Developing machine-learned interatomic potentials for Li-based disordered rocksalts

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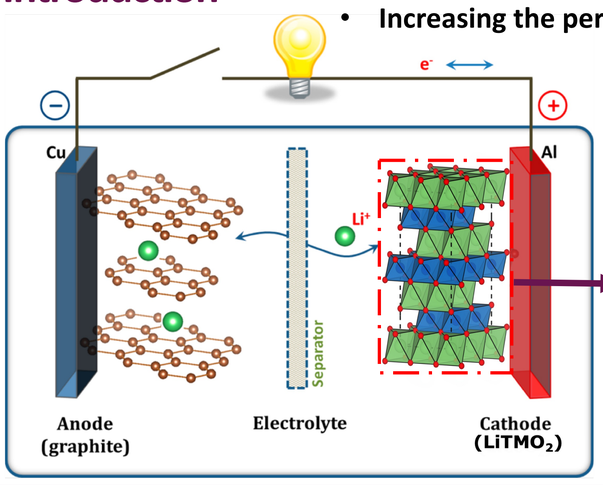
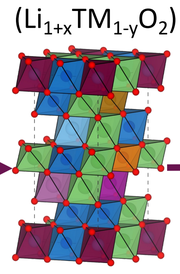
Introduction

- **Growing demands for electric power: need high energy and power density energy storage devices[1]**
- **Increasing the performance of cathode materials of Lithium ion batteries (LIBs) : ongoing and active area of research[2]**



To increase the energy density of LIB cathodes is to utilize anionic redox (i.e., oxygen redox), which can be reversibly accessed in cathode materials with a Li-excess composition[3]

Cathode ($Li_{1+x}TM_{1-y}O_2$)



Disordered rocksalt structure (DRX)

Difficulties modelling DRX using density functional theory (DFT)
- Many possible configurations
- High computational costs for **large supercells**

Advantages of using DRX compared to layered rocksalts
- Better structural stability upon Li removal
- Isotropic; hence Li can diffuse in 3D

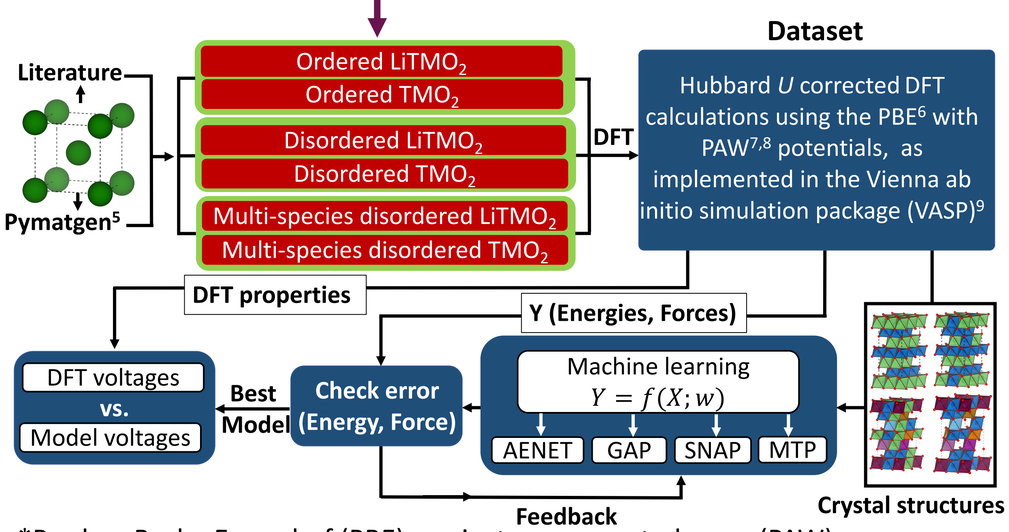
Need a **computational technique** which can provide **'quick'** and **'accurate'** estimates of energies and atomic forces to model disordered multi-component systems[4]

Machine-learning interatomic potentials (MLIPs)

- Mathematical representation of the **potential energy surface (PES)[4]**
- Map the atomic configuration of a structure to its total energy (by minimizing the **loss function**)

Methodology

The $LiTMO_2$ DRX data set was generated by enumerating Li and TM (transition metals) arrangements within the cation sublattice of the rocksalt structure (TM = Sc, Ti, V, Cr, Mn, Fe, Co, Ni, and Cu), Total Structures = 10842

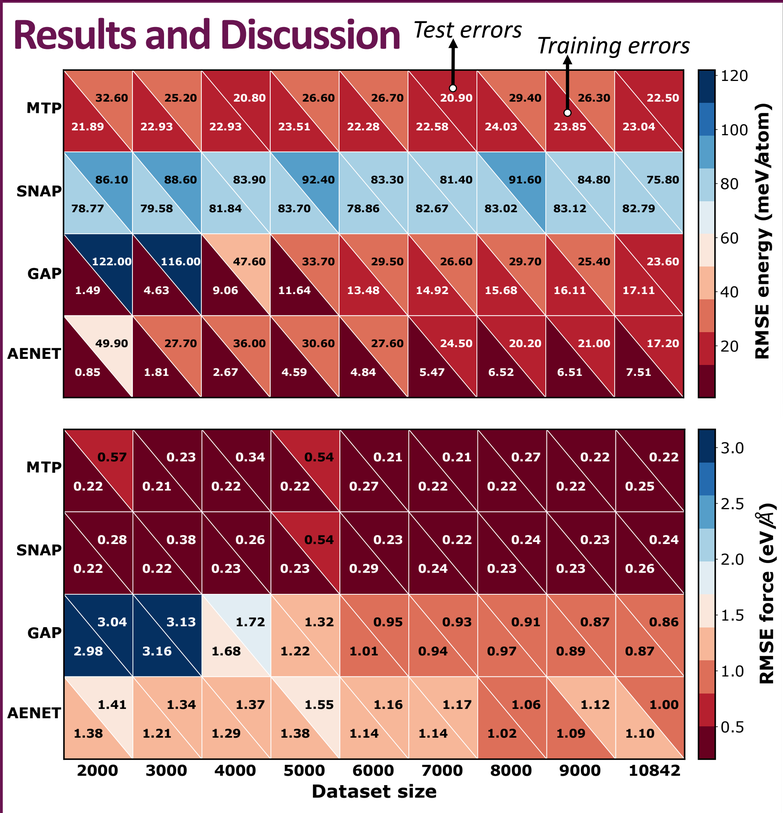


*Perdew-Burke-Ernzerhof (PBE), projector-augmented wave (PAW)

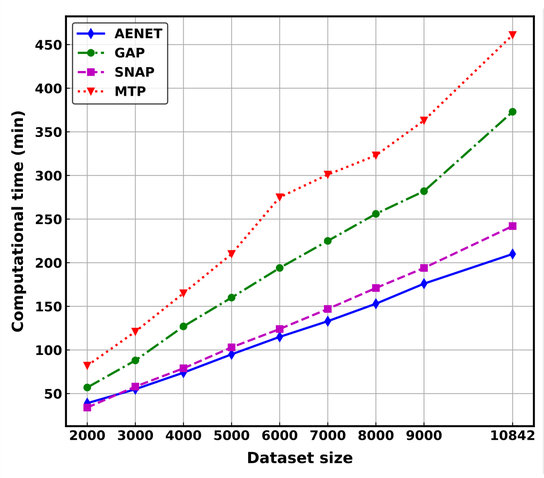
MLIP	MTP (moment tensor potential)[10]	SNAP (spectral neighbor analysis potential)[11]	GAP (Gaussian approximation potential)[12]	AENET (atomic energy network)[13]
Idea	Many-body interactions within a cut-off radius represented via moment tensors	Local atomic density (weighted delta functions) projected on a 4D hypersphere	Local atomic density modelled via a smooth overlap of atomic positions (SOAP) kernel	Feed forward neural network with local bonding environment as the input layer
Descriptor	Moment tensors consisting of radial distribution functions and outer products of position vectors of neigboring atoms	Hyperspherical projection of atomic density expanded in terms of bispectrum components	Atomic density as weighted sum of Gaussians	Radial and angular distribution functions
Training algorithm	Broyden-Fletcher-Goldfarb-Shanno (BFGS)	Linear regression	Gaussian process regression	Limited memory BFGS
Basis functions	Chebychev polynomials (for radial basis) and contracted moment tensors	Hyperspherical harmonics	Equispaced Gaussians (for radial basis) and spherical harmonics (for angular basis)	Chebychev polynomials

Used a single core of a **Intel® Xeon® Gold 6271 CPU**, with a maximum random access memory of 128 Gigabytes, without any hyperthreading for training all MLIPs

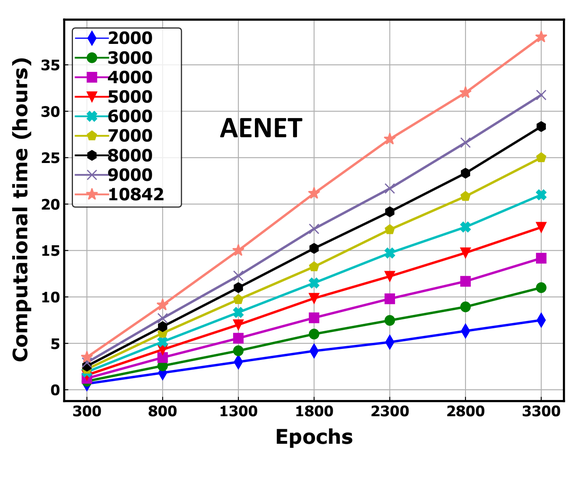
Results and Discussion



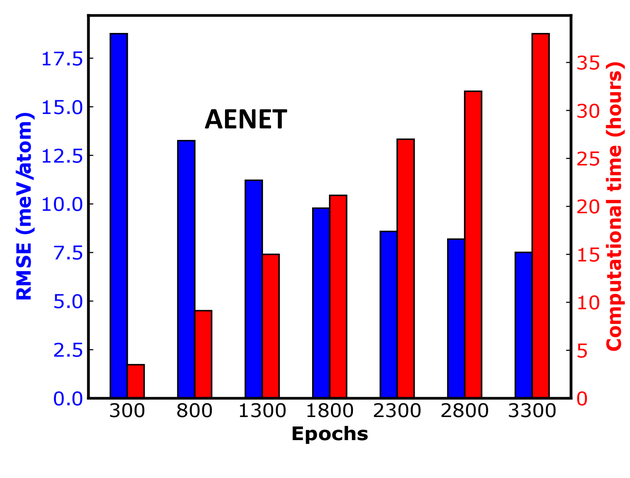
- AENET's **root mean squared errors (RMSE)** ~7.5 meV/atom on energies: similar to DFT (~1 meV/atom)
- SNAP: **largest errors** on energies
- Energy **errors decrease** with increasing dataset size for all MLIPs (**except MTP**): improvement in accuracy
- AENET and GAP display **similar energy** RMSEs in training and testing for all large datasets: **improvement in transferability**
- MTP and SNAP: good **accuracy** and **transferability** on **force** predictions



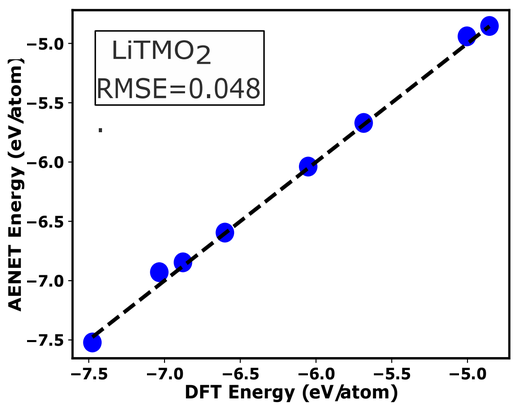
- MTP train time ~ 2 X (AENET train time)
- MTP is the **slowest** to train for all dataset sizes, followed by GAP
- **MTP** and **GAP**: harder to train with increasing dataset sizes

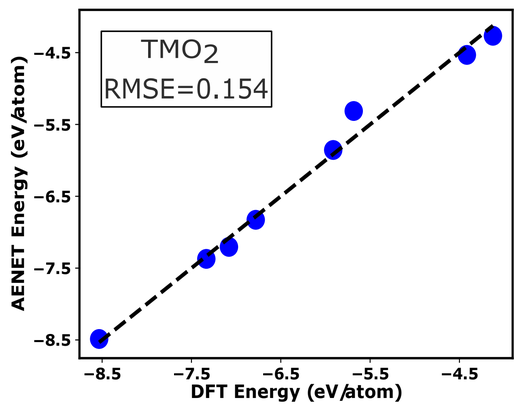


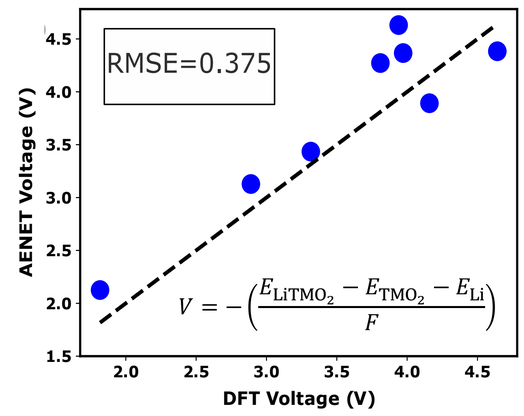
- **AENET:** training time depends on number of epochs
- Increase in training **time** is more rapid with increasing **epochs** for larger datasets



- **Energy RMSEs** for the training set decreases steadily with increasing epochs
- Rapid increase in computational time for the full **10842 dataset** may not be worth the marginal gain in accuracy, after **2300 epochs**







- The accuracy in predicting **material properties** is critical for evaluating the performance and determining the **utility of MLIPs**
- Prediction of **average intercalation voltages**, in ordered, layered, single-TM $LiTMO_2$ as a test of accuracy, versus DFT calculations
- AENET does suffer from a compounding of error versus DFT, **voltage errors: 10.05%** against DFT, largest voltage errors: **$LiFeO_2$ and $LiTiO_2$**

Conclusions

- We have quantified the **accuracy, transferability**, and **ease of training** of five atom-centered MLIPs **(MTP, SNAP, GAP, and AENET)**, in their ability to model the **PES** of disordered, **11-component**, $LiTMO_2$ compositions
- **AENET :** best potential for predicting total **energies. MTP:** the best performer for atomic **forces**
- **AENET** and **GAP** overfit for small datasets, **improve** considerably with **increase** in dataset size
- **AENET (MTP)** exhibit the **smallest (largest)** computational training time
- Our work should aid in the discovery of **novel DRX cathodes** and in modelling **complex, disordered systems**

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