Exploration of New Materials for All-solid-state Lithium-ion Batteries by Materials Informatics

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ABSTRACT: A key challenge of an all-solid-state lithium (Li)-ion battery (ASSLiB) development is to prevent crack formation in the electrodes during the charge and discharge. Such cracks block the smooth Li-ion transport between negative and positive electrodes and lower the output power. A possible measure is employing a new functional material, which shows higher durability against the crack formation but does not hinder the battery performance. A lot of simulation techniques have been proposed to assist experimental efforts for the new material search. Currently a simulation method consists of three parts has been widely used; candidate generation, synthesizability screening, and performance prediction. However, the ideal materials for ASSLiB have not been reported to the best of our knowledge due to the limitation that a rapid material screening can be done within the conventional material databases. It is known that exploration of unknown materials needs prohibitable computational costs. In this paper, we propose a practical method for unknown material exploration. We combine an unknown crystal structure generation technique using a genetic algorithm, which is known for heavy computational costs, and a machine learning potential to reduce the calculation costs. We demonstrate the performance of the scheme by raising some case studies of new material searches.

KEY WORDS: electrified vehicle, all-solid-state lithium-ion battery, material discovery platform

1. BACKGROUND AND OBJECTIVES

Electrified vehicles such as hybrid electric vehicles (HEV), plugin hybrid electric vehicles (PHEV), battery electric vehicles (BEV), and fuel cell electric vehicles (FCEV) have been seen as the key technologies that can realize a carbon neutral society. Batteries are one of the common and important unites among these. All-solid-state lithium (Li)-ion battery (ASSLiB) attracts significant attention for their enhanced chemical stability against high temperature operations and energy density compared with conventional batteries employing liquid electrolytes [1]. Higher chemical stability of the solid-state electrolytes can realize enhanced energy density since it can simplify and downsize cooling unites. A key challenge in ASSLiB developments is the battery performance degradation caused by the crack formation in the electrodes during charge and discharge. The volume of the active material powders changes as the (de)-lithiation, resulting in the peelings on the powder interfaces and crack formation in the electrodes (Figure 1) [2]. These structural changes in the electrodes can hinder the Li-ion conduction between positive and negative electrodes and lower the output power.

Electrode design optimization to minimize the impact of the crack formation is the essential task in the ASSLiB developments. Several approaches are possible in the design optimization (Figure 2). In the micrometer to millimeter scale, design parameters such as thickness of electrode layers, mixing ratios of powders, powder shape, size etc. can be optimized. To decrease the number of the trial production and experimental tests, we previously reported a

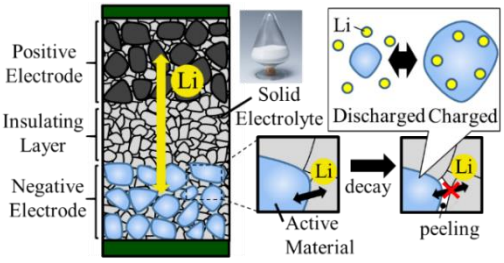

Figure 1. Schematic images of ASSLiB and the volume change of an active material as lithium insertion and ejection. Volume change of active materials causes powder interface peelings and cracks during the charge/discharge processes.

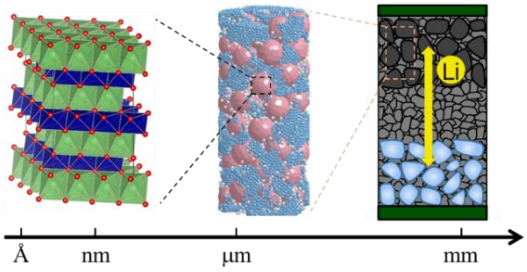

Figure 2. Multi-scale illustration of ASSLiB.

meso-scale simulation model based on a finite element method and demonstrated a successful case of design optimization [3]. In the scale of angstrom to nanometer designs, we select the functional materials that possess high durability against the crack formation as well as nice battery performance. Currently a simulation scheme consists of three parts is used in many cases to assist experimental works; candidate generation, synthesizability screening, and performance prediction (Figure 3) [4]. Firstly, a list of candidate materials is generated, and the candidates are screened by the synthesizability that is evaluated by decomposition energy. The candidates are further screened by the properties required to the batteries. Although there have been many simulation efforts for the material search, the ideal materials for ASSLiB have not been reported to the best of our knowledge. This is partly due to the limitation that a quick material screening can be done within the known materials that are listed in the conventional material databases. We believe exploration of unknown materials largely progresses the ASSLiB developments.

In this paper, we propose a practical method for the unknown material exploration. We combine an unknown crystal structure generation technique using a genetic algorithm, which is known for heavy computational costs, and a machine learning potential as a measure to the large calculation costs. We demonstrate the performance of the method by raising several case studies of new material searches.

2. METHODOLOGY

2.1. Listing theoretical material models

We generate a list of theoretical material models as the first step. We have developed two programs for the model generation. The first method fixes the crystal structure and substitutes the element of each atomic position in the target models. The second approach fixes chemical compositions but explores crystal structures. Both programs utilize a genetic algorithm implemented in the Atomic Simulations Environment (ASE) software package to produce new material models [5]. We choose the programs according to the needs and the situations of our developments. The flow of the structure exploration is described in the figure 4. The program creates theoretical models with random atomic positions from input chemical composition, and it relaxes the structures along the potential surfaces. Then, the optimized structures are converted to new structures by a mutation scheme where children structures keep some features of their parent structures. Then, the children are relaxed again. After we repeat the cycle many times, the algorithm proposes new crystal structures.

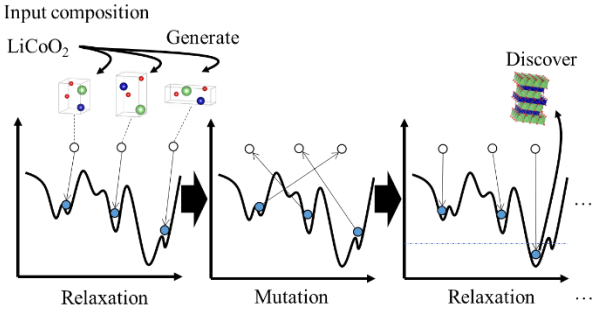

Figure 4. Structure generation by a genetic algorithm.

2.2. Screen candidates by synthesizability

The second step is to check the synthesizability of the generated material models by an indicator of decomposition energy. The decomposition energy is evaluated by an “energy above hull” scheme referring to a large energy data set of known compounds (Figure 5). Smaller decomposition energy indicates a less tendency to decompose into the most stable phases and easier synthesis. We have applied our original material energy database containing more than 300,000 compounds whose data has been derived from a unified calculation condition. We are still expanding the database by adding material data from our developments of not only batteries but also catalysts, semi-

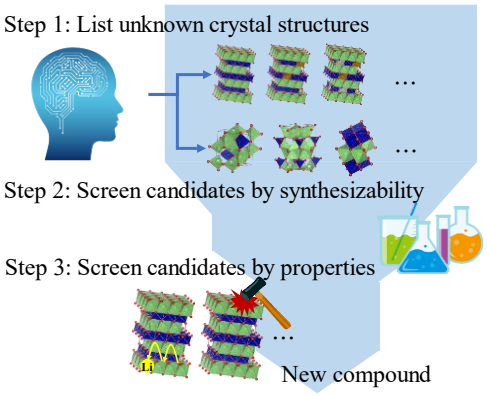

Figure 3. Flow of material exploration.

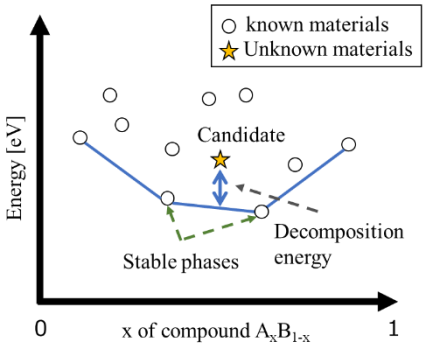

Figure 5. Synthesizability evaluation.

conductors, magnets, and so on related with automobile developments.

2.3. Screen candidates by properties

The third step is to evaluate material properties required to ASSLiB components. In the case of an electrolyte search, for example, we evaluate Li-ion conductivity and elastic constants. Li-ion conductivity can be predicted by a molecular dynamics (MD) simulation. Elastic constants can be theoretically determined by analyzing the energy variation dependent on the lattice constants of the crystal models. MD is a method that predicts dynamical behaviors of ions by continuously calculating the forces on each atom at each snapshot and moves the ions along the forces (Figure 6). The diffusion coefficient (D) of Li-ion can be calculated from the obtained mean-square displacements (MSD) of Li-ions:

$$\mathrm{MSD}(t) = \frac{1}{N}\sum_{i}^{N}[r_i(0) - r_i(t)]^2 \quad (1)$$

$$D = \frac{1}{6}\lim_{t\to\infty}\frac{d\langle \mathrm{MSD}\rangle}{dt} \quad (2)$$

where N is the total number of diffusing Li-ions, $r(t)$ is the position of the ith Li-ion.

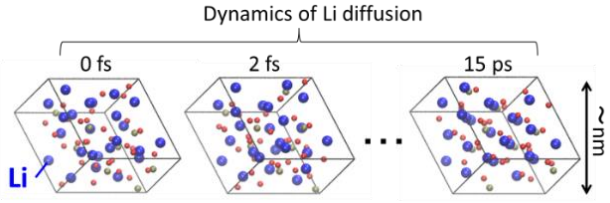

Figure 6. Schematic image of a molecular dynamics.

2.4. Simulation method

Above unknown material search flow is very slow due to the heavy computational costs of the atomic simulations. The biggest bottleneck is the material model generation by the genetic algorithm. Second bottleneck is the MD simulations for Li-ion conductivity evaluation. Both processes need DFT calculations repeated many times. To accelerate the calculation, we adopted an atomic simulator using machine learning potentials (MLPs). MLP is a machine learning model that predict energy and forces from the atomic configurations of target material models. Large DFT calculation databases are used to train the MLPs. MLPs can achieve faster calculation than DFT as well as keeping comparable calculation accuracy. We have selected Preferred Potential (PFP) as a MLP which is provided in a calculation environment of Matlantis because the model is trained by a variety of atomic configurations and chemical compositions, and active improvements are in progress as a universal force field [6, 7].

We can achieve both high speed and accuracy by applying accurate DFT simulations after a quick screening by the MLP simulations. In DFT simulations, the Vienna Ab initio simulation package (VASP) was selected as a solver [8-10]. Inner core electrons were represented by the projector-augmented wave (PAW) potentials. Electron exchange-correlation energy functionals were represented with the generalized gradient approximation (GGA), and the model of Perdew, Burke, and Ernzerhof (PBE) was used for the semi-local corrections.

3. RESULTS AND DISCUSSION

3.1. Material generation by element substitution

The first trial is to generate new Li-ion conducting materials. We explored Li_2MCl_4 with a spinel structure where M is a transition metal [11]. We built a supercell and substituted the transition metal sites by various elements with various ratios (Figure 7). About 100 models were generated to each elemental compositions to investigate various substituted-site distribution. Around 50000 substituted models were generated in total. All structures were relaxed, and the formation energy were evaluated by a PFP force field (figure 7). Calculation time was much shorter than the same algorithm using DFT calculation by around 70 times in our computational environments. We extracted stable compositions (+ 0.1 eV/atom than local minimum) from the calculation results as candidate materials for future experimental tests. These results indicate that the method can help us to explore new materials in a practical time.

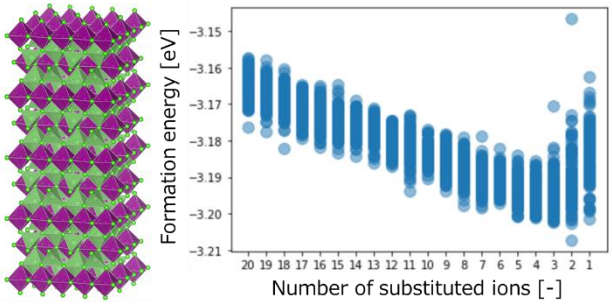

Figure 7. 2x2x4 supercell of Li_2MnCl_4 visualized by VESTA [12] (left), and formation energy of each composition (right).

3.2. Materials generation with new crystal structures

Next, we performed a material model generation without crystal structure templates. We searched stable crystal structures by inputting $LiCoO_2$ which is the chemical formula of a well-

known battery cathode active material. Figure 8 shows the energy variation during the new crystal structure search process. At the end of the calculation, the algorithm successfully discovered the crystal structure of "R-3m" as the most stable, which is the same with the existing cathode. The result implies that this scheme is applicable in exploring new crystal structures.

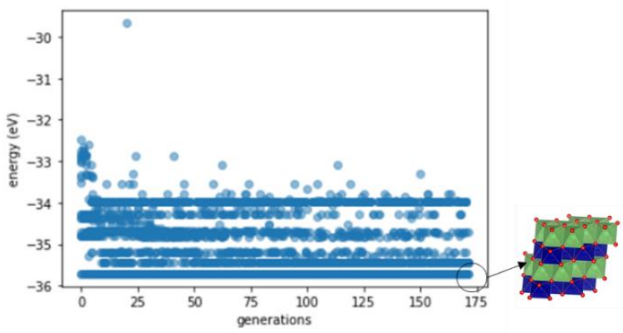

Figure 8. Progress of stable crystal structure search of $LiCoO_2$.

3.3. Material property evaluation

Promising materials can be extracted from the generated candidates above by evaluating material properties. In the exploration of oxygen (O)-ion conducting materials, we evaluated O-ion diffusion constants by MD simulations. Figure 9 shows MSDs and the Arrhenius plot of CeO_2 evaluated by a PFP force field. Because O-ion hopping from one site to the neighboring site is known to be a rare event, we accelerated the phenomenon by raising simulation temperature and by creating O-vacancies in the supercells. In our trial, the MSDs and Arrhenius plot can be produced within a day, which is much faster than the conventional DFT calculation. This indicate that we can accelerate the expansion of material property database with MPLs.

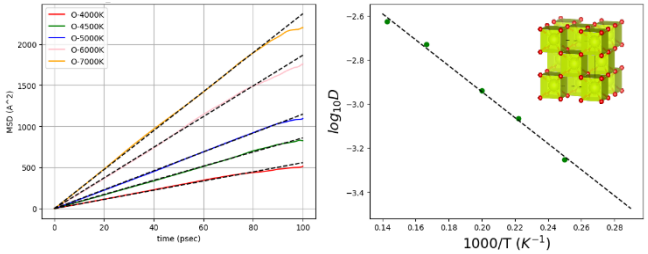

Figure 9. O-ion diffusion in CeO_2.

4. CONCLUSION

We have developed a practical scheme to discover unknown materials for ASSLiB. The method consists of three parts; candidate generation, synthesizability screening, and performance prediction. We have overcome the large calculation costs of unknown model generation and the property evaluation by MLP technology. We believe that the accelerated material data expansion can help machine learning research, and it can further accelerate material research of ASSLiB materials.

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