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# Development of DFT simulation of charging for amorphous anode materials with Bayesian Optimization

*S. Nogami, R. Shintaku, T. Tamura and M. Karasuyama
Nagoya Institute of Technology, Gokiso-cho, Showa-ku, Nagoya-shi, Aichi

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**Corresponding author***: clz12076@ict.nitech.ac.jp

## Abstract

In order to improve the performance of amorphous SiO (a-SiO), which is the next-generation anode material for lithium-ion batteries, we developed a more accurate charging simulation. As a result, we succeeded in developing a more realistic charging simulation method.

## 1. Introduction

Lithium-ion secondary batteries (LIB) with a high energy density have been developed mainly for use in small mobile devices. One possible high-energy density solution is the use of highcapacity negative electrodes fabricated from tin, silicon, or other materials, and a-SiO materials have been already commercialized. However, a-SiO materials has the issue of capacity degradation during charge-discharge cycles. Several atomistic studies based on density functional theory (DFT) have reported on the lithiation behavior of silicon-related amorphous negative-electrode materials. Some studies have employed a scheme wherein lithium (Li) atoms are arranged in the center of the largest spherical void and atomically relaxed. [1] However, there is no assurance that the largest void is an energetically stable site. Other studies have employed a scheme wherein Li atoms are randomly arranged in amorphous models, which are then melted at high temperatures and cooled to generate atomic configurations during the charging process. [2] However, because the actual charging process does not involve such high temperatures to melt the material, there is no assurance that this scheme accurately reproduces the chemical reactions occurring. It is essential to place Li atoms at stable sites in amorphous models rather than random ones.

In this study, a more realistic charging simulation scheme was developed by using Bayesian optimisation to efficiently search for stable sites for Li atoms and to place Li atoms.

## 2. Computational method

The a-SiO model (Fig. 1) was created using a simulation code based on machine learning potential. [3] We used the SIESTA first-principles calculation software with localized basis sets, for energy calculations and structural relaxation.

Mesh points divided into 0.2 Å increments along all axes were considered for the a-SiO model. The objective quantity was set as the total energy of the system, and the stable insertion sites of Li were searched for at each mesh point using Bayesian optimization. Li was placed at the most stable site. The feature value used was the smooth overlap of atomic positions (SOAP) of the inserted Li center. The feature values used were based on the smooth overlap of atomic positions (SOAP) centered on each mesh point. After performing the same process 10 times, we performed structural relaxation. This was repeated until there were 200 Li to be inserted (Fig.2). However, it was very inefficient because the training data obtained during the search was not reused. We considered using the training data obtained in the search for the next and subsequent searches. However, the total energy of the system is not appropriate as the objective function because the number of atoms is different. Therefore, we reused the training data by setting the

objective function as the formation energy $E_n^{form} = E^{SiOLi_n} - \left(E^{SiOLi_{n-1}} + E^{Li}\right)$, which is the ease of lithium insertion.

## 3. Results and discussion

Efforts to reuse the training data significantly reduced the simulation time. The structure was more energetically stable than when Li was randomly inserted. In addition, the number of $Li_6O$ structures that were generated in the random case was greatly reduced. This indicates that the final structure obtained differs greatly depending on the lithium insertion process.

## 4. Conclusions (or Summary)

We have developed a more accurate simulation method for charging lithium-ion battery anode materials using Bayesian optimization. As a result, we succeeded in obtaining a stable terminal structure more efficiently than the conventional method. It was also found that the structural change changed significantly depending on the charging process. These results indicate that the charging process is important.

## References

[1] V. L. Chevrier *et al*., J. Electrochem. Soc., 156 A454 (2006).
[2] C.-Y. Chou and G. S. Hwang, Surf. Sci., 612, 16 (2013).
[3] H. Hirai *et al*., Phys. Rev. Materials 6, 115601 (2022).

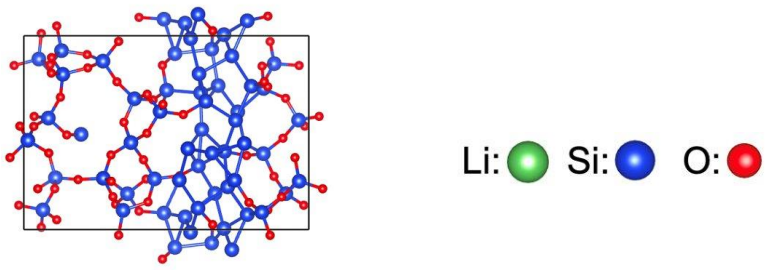


Fig.1: Model of a-SiO($Si_{50}O_{50}$).

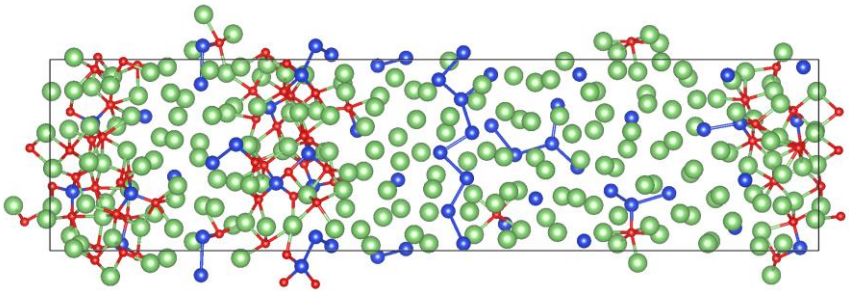

Fig.2: Fully charged model of a-SiO($Li_{200}Si_{50}O_{50}$).