Predicting Li Transport Activation Energy with Graph Convolutional Neural Network

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Abstract. Exploring activation energy in ionic transport is one of the critical pathways to discovering high-performance inorganic solid electrolytes (ISEs). Although traditional machine learning methods have achieved relatively accurate activation energy predictions, they suffer from issues such as complex descriptor construction and poor generalization. Graph neural network (GNN) has gained widespread usage in accurate material property prediction due to their ability to uncover structure-property relationships latent in materials data in an end-to-end way. However, current graph representation methods and corresponding GNN models have not been widely applied to the ion transport properties of materials. Here, we introduce the interstitial network graph representation method, and design a GNN model to predict activation energy in Li-containing compounds. As a result, the dynamic ion migration process is characterized, enabling the GNN to automatically capture the inherent mechanisms of ion transport. Performance tests demonstrate that interstitial network representation method achieves high prediction accuracy, with a 10% improvement in prediction accuracy compared with the crystal structure representation method. The developed model can be used to screen and design ISEs and in general providing new ideas for applying machine learning in materials science.

Keywords: Inorganic Solid Electrolytes · Activation Energy · Interstitial Network · Deep Learning · Graph Convolutional Neural Network

1 Introduction

All-solid-state batteries (ASSBs), as a hot topic of research on electrochemical energy storage, have drawn widespread attention for various studies of performance characterization and prediction. One of the primary challenges in the

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advancement of inorganic solid electrolytes (ISEs) pertains to ion transport. Lower activation energy facilitates ion transport and also widens the range of operating temperatures [1]. Therefore, exploring materials with low activation energy (E_a) provides an effective approach to the development of high-performance ISEs.

Nowadays, there are two methods commonly used to derive activation energy. One is to conduct experiment, where electrical impedance spectroscopy is performed to obtain the conductivity data combined with the Arrhenius equation to calculate activation energy. The other is to carry out theoretical simulation, such as climbing-image nudged elastic band (CI-NEB) [2], molecular dynamic simulation (MD) [3], and others. Nevertheless, these methods have demanding requirements for experimental equipment and conditions. Also, they tend to incur high resource costs, which makes them unfit for large-scale search for new materials. Therefore, data-driven machine learning methods have attracted increasing attention from researchers due to their lower computational costs, faster processing speeds, and high predictive accuracy.

Machine learning (ML) has already been widely used for large-scale materials property prediction, particularly the prediction of activation energy [4,5]. Some research has been conducted to explore the approaches based on crystal structure descriptors. For example, Katcho et al. [6] used ion coordination numbers, ion site energies, polyhedral volumes, and compound density as descriptors and utilized a random forest method to model the structure-property relationship between these descriptors and activation energy. Liu et al. [7] performed feature engineering, with 30 descriptors relevant to activation energy prediction selected for ISEs, enabling accurate prediction of activation energy. However, traditional machine learning models are poor at predicting the properties of compounds with composition and structure varying in a wide range.

In recent years, graph neural network (GNN), such as deep learning models, has emerged as a powerful approach to the direct extraction of useful information from raw, unstructured graph data, which removes the need for laborious yet essential design of descriptors. Moreover, graph representation is a powerful method of non-Euclidean data representation that is commonly used to explore various complex properties of the material. Xie et al. [8] represented crystal structures by encoding atomic information and bonding interactions between atoms in the form of crystal graphs, and then proposed a crystal graph convolutional neural network (CGCNN) to accurately predict such properties as formation energy, bandgap, Fermi energy level, and elastic modulus. Based on the crystal structure graph representation, various GNNs have been proposed to improve prediction performance, such as ALIGNN [9], GATGNN [10], and DeeperGATGNN [11]. In addition, Gariepy et al. [12] developed an automatic graph representation algorithm (AGRA) tool that can be used for multi-phase catalysis to extract the local chemical environment of metallic surface adsorption sites. However, as far as we know, there is still no research conducted on the use of GNN to predict activation energy for ion transport in ISEs. Moreover, the mechanism that can affect activation energy is complicated. It is worth noting that the use of the representation methods in the studies cited above

focuses on atomic and space information, which is insufficient to fully capture the underlying mechanisms of ion conduction. As for describing mechanisms of ion conduction, interstitial network (IN) is proposed to adequately characterize the essential geometric and topological attributes of ion transport properties, which are obtained from the network of transport paths formed by skeleton ions and bottle-neck connections in the crystal structure [14].

In this study, we propose a novel graph representation method based on the IN, to achieve an accurate prediction of ISEs activation energy. Then, to mine latent information comprehensively, a GNN model is designed and optimized according to the characteristics of IN. The results demonstrate that the IN representation method outperforms the crystal structure representation method by 10% in predicting activation energy, and it fits well with experimental and simulation results. This work can be adopted to substantially reduce the screening space required for high-throughput computations, contributing a novel solution to the development of machine learning methods guided by domain knowledge.

2 Method

2.1 IN Calculation Method

IN calculations are derived from the screening platform for solid electrolytes (SPSE) [15]. Within ionic crystals, larger-radius anions form a relatively stable framework, while smaller-radius cations are distributed over the created voids. The IN is constructed by connecting the voids and this network is essential for investigating ion transport characteristics. The Voronoi decomposition algorithm represents a spatial partitioning technique widely applied in materials science to analyze crystal interstitial space [16] and is implemented in the Crystal structure Analysis by Voronoi Decomposition (CAVD) geometric analysis program, which can be used to efficiently calculated IN data for crystal structures [13].

The workflow of IN data calculation is shown in Fig. 1. For illustration, we used tetragonal $Li_7La_3Zr_2O_{12}$ (LLZO, icsd-246817) as an example. CAVD encodes the crystal structure using the material information from crystallographic information files (CIF) [17] , including chemical formulae, atomic valence states, and atomic positions. Through Voronoi decomposition, the voids within the crystal structure are transformed into an IN. Then, geometric and topological analyses are performed for this network, through which descriptors are obtained for the geometric structure of solid electrolytes, such as ion migration pathways topology and channel dimensions. Simultaneously, the activation energy values corresponding to the data for each compound are obtained through bond valence site energy (BVSE) [14]. The BVSE program uses CIF files to compute the energy potential field for migrating ions within the three-dimensional crystal structure space. Both CAVD and BVSE have been integrated into our independently developed SPSE. Users can retrieve or upload compounds of interest through the platform and generate the corresponding interstitial network files through CAVD calculations. Through the above calculations, the IN data and activation energy data are collected.

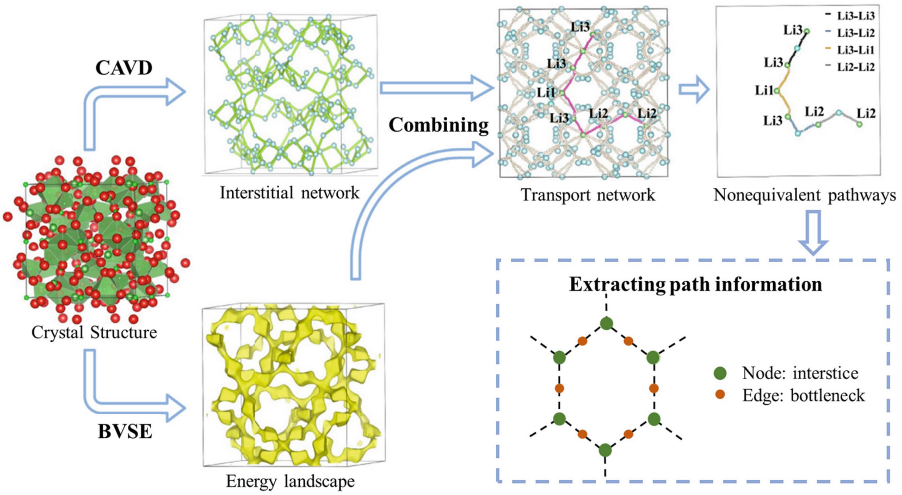

Fig. 1. The workflow of calculate the IN through SPSE. To obtain the IN data, CIF is processed through CAVD, and this information is combined with energy landscape calculated by BVSE to construct the transport network. Subsequently, a nonequivalent path calculation method is employed to filter out redundant data, allowing for the extraction of interstice and bottleneck information along the paths. This process resulted in the generation of IN data samples.

2.2 IN Representation Method

The IN representation method is based on the analysis of interstices and bottlenecks characteristics. In the Voronoi decomposition of the crystal structure, the interstices correspond to Voronoi polyhedra vertices or centers of Voronoi polyhedra faces. The bottlenecks correspond to the position of the minimum radius along each Voronoi polyhedra edge. After obtaining IN data, we utilized interstices as nodes and bottlenecks as edges. For each interstice or bottleneck, we choose the 12 nearest atoms to represent a local chemical environment. High-quality descriptors can greatly improve the accuracy of the model. Hence, we extracted the interstice size and bottleneck size from the IN file and added atomic information descriptors such as atomic numbers and electronegativity. In this process, the nonequivalent paths are calculated, and the bottlenecks and interstices located at the equivalent sites are filtered out to reduce the memory required for the calculation. The construction of the IN representation of the ISEs was then completed. The flowchart of the IN representation method is shown in Fig. 2.

The advantage of IN lies in the fact that the ion transport channels geometric characteristics, conduction thresholds, and ions transport descriptors (e.g., transport channel dimensionality) contained therein are critical to the ion transport performance. The geometric and topological features of the material are extracted and used to calculate the ion transport path information contained in the IN to predict the ion transport properties.

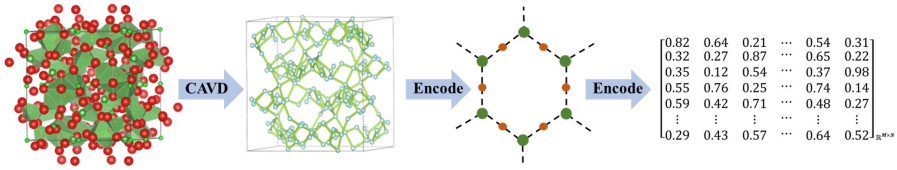

Fig. 2. IN representation method transformation flow. M means the number of nodes; N means the number of features.

2.3 Construction of GCN-Based Activation Energy Prediction Model

Graph Convolutional Neural Network. In this study, graph convolutional neural network (GCN) [18] is employed to extract features of nodes from interstitial network. Sketch of GCN architecture is shown in Fig. 3. For the nth layer in GCN, it takes adjacent matrix A of IN and hidden representation matrix $H_{(n+1)}$ as input, then the output of the next layer will be generated as follows:

$$H_{n+1} = \sigma(\tilde{D}^{-\frac{1}{2}}\tilde{A}\tilde{D}^{-\frac{1}{2}}H_n W^n) \tag{1}$$

where $\sigma(\cdot)$ is the sigmoid function and $H_0 = X$, $\tilde{A} = A + I$ is the adjacent matrix with self-connections.$\tilde{D}$ is the diagonal degree matrix of $\tilde{A}$, and $W^n \in \mathbb{R}^{d_n \times d_{n+1}}$ is a trainable weight matrix. For the ease of parameter tuning, we set output dimension $d_{n+1} = d_n = d$ for all layers.

Graph Pooling Operation. In order to select the key nodes that have great influence on ion transport performance, we adopted the graph pooling operation to simplify the structure of the IN. Through the graph pooling operation, we can eliminate some of the less significant nodes and retain the more valuable nodes. This strategy not only effectively reduces the redundancy of data, but also improves the computational efficiency and provides more refined graph structure data for subsequent analysis.

The Output Layer. After repeating the graph convolution and pooling operations for several times, the final graph level representation Z can be obtained. Finally, we fed the graph level representation into a Multilayer Perceptron (MLP) to perform the activation energy prediction task. The loss function is defined as the Mean Square Error of predictions over the targets:

$$\tilde{Y} = MLP(Z), \tag{2}$$

$$\mathcal{L} = \frac{\sum_i^N (\tilde{Y}_i - Yi)^2}{N}, \tag{3}$$

where $\tilde{Y}_i$ represents the predicted activation energy values and Y_i is the Activation energy values calculated from SPSE. N denotes the training sets of graphs that have targets.

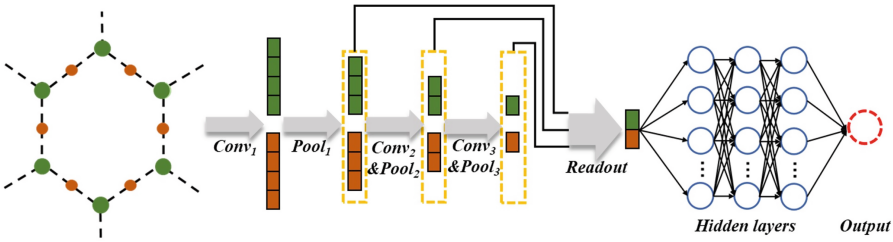

Fig. 3. Structure of GCN. On the left figure, green indicates interstitial; red indicates bottleneck. (Color figure online)

3 Experiments

3.1 Dataset

The IN dataset is collected from the SPSE, which comprises a total of 2150 lithium-containing compound entries. The CIF data is collected from the SPSE and Inorganic Crystal Structure Database (ICSD) [19]. Initial preparations involved organizing the CIF of target compounds and uploading to SPSE for calculation to get IN files. In addition, we collected data from some of the published literature for the comparison of results to validate our method for predicting activation energy in ISEs.

3.2 Experimental Setup

In all experiments, we employed mean squared error (MSE) loss function for training. To assess the accuracy of the model in predicting activation energy, we used determination coefficient (R^2) to evaluate the performance of model. The preprocessed interstitial network files and CIF files are divided into the training/testing/validation sets with a ratio of 8:1:1. We repeated this random splitting process 10 times, and the average performance is reported. Section 2.3 provides a comprehensive description of our model architecture. Table 1 details the parameter configuration.

Table 1. The parameter configuration of the model.

Parameter	Value
$Hidden1\_units$	128
$Hidden2\_units$	128
$Hidden3\_units$	128
$Pooling1\_ratio$	0.9
$Pooling2\_ratio$	0.8
$Pooling3\_ratio$	0.9
Epoch	150
Optimizer	Adam

Hidden unit means the output feature dimension after performing feature transformation and extraction on nodes in each hidden layer; Pooling ratio means the proportion of retained nodes compared to the total number of nodes after a pooling operation.

3.3 Experimental Results

The comparison between the proposed model and state-of-the-art models is shown in Fig. 4. The model based on IN significantly outperforms that based on crystal structures. The results of the models show that when the crystal structure is represented by atomic numbers as nodes, it is less effective information for predicting the activation energy. In contrast, the interstitial space is better representation of the crystal structure relevant for ionic transport, since IN contains additional geometric features and topological logic features, allowing the model to better identify their influence on the activation energy.

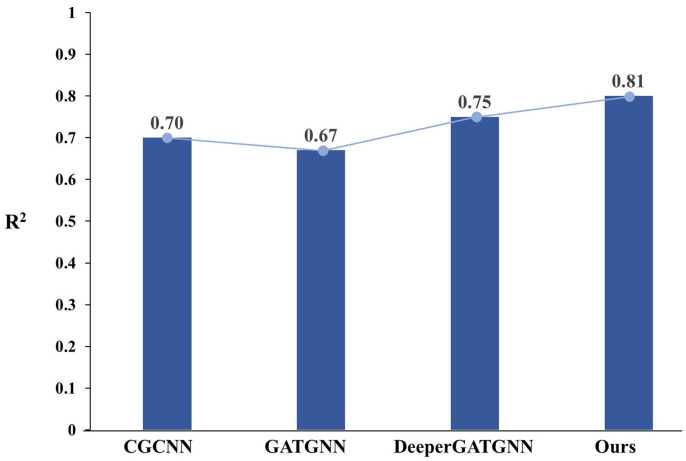

Fig. 4. The performance of different graph representation on the test set.

Partial prediction results are compared, as shown in Fig. 5. Under the guidance of materials domain knowledge, the data set is divided based on the activation energy value. From the accuracy of the activation energy predictions for various material subsets, it is evident that the model excels at accurately predicting materials with low activation energies. While the precision diminishes for materials with higher activation energies, the consistent predictive trends remain unaffected, ensuring the validity of the results. This validates the feasibility of the method for identifying materials with low activation energies. To demonstrate the accuracy of the model predictions clearer, we selected three crystals: Li_3N, $Li_7La_3Zr_2O_{12}$, and $LiFePO_4$, all of which are popular materials in study. As demonstrated in Table 2, a comparison is made among partial prediction results, BVSE results, and published data.

The time required for obtaining activation energy data using three different methods is as follows: Conventional experimental methods demand 48 h from

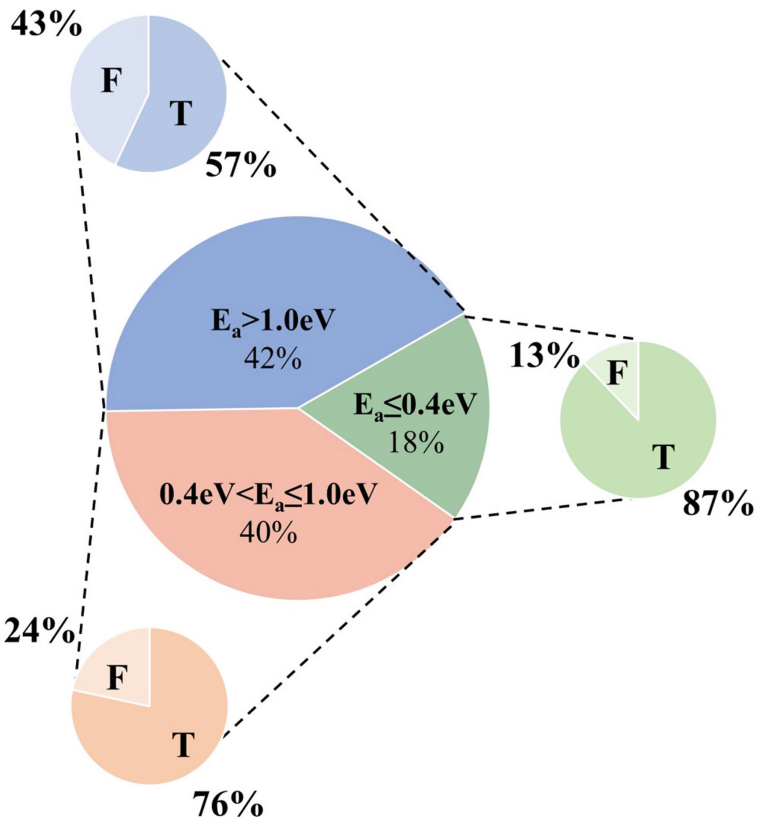

Fig. 5. The percentage of materials with different activation energies and the accuracy of predictions. "T" indicates errors below the threshold; "F" indicates errors above the threshold.

experimental setup preparation to testing for single activation energy value; calculations using the SPSE require 5 min, and lastly, our well-trained model completes the task within a matter of seconds. As a result of screening by this model, the material search space is considerably narrowed down, and experiment time is reduced by orders of magnitude.

Table 2. Comparison of predicted, BVSE-based, and published experimental E_a.

ID	Formula	Prediction(eV)	BVSE(eV)	Published(eV)	Ref
icsd_156898	Li_3N	0.21	0.21	0.13	[20]
icsd_183685	$Li_7La_3Zr_2O_{12}$	0.39	0.46	0.32	[21]
icsd_193797	$LiFePO_4$	0.38	0.39	0.48	[22]

3.4 Parameter Sensitivity Analysis

Performance and generalization ability of a deep learning model are significantly influenced by selection of hyperparameters. Proper hyperparameter choices can enhance model performance, while incorrect selections can result in issues like overfitting or underfitting. Two crucial hyperparameters are the learning rate and batch size. The learning rate dictates the magnitude of weight updates during model training, and an illsuited learning rate can hinder model convergence. On the other hand, batch size determines the number of samples processed in each training iteration, impacting training speed and convergence; an inappropriate batch size can result in slow convergence or training instability.

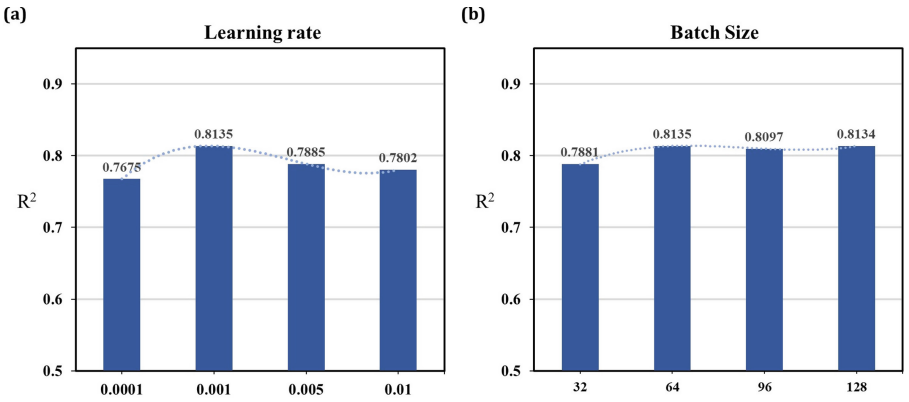

Fig. 6. The performance of the model on different hyperparameters. (a) Learning rate; (b) Batch size.

We conducted a sensitivity analysis on the hyperparameters of learning rate and batch size. Figure 6(a) illustrates how the performance of the model changes with learning rate. When the learning rate was set at 0.0001, the model exhibited its poorest performance, primarily due to the constrained magnitude of weight updates, making it unable to reach an optimal state within the same number of training iterations. Conversely, increasing the learning rate to 0.001 yielded the best performance. However, further increase to 0.005 and 0.01 led to a gradual performance deterioration. This was attributed to the larger learning rate, which induced substantial weight updates, causing the model to oscillate near the optimal point and impeding its convergence. Figure 6(b) illustrates how the performance of the model varied with changes in batch size. The model performed poorly when the batch size was set at 32. This can be ascribed to the smaller batch size, which increased sensitivity to effects of individual samples and reduced training speed. As the batch size increased, model performance gradually improved. Nonetheless, an excessively large batch size consumed more computational resources which may lead to potential scalability issues.

4 Conclusion

In summary, we proposed a graph representation method based on interstitial network (IN) and constructed a graph convolutional neural network (GCN), aiming to predict the activation energy of ISEs. By utilizing the geometric and topological features of the IN, we realized the high-accuracy prediction of activation energy through the graph representation method. Compared with the state-of-the-art crystal structure graph representation method, our method has better predictive accuracy and the efficiency of material screening is orders of magnitude higher compared with conventional calculations. In the future, we will extend the method to other migrating ions, realize the prediction of activation energy of multi-component inorganic solid-state electrolytes and develop the application of IN for predicting additional material properties.

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