論 文 の 内 容 の 要 旨

論文題目　**Development of Neural Network Potentials to Study Atomic Diffusion Behaviors in Amorphous Materials**

（アモルファス材料中の原子拡散挙動の研究のためのニューラルネットワーク・ポテンシャルの開発）

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1. Introduction

Atom/ion diffusion in amorphous materials is an important phenomenon in many nanoscale information and energy devices, and the atom diffusion rate in amorphous materials has great influence on the performance of the devices. The systematical investigation of such issue is difficult for the computational demanding density functional theory (DFT) calculation for the following reasons. First, the computational cost of popular atomic simulation techniques, such as the nudged elastic band (NEB), becomes much heavier in the amorphous materials compared with the crystalline case due to the lack of structural symmetry. Second, it is strongly desirable to take account of the variation of density and composition, which is often seen in the amorphous materials, in simulations. Because of the factors mentioned above, a systematical investigation of diffusion in amorphous materials is too burdensome for the DFT calculation, and the development of computationally more efficient simulation techniques is in dire need.

Recently, the high-dimensional neural network (NN) potential proposed by J. Behler and coworkers has attracted much attention as a promising way of achieving high computational accuracy and speed [1]. Such neural network-based interatomic potentials were found to be much more accurate than the conventional interatomic potentials while the speed of computations with them is usually several orders of magnitude faster than DFT calculations. Thus they were utilized for examining various materials. However, their application to atomic diffusion is still rare, and none for the diffusion in amorphous materials as far as we know.

In this dissertation, we tried to apply the neural network (NN) potential to tackle this issue. We proposed the simplified NN potential method and explored the applicability of high-dimensional NN potential in simulating atomic diffusion in amorphous materials. The material systems we investigated include 1) the amorphous oxides (*a*-Ta_2O_5 and *a*-AlO_x) with single Cu atoms for the atomic switch; and 2) the amorphous Li_3PO_4 (*a*-Li_3PO_4) for all-solid-state Li ion battery and a novel memory device.

2. Potential for Cu diffusion in amorphous Ta_2O_5

Considering the fact that the high-dimensional NN potential needs a large amount of DFT calculation (10000~100000) results as reference data, we proposed the simplified NN potential, which can be used to predict interstitial diffusion paths and barrier energies. The simplified NN potential is constructed for Cu/*a*-Ta_2O_5 system. The basic idea is to express the total energy of a structure containing

the amorphous Ta_2O_5 matrix and a single Cu atom, $E_{Ta2O5+Cu}$, as the sum of the energy of the pure amorphous Ta_2O_5 matrix, E_{Ta2O5}, and the energy change caused by the Cu atom insertion, ΔE. E_{Ta2O5} can be calculated from DFT. An NN is constructed to predict the energy change due to Cu insertion ΔE according to the local atomic environment of Cu atom.

The potential for Cu/*a*-Ta_2O_5 was constructed using 2000 DFT reference calculations, which is much less than a typical ternary high-dimensional NN potential. The reliability of the utilized NN potential was validated via energy predictions. Its root mean square error (RMSE) for energy predictions was equal to 23 meV/structure for the training set and 39 meV/structure for the independent testing set. To test the reliability of the NN potential for describing the atomic diffusion process, the former was used to predict a path of the Cu diffusion in the amorphous Ta_2O_5 matrix via NEB method. The locations of the diffusion path and the energy variations along the path are shown in Fig. 1. The results obtained with the NN potential was in good agreement with the DFT results, which demonstrated the accuracy of simplified NN potential in predicting diffusion paths and corresponding barrier energies. By comparing the time needed to calculate the energy of a single geometric configuration, we roughly estimated that the simplified NN potential was 10^7 times faster than DFT.

Owing to the high computational efficiency, the equilibrium positions and diffusion paths of Cu atoms in the amorphous Ta_2O_5 structure can be easily identified and characterized. Afterward, the Cu diffusion coefficients at various temperatures can be examined using the kinetic Monte Carlo method. We found that the Cu diffusion activation at the temperature range 500−800 K is 0.67 eV, which agrees well the experimental measurement, 0.64 eV. [2]

Since the simplified NN potential demands relatively few DFT calculations for the reference data, it is easy to construct. However, its application may be limited to the amorphous matrix from which reference data are obtained. Applying the potential to a different amorphous matrix may need considerable compromise on its accuracy. For this reason, we regard the simplified NN potential as a complementary technique to the high-dimensional NN potential: From the simplified potential, a rough overview of atomic diffusion behavior can be obtained with much lower computational cost.

3. Potential for Li diffusion amorphous Li_3PO_4

The high accuracy and good transferability of high-dimensional NN potential make this potential a promising tool for the simulation of diffusion in amorphous material. However, it has never been used on this issue, and its accuracy for the diffusion in complicated amorphous structures is still unclear. For this reason, we constructed the high-dimensional NN potential for amorphous Li_3PO_4 (*a*-Li_3PO_4), and used it to study Li atom diffusion. The *a*-Li_3PO_4 was chosen as the benchmark materials because it is an important electrolyte but the theoretical studies on its structure and atomic transport properties are rare.

The high-dimensional NN potential for *a*-Li_3PO_4 was constructed using 38592 structures and corresponding energies. The structural and energetic properties of crystalline Li_3PO_4 calculated with the constructed NN potential are in good agreement with DFT calculation and experiment. To test the

reliability of NN potential in simulating atomic diffusion, we computed Li vacancy formation energies, diffusion pathways and barrier energies, diffusion coefficients and activation energies using a small amorphous Li_3PO_4 model. By comparing these results with corresponding DFT calculations, we found that the average error of NN potential is 0.029 eV in the calculation of Li vacancy formation energies, 0.048 eV in the barrier energies, and 0.04 eV in the activation energy. Moreover, the diffusion coefficients obtained from molecular dynamics and kinetic Monte Carlo simulation (based on diffusion barriers). As shown in Fig 2, the diffusion coefficient obtains from different simulation approaches are always consistent with DFT results.The computation speed of NN potential is about 4000 times faster than DFT.

In addition, we constructed a large-scale amorphous Li_3PO_4 structure containing 1006 atoms. The formation of P_2O_7 units in the *a*-Li_3PO_4 was observed, which is consistent with the experimental characterization. The Li diffusion activation energy in it is estimated to be 0.55 eV, which agrees with the experimental measurements (0.55 ~ 0.58 eV). [3]

4. Potential for Cu diffusion in amorphous non-stoichiometric alumina

As mentioned, the structural properties of amorphous materials, such as density and atomic composition, are subject to vary depending on the fabrication conditions. Such structure variation should be considered in the simulation of atomic diffusion. However, there is no previous research on the high-dimensional NN potential constructed for bulk material with large density variation or highly off-stoichiometric composition as far as we know. Thus, here we tried 1) to develop the high-dimensional NN potential that can adapt considerable structure variation, and 2) to use the developed potential to study the effect of density and composition variation on the atomic diffusion behavior. The material system adopted for this is Cu/ *a*-AlO_x.

The high-dimensional NN potential for the Cu/*a*-AlO_x was constructed using 41495 reference structures. These structures have different density and O/Al ratio. The variation of their density ρ is in the range of 2.7 ~3.3 g/cm^3, while the variation of O/Al ratio (the x value) is in the range of 1.0 ~ 1.5. The NN potential trained using these reference structures can adapt the density and composition variation in the aforementioned range. The RMSE of such NN potential is 13.8 meV/atom in the training set, and 13.4 meV/atom in the testing set.

The *a*-AlO_x structures were constructed with melt quenching method using the NN potential. The structural properties, such as pair correlation function, bond length and coordination number, are consistent with the experimental observations and other theoretical models. To study the effect of density and composition variation on the Cu diffusion, the Cu diffusion coefficients in different *a*-AlO_x matrices were calculated with molecular dynamics. The states of these *a*-AlO_x matrices are (1) ρ=3.1 g/cm^3, x = 1.5; (2) ρ=2.9 g/cm^3, x = 1.5; (3) ρ=2.7 g/cm^3, x = 1.5; (4) ρ=2.9 g/cm^3, x = 1.25; (4) ρ=2.9 g/cm^3, x = 1.0. The results are shown in Fig 2. With the decrease of *a*-AlO_x density from 3.1 to 2.7 g/cm^3, the activation energies decreased from 1.02 eV to 0.79 eV. By extrapolating the diffusivities with the Arrhenius

relationship, we found that the room temperature diffusivities of Cu increase with the decreasing of *a*-AlO_x density. This result can provide the theoretical explanation for the experimental phenomenon found in the Cu/Ta_2O_5/Pt atomic switch by T. Tsuruoka, that is, the formation voltage of atomic switch drops with the decrease in the density of oxides thin film. [4] The decrease of formation voltage is due to the increase of Cu diffuse in the low-density oxides. On the other hand, the variation of O/Al ratio does not have a significant impact on the Cu diffusion activation energy.

5. Concluding remarks

In this work, we developed several neural network potentials. First, we proposed the simplified NN potential method, which is easy to use, and required relatively few training data. The method can accurately prediction atomic diffusion paths and barrier energies. Though its transferability is limited at the present stage, it can be used as an important complementary technique to obtain rough overview with lower computational cost. Next, the reliability of high-dimensional NN potential in the amorphous diffusion simulation is comprehensively investigated. We found that the high-dimensional NN potential can accurately reproduce the DFT results in the calculation of formation energies, diffusion pathways and barrier energies, diffusion coefficients and activation energies. Finally, we successfully developed the NN potential that can adapt to the considerable variation in density and composition. Using the developed NN potential, the effects of density and composition variation on the atomic diffusion behavior are investigated. All these aforementioned NN potentials have much high computational efficiency than DFT calculation, and can be powerful tools for the theoretical investigation of diffusion behavior in amorphous.

In addition, we provided many simulation results about Cu diffusion in amorphous Ta_2O_5 and AlO_x and Li diffusion in amorphous Li_3PO_4. These results can be useful information for understanding the operation of atomic switch and solid-state batteries. In the future, we expect the NN potential can be a useful tool to investigate other interesting topics in the related fields, such as the Cu diffusion in oxides with the presence of water molecules, the mechanism of Li diffusion in amorphous Li3PO4 or LiPON, etc.

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