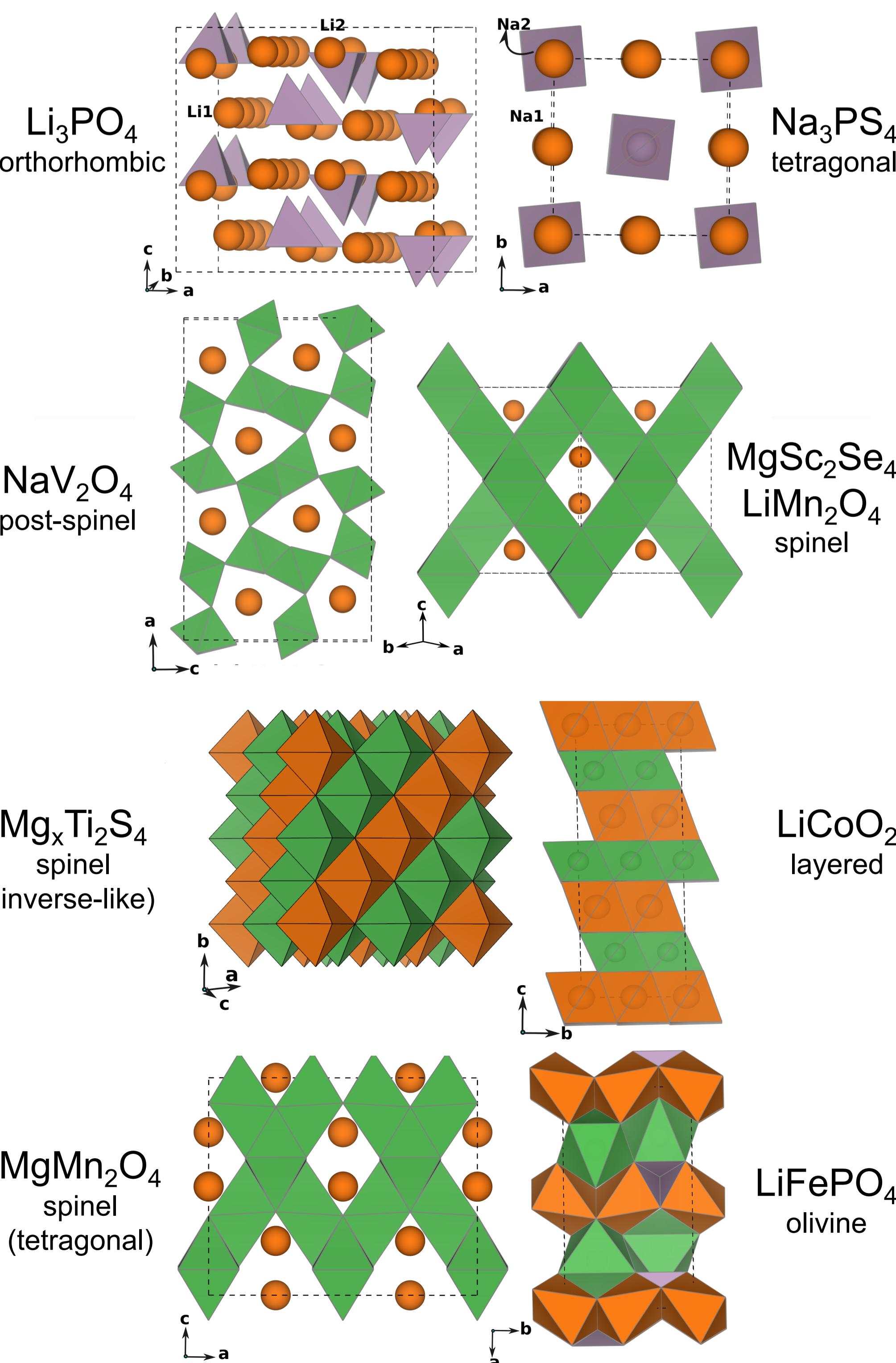
- For solid electrolytes only

Addition of climbing image (CI) approximation
 

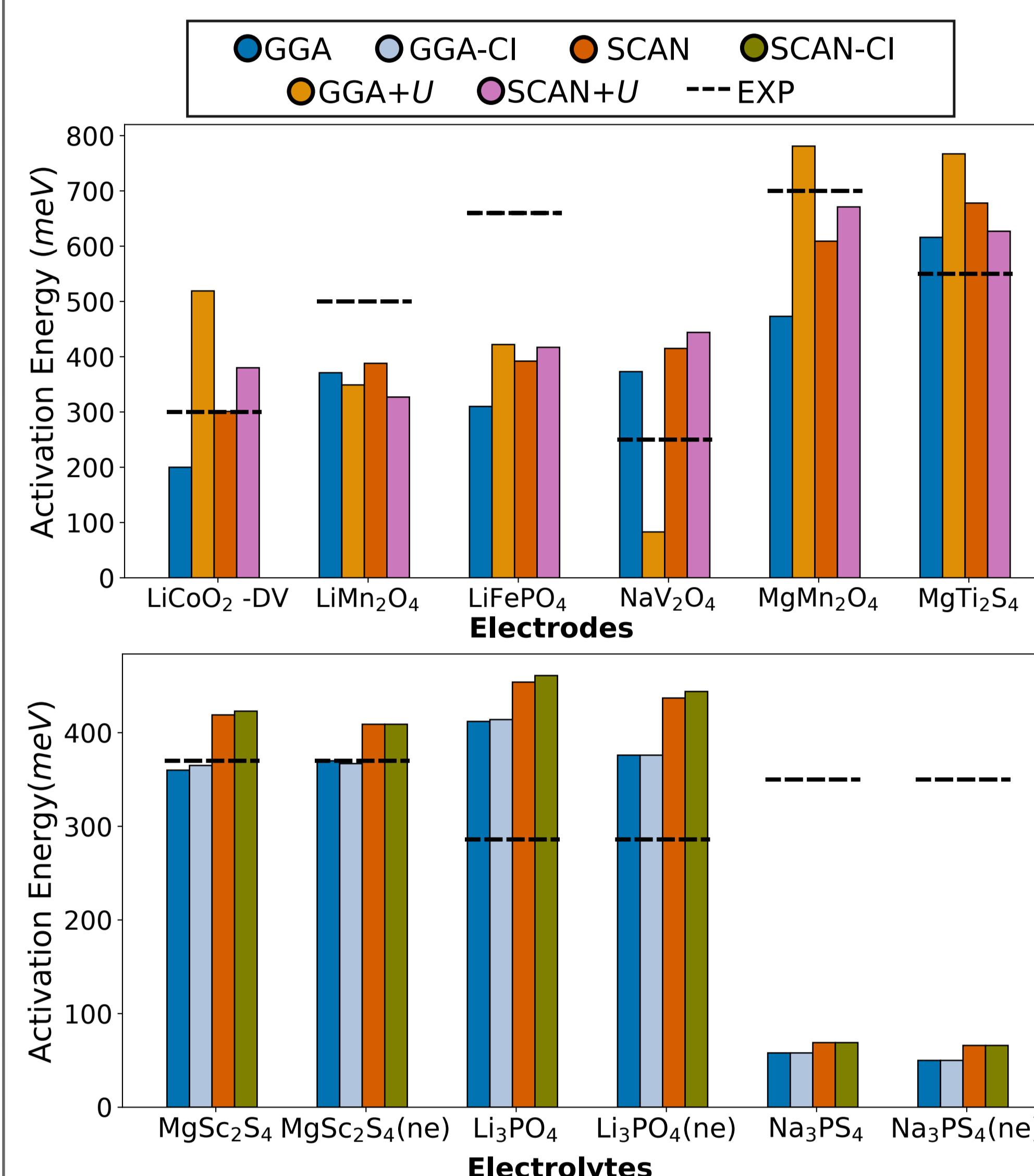
- For solid electrolytes only

## 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 database<sup>10</sup>



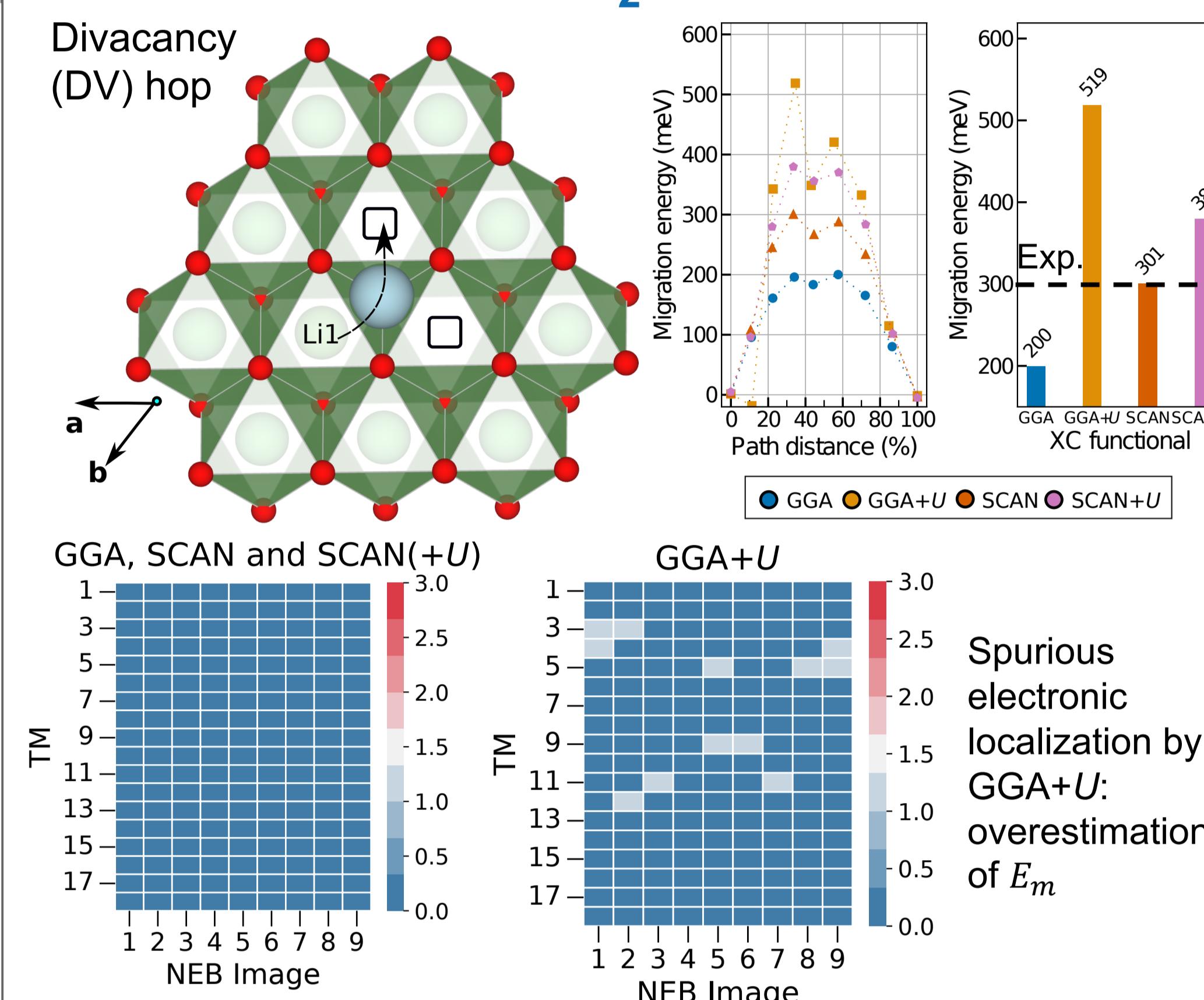
## RESULTS



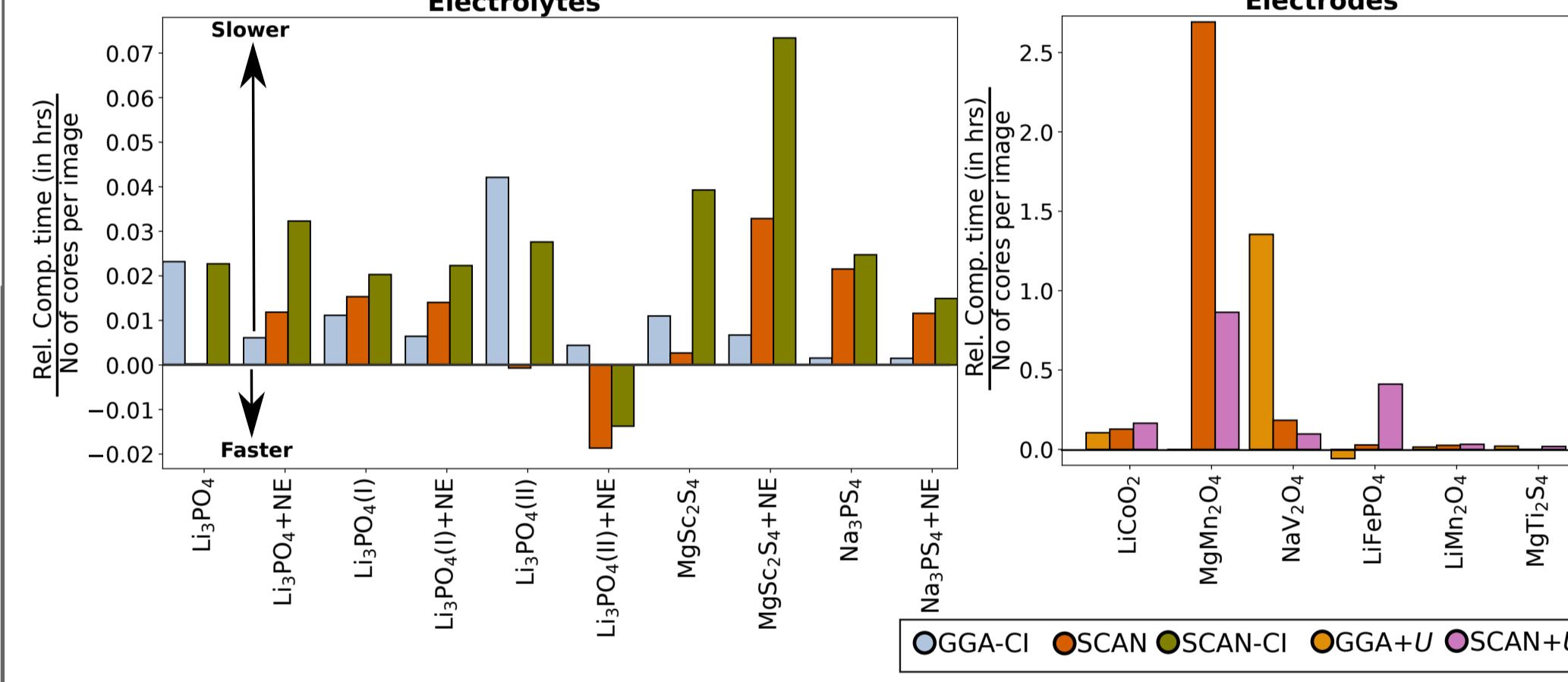
Activation Energy (meV)

Electrodes

## EXAMPLE 2: LiCoO<sub>2</sub>



## COMPUTATIONAL PERFORMANCE



- Computational time with GGA/GGA+U ~75% faster than SCAN
- SCAN faster than SCAN+U
- Significant convergence difficulties with SCAN and SCAN+U

## 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

## ACKNOWLEDGEMENTS

- Science and Engineering Research Board, Government of India
- National Research Foundation, Singapore
- Ministry of Education, Singapore
- Supercomputer Education and Research Centre, Indian Institute of Science
- National Supercomputing Centre, Singapore

## REFERENCES

- G.S. Gautam and P. Canepa, Magnesium Batteries: Chap. 4 (2019)
- D. Sheppard et al., J. Chem. Phys. 128, 134106 (2008)
- G. Kresse and J. Hafner, Phys. Rev. B 48, 13115 (1993)
- J. Nocedal, Math. Comput. 35, 773-782 (1980)
- J.P. Perdew et al., Phys. Rev. Lett. 77, 3865 (1996)
- J. Sun et al., Phys. Rev. Lett. 115, 036402 (2015)
- V. Anisimov et al., Phys. Rev. B 44, 943 (1991)
- A. Jain et al. APL Mater. 1, 011002 (2013)
- O. Long et al., Phys. Rev. Mater. 4, 054101 (2020)
- M. Hellenbrandt, Crystallogr. Rev. 10, 17-22 (2004)

