Composite polymer solid ionic conductivity calculation software V0.1.0

User Documentation

2023-02-24

Catalogue

1 Introduction

1.1 Background

Rechargeable lithium-ion batteries have high energy density and are widely used in electric vehicles and portable electronic devices. General application. However, due to the flammability of organic liquid electrolytes, commercial lithium-ion batteries are facing severe challenges.

Inorganic solid electrolytes and polymer electrolytes are commonly used in all-solid-state lithium ion batteries. For example, $Li_{0.33}La_{0.557}TiO_3$(LLTO), $Li7La_3Zr_2O_{12}$(LLZO), $Li_{1.3}Al_{0.3}Ti_{1.7}(PO_4)_3$(LATP), and $Li_{10}GeP_2S_{12}$(LGPS) are inorganic solid electrolytes. They usually have high lithium ion conductivity (higher than 1×10^{-3} S cm^{-1} at room temperature), wide electrochemical window (>5V), and good thermal stability. However, inorganic solid electrolytes have problems such as high brittleness and large interface impedance between electrolyte and electrode. On the contrary, polymer electrolytes, such as polyethylene oxide (PEO), polyacrylonitrile (PAN). Polypropylene carbonate (PPC) and polyvinyl carbonate (PVCA) have high flexibility, light weight and relatively high interfacial resistance. However, polymer electrolytes usually have low lithium ion conductivity, small ion transfer number (< 0.5), and poor thermal and electrochemical stability.

The development of inorganic and polymer electrolyte composite materials, namely composite polymer electrolyte, is to solve the above problems. Effective strategy of the problem. In the composite polymer electrolyte, the inorganic solid electrolyte particles are dispersed in the polymer matrix, and the commonly used inorganic fillers are LLZO and LLTO. In the composite polymer electrolyte, the polyether-based composite material has the advantages of low cost, good mechanical stability, good compatibility with the electrode and good film forming performance.

1.2 Theoretical basis

The incorporation of a second phase into a single-phase solid electrolyte disrupts the thermodynamic equilibrium of the crystal defects, changes the ion conduction path and ion migration number, and, due to mechanical stress, a third phase is created at

the interface; this new phase is known as the interfacial phase. The interfacial phase arises mainly because some lithium ions located in regular lattice sites in inorganic fillers move to surface sites and leave negatively charged vacancies in the lattice while positively charged ions appear on the surface. The movement of lithium ions to surface positions leaves negatively charged vacancies in the lattice while positively charged lithium ions appear on the surface. This process is known as the defect reaction. These interfacial phases are highly conductive and provide new conduction paths for ion transport. These interfacial phases are highly conductive and provide new conduction paths for ion transport.

Li^+ therefore involves three diffusion pathways in composite polymer electrolytes, namely within the matrix material (i.e. polymer) internally, inside the inorganic filled phase, and the interfacial phase between the filled phase and the matrix. For the different conduction pathways, continuous channels need to be formed to constitute a percolating ion channel, and a high ionic conductivity complex polymer electrolytes with high ionic conductivity must have at least one percolation pathway with fast conduction characteristics. Studies have shown that the enhanced conductivity of composite polymer electrolyte conductivity is enhanced by the formation of a space charge layer at the internal interface between the two phases, resulting in The increase in carrier density and the corresponding increase in interfacial conductivity.

Therefore, the dispersion of the secondary phase is an effective strategy to improve the ionic conductivity of solid electrolytes, and the percolation effect is an important factor in improving the ionic conductivity of composite polymer solid electrolytes. Achieving quantitative predictions of conductivity This is of great importance for the design and development of future composite solid state electrolytes. This procedure uses percolation theory to predict the electrical conductivity of polymer-based composite solid state electrolytes and to target the amount of free flow required for the highest electrical conductivity of such hybrid solid state electrolytes. The procedure uses percolation theory to predict the conductivity of polymer-based composite solid state electrolytes and to target the concentration range of inorganic

dopants required for the highest electrical performance of such hybrid solid state electrolytes.

1.2.2 Development and application of percolation theory

The percolation model is a statistical model developed by Boradbent and Hammersley in 1957 where the flow of a fluid The flow of a fluid through a porous medium is called percolation and is used to describe the movement of a fluid in a random medium. The model is similar to that of ordinary stochastic processes such as diffusion. The model differs from the usual stochastic processes (e.g. diffusion) in that the fluid motion itself is not stochastic, only the medium is. It is only the medium that has a random nature. Percolation theory can describe many social and natural phenomena, such as the infection of trees with diseases in orchards, the spread of forest fires and the dissemination of information. The theory of percolation can describe many social and natural phenomena, such as the infection of trees in orchards, the spread of forest fires and the dissemination of information.

percolation is also a common problem in engineering fields such as hydropower, geotechnical, oil and gas extraction and geothermal development, and It can lead to engineering damage failure or poor energy recovery. By constructing a Percolation model to analyse the movement pattern of fluids in the medium, the flow rate and the resulting permeability stability and recovery rate, we can guide the design and construction of Percolation control for relevant projects. It also provides a scientific basis for geohazard prediction and efficient energy extraction.

The classical Percolation models are mainly key Percolation and point Percolation on a grid point diagram. In a key percolation model, the space is divided into a series of independent points, each of which has the potential to be connected to each other. As the size of the connections increases, a series of clusters of connections will be formed in the space. Figure 1(a)(b) shows the relationship between a series of points in a two-dimensional plane. (b) shows a series of connections between points in a two-dimensional plane. As the number of connections increases, a network of connections to boundaries will be formed. network. In addition to bonded Percolation, point Percolation is also a common Percolation model (e.g. Figure 1(c)(d)). It is

important to emphasise that Percolation models do not necessarily have to be based on standard grid points, and that arbitrary local interconnections lead to global connectivity analysis. Any global connectivity analysis resulting from local interconnections can be called a Percolation simulation.
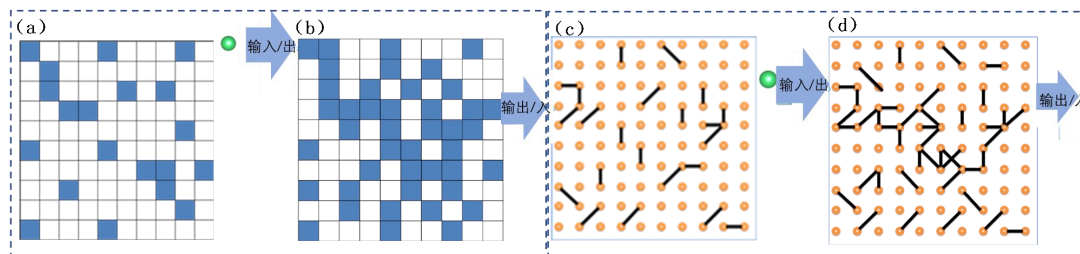

Fig. 1 Two-dimensional diagram of several cases regarding percolation. (a) Bond percolation model with no conduction channel formed; (b) Bond percolation model with conduction channel formed; (c) Point percolation model with no conduction channel formed; (d) Bond percolation model with conduction channel formed. (c) Point percolation model without a conduction channel; (d) Bond percolation model with a conduction channel

In the 1980s, percolation theory was applied to the study of the electrical conductivity of ionic conductors. For composite solid conductors, such as AgI or LiI doped with a second phase of Al2O3, the ionic conductivity of the resulting hybrid conductor increases, a phenomenon that can be explained by percolation theory. The researchers believe that the interface between the first and second phases is highly conductive and that with the addition of the second phase a long-range conductive interfacial channel emerges, thus giving the ions a highly conductive transport channel, the emergence of this long-range conductive interfacial channel is called "interfacial percolation". In the 21st century, researchers have also identified this phenomenon in polymer-based composite solid-state electrolytes. The addition of nanoscale inorganic dopants to polymers can increase the ionic conductivity of the electrolyte.

Based on this finding, our procedure is to use percolation theory to predict the conductivity of polymer-based composite solid-state electrolytes, targeting the range of inorganic dopant concentrations required for the highest conductivity of such hybrid solid-state electrolytes. It is divided into two main parts, building a conductivity model based on two-phase mixture theory and solving for the diffusion

coefficient of the polymer composite solid state electrolyte through a phase stochastic resistance model and Monte Carlo simulations.

1.3 Main functions

(1) Calculate the diffusion coefficient of the composite solid electrolyte system for different doping concentrations

(2) Determine the optimum range of filler doping concentrations for the composite solid electrolyte to achieve the highest conductivity

2 Functional modules and key algorithms

2.1 Functional modules

The main functional module of the program is divided into two parts: the first part is based on a random resistance model to build a two-phase lattice model based on a random resistance model; the second part is a Monte Carlo simulation in which walkers are randomly The second part is a Monte Carlo simulation in which the walkers are randomly walked over the lattice model, sample data is recorded and physical parameters are calculated.
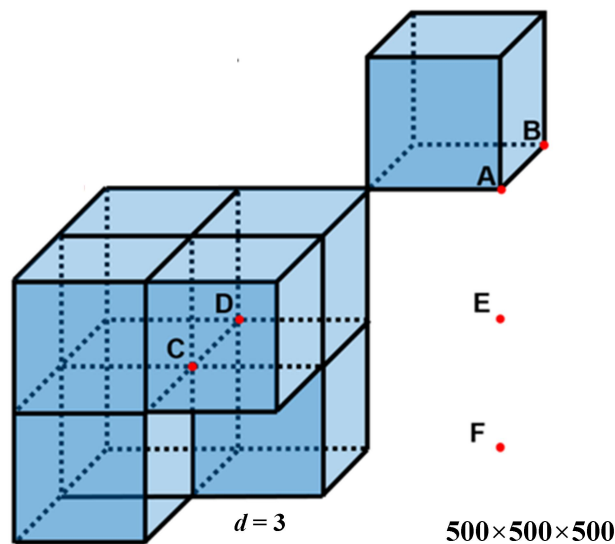

Figure 2 Schematic diagram of the two-phase hybrid lattice model

Firstly, regarding the construction of the two-phase hybrid lattice model, a

500*500*500 lattice gas model is constructed in 3D space (as shown in Figure 2), in which 500*500*500*P lattice sites are randomly occupied (P denotes the doping concentration of inorganic substances) to represent the randomly filled inorganic substances in the polymer matrix. The bonds connecting two adjacent lattice sites can be considered as resistors and three types of bonds exist in the model. (1) Highly conductive bonds AB bond, the number of its surrounding four lattice sites occupied by inorganic substances can be one, two or three, the bond (2) CD bond, where all four surrounding lattice sites are occupied by dopants, indicating an inorganic bond; (3) the last type is a polymer bond, where none of the four surrounding sites are occupied by inorganic dopants. (3) the last type (EF) is a polymer bond where none of the four surrounding sites are occupied by inorganic matter. The walkers in the system migrate along these three bonds.

Once the model has been constructed, Monte Carlo simulations are used to solve for the diffusion constants of the system. In order to quantitatively determine the diffusion constants of the composite conductor, the main input parameters of the program are three τ, which represent the time steps required for walkers to successfully pass through each of the three types of bonds. After initialising the structure, the walkers are allowed to perform random walks, and when enough steps have been migrated, the structure is then used as a base. When the number of steps is large enough, the mean square displacement of the walkers is proportional to the diffusion coefficient. The Nernst-Einstein equation is satisfied. Therefore, we can record the location of the physical coordinates of the walkers' migration and the corresponding time. The mean square displacement of the system can be calculated by recording the physical coordinate positions of the walkers and the corresponding time, and furthermore, the diffusion coefficient can be found. From this This allows us to predict the conductivity of polymer-based composite solid state electrolytes.

2.2 Key algorithms

（1）initial_structure

The module implements the function of initializing the composite polymer conductor

structure, including the size of the model, the occupation of the inorganic phase, and the initial site state of the walkers.

(2) ions_jumping_process

This module implements the algorithm of how walkers choose to migrate.

(3) samples_to_generate

The module is used to record the information of each step of walkers migration, including time step and site coordinates.

(4) parameter_calculation

The module implements the ionic conductivity calculation algorithm, and solves the ionic conductivity according to the Nernst Einstein equation by recording enough walkers migration information.
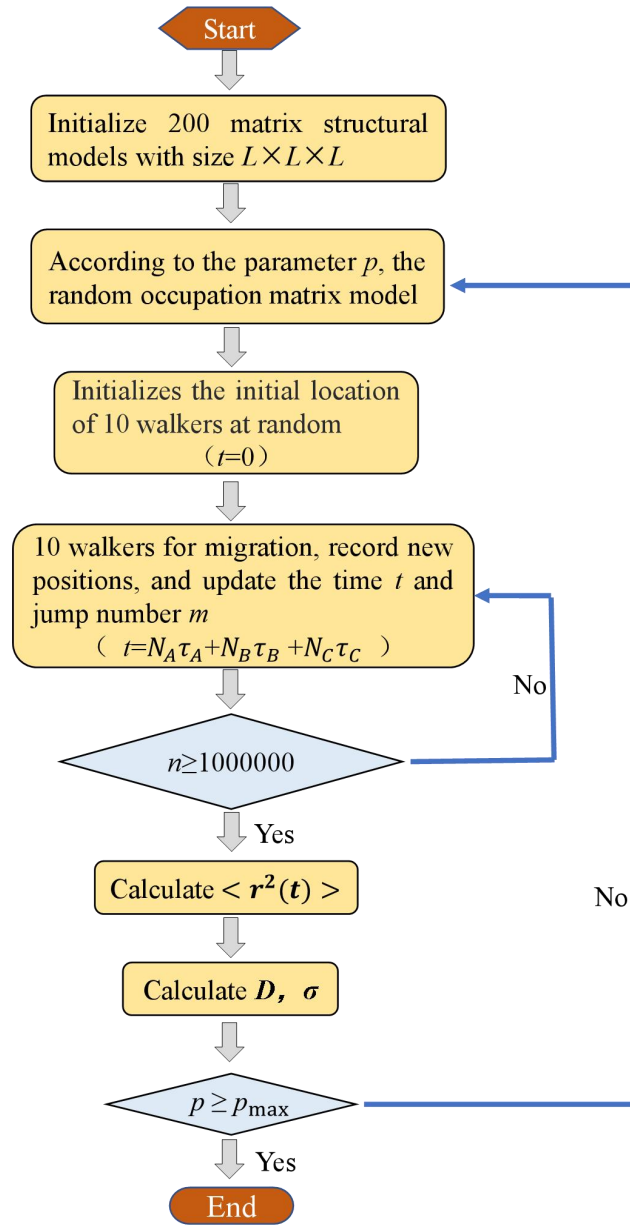
2.3 programming controls

Figure 3 Program design flow chart

3 Operating environment and usage method

3.1 Operating environment

Hardware requirements:

● Processor: Intel or AMD dual-core, frequency 1G and above

● Memory: 4GB and above

Software requirements:

● Operating system: Windows 7 and above

- Python 3
- pandas 1.3.2
- pip 21.2.2
- python-dateutil 2.8.2
- pytz 2021.1
- setuptool 57.4.0
- six 1.16.0

3.2 Installation tutorial

The dependent packet information is stored in the requirements.txt file.

Installation command: pip intall erpipc

3.3Instructions for use

After the installation is completed according to 3.1 and 3.2, the parameters P, tao_a, tao_b, tao_c are set in the parameter_calculation module, and then the program is run to generate a file of sample0, which saves the calculation results of ionic conductivity.