Quest for outperforming cathode materials for Sodium-ion batteries.

Martin Hoffmann Petersen[1], Arghya Bhowmik[1], Jin Hyun Chang[1] and Juan Maria Garcia Lastra[1]
[1]Department of Energy Conversion and Storage, Technical University of Denmark, Anker Engelunds Vej , Kgs. Lyngby, 2800, Denmark
mahpe@dtu.dk

Na-ion batteries (NIBs) are considered sustainable and lower-cost alternatives to Li-ion batteries (LIB) [1]. Currently, no single NIB displays all the desirable characteristics needed for high performance. We aim to search across the polyanionic materials (PAM) universe comprising all chemical composition and structural variations to uncover compositions that are easy to synthesize, contain little or no elements with supply risk and have good electronic and ionic transport properties to achieve this goal. In Fig. 1, we illustrate the tremendous phase space of the PAM universe.

Researchers (including the Nobel laureates Goodenough[2] and Whittingham[3]) acknowledge that more sophisticated theoretical guidance is needed to uncover the phase space and find optimal metal/polyanion combinations since compositions with few types of elements (4 to 6) have yielded limited success[4]. High throughput computation has been tried to screen through a large pool of candidate battery materials to identify suitable candidates for synthesis and application[5].
The size of such candidate libraries depends on the type of property, chemical complexity and simulation system size requirements. Because DFT is an O(n3) method only ~104 configurations of ~100 atom transition metals oxide supercells can be handled with tier-0 supercomputing resources.
Unlike unsubstituted pristine systems, substituted systems need larger simulation boxes and require statistical sampling of atomic configurations for each composition and degree of sodiation[6]. Even with state-of-the-art supercomputing and workflow infrastructure, we cannot explore target PAM phase space with DFT or even with ML potentials. By using conditional generative models we should be able to inversely design cathode materials based on target properties and reduce the amount of computational time needed to find the optimal configuration in the enormous PAM phase space.

Before leveraging generative models for inverse designing promising candidates for cathode materials, it is crucial to establish a comprehensive database of sodium-ion cathode materials. The computational demands of DFT and ab initio molecular dynamics (AIMD) exceed our data collection capabilities, leading us to employ Graphical Neural Networks (GNNs) to develop a Machine Learning Potential (MLP). This approach enables us to study dynamics over extended time scales and large systems[7]. Through an Active Learning (AL) workflow, we refine our MLP to suit our specific system needs. For that, we have recently published a package known as CURATOR [8]. With CURATOR, we have built an autonomous workflow, where we train a MLP, then deploy the model to describe the dynamics of several systems and then we use batch active learning to pick out candidate samples from the MLP driven simulations which needs to be relabelled using DFT to improve our MLP.

Given the disorder within the system, Cluster Expansion (CE)[9] is employed for the initial training set generation. CE also facilitates the modeling of initial and final states of diffusion using the Nudged Elastic Band (NEB) method to estimate energy barriers. With an estimation of energy barriers, we can deploy Kinetic Monte Carlo (KMC)[10] methods to model the ensemble dynamics of the system, shown in Fig. 2. The training of a suitable machine learning model for energy barrier estimation is in progress and done soon.

Focusing on the Olivine and Maricite NaMPO4 (M=Fe, Mn, Ni, and Co), we have successfully trained a MLP using the PAINN[11] architecture to model the dynamics of these materials on the same accuracy level as DFT. From Monte Carlo, molecular dynamics, and NEB simulations we hope to find the perfect doping range of transition metal ions giving us the most stable and energetically favorable system. Proving our methodology in this limited phase space, we can exploit it to the large phase space of the PAM universe and thus expand our search range even further obtaining enough data for the generative model.

References

[1] H. S. Hirsh et al., Advanced Energy Materials, 10 (2020) 2001274
[2] M. Xu, J.B. Goodenough et al., Chem. Mater, 26 (2014) 3089-3097
[3] H. Zhou, M. S. Whittingham et al., Chem. Mater, 23 (2011) 293-300
[4] M. Chen et al., Advanced Energy Materials, 9 (2019), 1803609
[5] S. P. Ong, Computational Materials Science 161 (20198), 143-150
[6] K. Okhotnikov, T. Charpentier and S. Cadars, J Cheminform, 8 (2016), 17
[7] O. T. Unke, et al., Chemical Reviews 121.16 (2021), 10142-10186.
[8] X. Yang, M. H. Petersen et al. ChemRxiv (2024)
[9] J. H. Chang, et al., Journal of Physics: Condensed Matter, 31.32 (2019), 325901.
[10] P. Canepa, ACS Materials Au 3.2(2022), 75-82.
[11] K. Schütt, O. Unke, and M. Gastegger, PMLR, (2021)

Figures

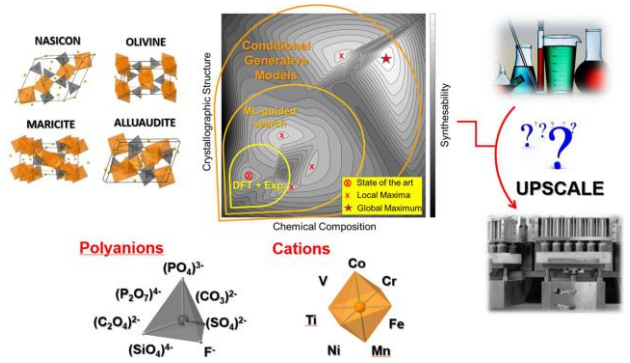

Figure 1. The polyanionic materials phase space, consisting of different crystalline crystallographic structures, anions and cations.

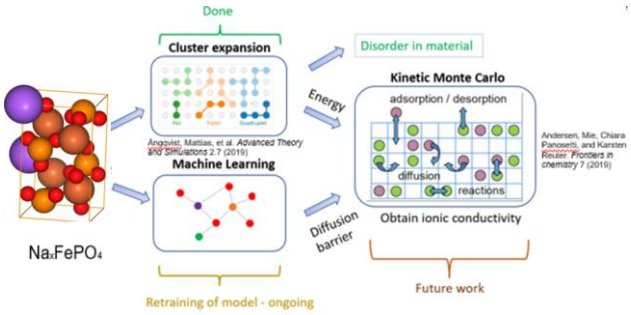

Figure 2. Conceptional idea of the workflow used to predict the diffusion barriers of ionic diffusion