Exploring dopant effects on cathode synthesizeability and voltage stability with high-throughput ML

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Abstract

Battery technology is essential to the clean energy transition, with applications ranging from consumer electronics to large-scale grid-scale energy storage.
Lithium-ion batteries, in particular, have proven durable, safe, and low-cost. Sustainable mining of raw materials and battery recycling are critical to further reducing the environmental impact of our energy needs. However, impurities in material feedstocks such as metal ores and recycled batteries are widely known to have (positive or negative) consequential effects on the performance of cathode materials[1,2]. The impact on phase stability and energy density are two primary quantities that dictate cathode viability in the market. A systematic evaluation of dopants in these cathode active material (CAM) with extrinsic elements, similar to common practices in the semiconductor industry, is key to developing optimal recycling and mining strategies.
However, the vast combinatorial space of CAMs and dopants makes brute-force experimental evaluation a resource and time intensive ordeal. Computational methods, such as density functional theory (DFT), have recently emerged as a new materials discovery paradigm, accelerating the screening of large chemical spaces, including battery applications[3,4]. However, while DFT provides state-of-the-art predictive capabilities, its computational cost prohibits large-scale screening of dopants and CAMs, limiting its application to targeted studies. Universal machine learning interatomic potentials (MLIPs) provides a viable proxy for DFT with moderate accuracy and generalizability across a broad range of chemical systems while dramatically reducing the computational expense.
In this work, we constructed an automated high-throughput screening pipeline that leverages the accuracy and efficiency of universal MLIPs to evaluate the phase stability and energy density of doped CAMs across 15 CAMs and 50 dopants and co-dopants. To bridge the gap between computational and experimental results, we also modelled dopants in varying supercell sizes to assess the effect of dopant concentrations ranging from 25% to 5% doping.
We also present an ensemble of experimental validation including synthesizeability, X-ray Diffraction (XRD) characterization, voltage profiles, and unit cell size. The cross-validation of these results highlights the potential of ML workflows as a viable method for accelerating scientific discovery in highly combinatorial search spaces with good predictive accuracy.

Methods

We employed UMA [5], a foundational MLIP, trained on the the Open Materials (OMat24) [6] dataset in our high-throughput screening of doped CAMs. Our framework is illustrated Figure 1 (top) where we begin by predicting the formation energy of each lithium depletion step in a pristine CAM structure in order to construct the full voltage profile using the following:

$$V = -\frac{\mu_{Li}^{cathode} - \mu_{Li}^{anode}}{zF}$$

where $\mu_{Li}^{cathode}$ and μ_{Li}^{anode} represent the chemical potential of lithium in the cathode and anode materials respectively, z is the number of electrons transferred per lithium ion, and F is the Faraday constant. In concert, we also assess the most stable dopant defect configuration in the CAM based on defect formation energy by considering both substitutional and interstitial defects with the following:

$$E^f(X) = E_{tot}(X) - E_{tot}(bulk) - \Sigma_i n_i \mu_i$$

where $E_{tot}(X)$ is the total energy of the CAM with dopant X, $E_{tot}(bulk)$ is the total energy of the pristine CAM, n_i is the number of species *i* in the doped structure, and μ_i is the chemical potential of species *i*. Likewise, from the most stable doped configurations, we also compute the full voltage profile. This allows us to compare both defect stability and the voltage of a doped CAM simultaneously as shown in Figure. 1 (bottom).
We also assessed the formation energies of undesirable impurity phases that may appear in the synthesis or charging/discharging of the CAM. This allows us to assess the phase diagram of charged and discharged doped CAMs to ensure phase purity throughout the voltage profile.

Results and analysis

Our ML-accelerated workflow enables the enumeration of doping and co-doping sites in the 15 CAM structures representing 300k MLIP calls. These initial computations determine the most stable doped

structures for electrochemical properties computations. Computing the full voltage profile requires about 1 million MLIP calls as we need to sequentially delithiate the structure by enumerating each possible next vacancy site and relaxing the structures. We generated this screening data for 15 CAMs across 50 dopants, demonstrating that universal MLIPs enable accurate, cost-effective large-scale screening of complex properties.
We highlight the first step of our workflow in Figure 2, where we show the formation energy computed for substitutional or interstitial doping of bulk LiFePO4. Our pipeline identifies stable substitutional doping sites across a large portion of the periodic table. We subsequently compute the full voltage profile for delithiation of the cathodes revealing that doping can improve electrochemical performances. We identify among the doped structures the one combining negative formation energy (stable doped configuration) and improved (higher) voltage that remain stable throughout delithiation. After validating our prediction running our pipeline with DFT energy predictions and relaxations, we select the top candidates for experimental synthesis and voltage profile characterization. We measure XRD spectra to confirm the synthesized material's structure, and characterize the electrochemical properties of the doped cathodes.

Outcome and Future Works

In this work, we have demonstrated the application of MLIP in cathode discovery by evaluating simple thermodynamic properties for 13 cathodes and 50 x 50 dopants. As an example, our pipeline proposes Zn, Cd (albeit with toxicity concerns) Pb as potential dopants for improving the energy density of LiFePO4 (LFP). Meanwhile, common contaminants found in feedstock and recycled materials such as Cu and Mn will have a negligible effect on energy density while potentially improving stability. Other common contaminants such as Ni and Co however, can potentially destabilise the CAM.
We hope to explore the effects of surface properties of cathodes with existing MLIP models in the future. The surface of cathodes and in particular, its interface with the electrolyte, is the origin of cathode degradation. We will focus on the impact of solvents on the stability of the cathode and electrolyte interface. A full understanding of both dopant diminished phases and voltage stability along with surface resistance to corrosion will provide a complete scope of overall cathode stability.

References

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Figures

Figure 1. (Top) High-throughput pipeline for discovering novel CAMs. After determining stable dopant configurations, the full voltage curve is computed by sequentially assessing the most stable cation vacancy until full delithiation. In parallel, formation energies of impurity phases are computed to assess phase stability. (Bottom) The resulting data is evaluated to assess the effect of the dopant on the voltage curve and defect stability in a cathode.

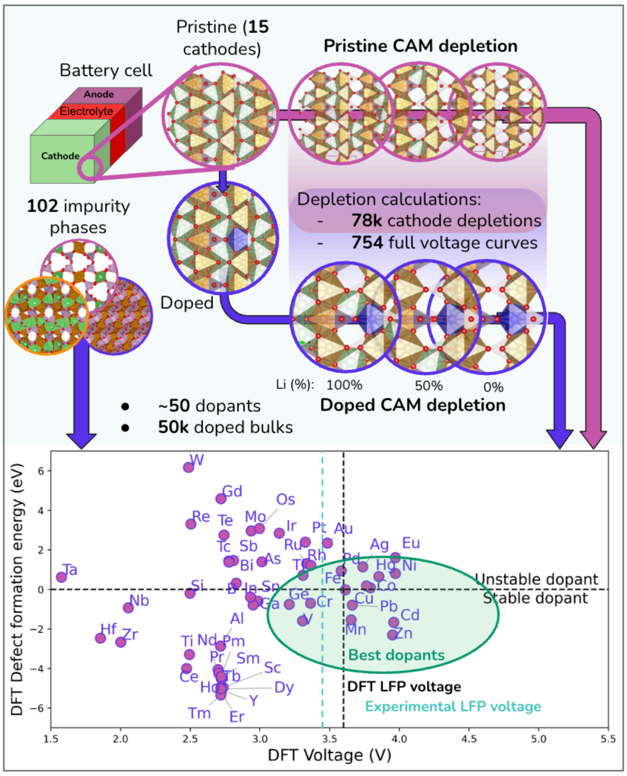

Figure 2. Formation energies of dopants in LiFePO4 at different lattice sites. Heatmap showing the formation energy (eV) for each dopant occupying four possible positions: Fe substitution (top), P substitution (right), Li substitution (bottom), or interstitial site (left). Colors indicate energy magnitude in electron-volt, with lower values corresponding to more favorable dopants incorporation: warm colors indicate favorable dopant incorporation.