Efficient Material Screening by Combining DFT Method and Multivariate Analysis

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Introduction

Exploration of new chemistries through DFT-based computational modeling has become a widely-adopted tool for the rapid discovery and screening of materials. However, evaluation of a vast chemical search space by stand-alone DFT method overwhelmingly becomes a bottleneck step in terms of time resource. In this study, a technique is developed by combining DFT method and multivariate partial least squares analysis in order to efficiently predict the Li ion jump energy within the olivine-type $LiMXO_4$ search space for evaluation as possible solid electrolyte materials.

Computational details

Atomic geometry optimization was carried out through the VASP code. The chemical search space investigated was the olivine-type $LiMXO_4$ composition; M and X are nontransition metals in the periodic table since the intended application is for solid electrolyte use. Initial atomic position data from published structural information on experimentally synthesized ordered olivine materials in Inorganic Crystal Structure Database (ICSD). For unreported compositions, atomic data from reported ones were used as templates. An energy cutoff of 500 eV is chosen to ensure that the total energies are converged within 3 meV per formula unit. Test calculations showed that the results for a $2 \times 3 \times 3$ Monkhorst-Pack kpoint grid in a unit cell showed a reasonable convergence and an error of <1 meV/$LiMXO_4$ unit in the total energy. For the exchange correlation energy, standard generalized gradient approximation (GGA) was used with parametrization of Perdew–Burke–Ernzernhof for solids (PBEsol). The nudged elastic band (NEB) method was used to determine migration pathway and its energy (EA). A $1 \times 2 \times 2$ supercell with a formula unit of $Li_{15}M_{16}X_{16}O_{64}$ (1 Li vacancy created along the diffusion channel), and numerical integration was performed over the Brillouin zone by sampling the Γ-point. Convergence was determined to be within 30 meV/formula unit.

The database used for EA prediction was built from a sample of DFT-accurate EA values (target) and variables (predictors) such as lattice parameters, born effective charge of cations, intra-polyhedron parameters, and inter-polyhedron parameters. For EA model building, partial least squares regression was used.

Results and discussion

Promising M-X pairs (<0.30 eV) with experimental data (from ICSD) according to Figure 1 include Mg-As (0.17 eV), Sc-Ge (0.22 eV), In-Ge (0.28 eV), and Mg-P (0.30 eV); Mg-As and Sc-Ge are reported here for the first time

as battery materials. The diffusion pathway is shown in Fig. 1b and 1c. Fig. 2a shows the fitting quality of the generated EA prediction showing good quality, the final model showed that 96.26% of the variation in the response variable EA can be explained by three new projected variables (RMSE = 0.316). Promising theoretical compositions are also determined for Group 13 Al-X, Ga-X, and In-X pairs, and for Ca-X pairs (Fig. 2b). In Fig. 3, the original variables are ranked by variable importance in projection (VIP) values. The major contributions to EA value came from M octahedron descriptors such as elongation of the M octahedron, bond angle variance of the M octahedron, and Li-O-M angle at the edge-sharing octahedra along the diffusion channel. It was also found out that the variables related to the M octahedron are the ones that were used to build the first new projected variable. Note that the M octahedron is in the immediate vicinity of the Li-ion pass and a strong influence is expected for it in terms of EA. The influence was found out to be expressed in terms of the distortion of the M octahedron that causes energy-penalizing local lattice distortion in the course of ionic transport. Hence, we determined the latter as the crucial parameter for Li ion migration.
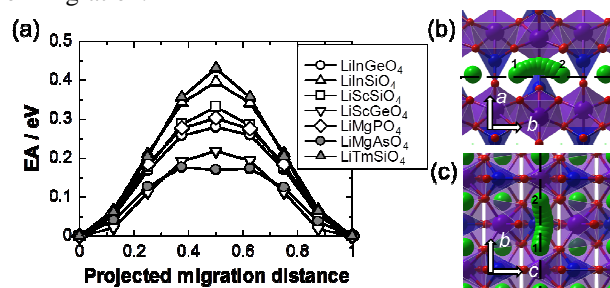

Figure 1. a) Li migration energy (EA) along the 1D-diffusion channel of ICSD-reported olivine-type $LiMXO_4$ compositions. b-c) Migration pathway of Li into an Li vacancy site (from position 1 to position 2) via an interstitial route.
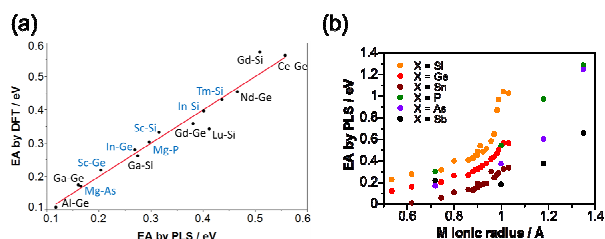

Figure 2. a) Plot of DFT-calculated EA against PLS-predicted EA for different M–X samples. Blue data points M–X pairs are reported in ICSD. b) Predicted Li-ion hopping EA for different M–X pair compositions, according to the final PLS model.
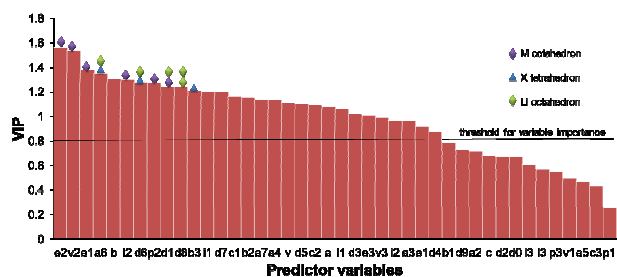

Figure 3. Variable importance in projection (VIP) ranking of predictor variables in the final PLS model.