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Analysis of Porosity and Conductivity of Cement-Based Electrolytes Based on Voronoi Algorithm

Yining Yang*, Xingbo Li

School of Urban Planning and Municipal Engineering, Xi'an Polytechnic University, Xi'an, Shaanxi, 710048, China

ABSTRACT
In this paper, to study the influence of porosity on the ionic conductivity of cement-based electrolytes, the Voronoi algorithm was proposed and adopted to generate cement-based electrolytes. Physical experiments were conducted and numerical simulations werecarried out using COMSOL. The results show that it is feasible to generate cement-based electrolytes by the Voronoi algorithm, and appropriately increasing the porosity can significantly improve the ionic conductivity. Through simulation experiments, the fitting formula of-the ionic conductivity and porosity of 5wt% KOH cement-based electrolyte was determined: $y = 0.129x + 0.394$.

KEYWORDS
Cement-based electrolyte; Lonic conductivity; Porosity; Voronoi algorithm

1 Introduction

As solar and wind energy gradually become the core of clean energy, the demand for efficient energy storage technologies continues to increase [1]. Solid-state batteries have attracted much attention due to their significant role in stabilizing the power grid and promoting the integration of renewable energy[2].

In common battery systems such as lithium-ion batteries, liquid electrolytes are widely used due-to their high ionic conductivity and specific capacitance, but they pose safety risks. Its flammability makes the battery prone to combustion or explosion under overcharging, overdischarging or external force impact. The liquid electrolyte has insufficient sealing performance. Leakage can lead to performance decline and environmental hazards. When a short circuit or malfunction occurs, the electrolyte decomposes and releases heat, causing thermal runaway and increasing the risk of fire or explosion. These problems limit its application in high-security scenarios.

Cement materials[3] have become the preferred material for the development of rechargeable cement-based solid-state batteries due to their alkaline properties and porous structure. Cement-based batteries[4-5] have advantages such as low cost, environmental friendliness, and integration of energy storage and structure. They can not only be used as energy storage units but also as structural components of buildings and infrastructure. Although itsunit energy density is relatively low, when integrated into the entire building, the total energy storagecapacity is considerable. However, the performance of the battery is mainly affected by the conductivity of electrolyte ions and the characteristics of theelectrolyte-electrode interface. Therefore, in-depth research on the influence of cement-based electrolyte pores on ionic conductivity is an important direction-for improving battery performance. Meng and Chung[6] were the first to propose the use of cement materials as electrolytes. Their research indicates that the pore structure formed internally after the hardening of cement materials can not only store ionic solutions but also provide channels for themigration of ions in the electrolyte, and the pore connectivity directly affects the ionic conductivity；Rampradheep[7] significantly enhanced the storage capacity of pore solutions by introducing self-curing agents into the cement-based electrolyte, forminga structure similar to a "reservoir" inside the cement-based electrolyte, which slowed down the evaporation of ionic solutions within the pores of the cement-based electrolyte, thereby improving the stability and practicality of the electrolyte；D. Zhang[8] et al. prepared a cement electrolyte with geopolymer and magnesium phosphate cement as the structural phase and KOH as the ionic conductive phase.Through experiments, they found that the pore structure of the cement-based electrolyte had a significant impact on its ionic conductivity, but they havenot yet quantitatively analyzed the mechanism of the pore structure's effect on the overall performance of the cement-based electrolyte in combination with numerical simulation methods。

The performance of cement-based electrolytes is closely related to the distribution and connectivity of their microscopic pore structure. These characteristics directly determine the balance between ion conduction efficiency and mechanical properties. The traditional methods for obtaining the microstructure of cement materials rely on three-dimensionalmeasurement techniques, such as X-ray computed tomography (CT) combined with focused ion beam(FIB) and scanning electron microscopy (SEM), which can generate high-precision microstructure models. However, these methods have a large amountof data and high costs, making it difficult to be widely used in numerical simulation to construct representative volume units (RVE). In contrast, this study adopts the Voronoi algorithm to generate artificial microstructures, which has significant advantages. This algorithm is based on random structural parameters (such as

volume fraction and pore size distribution), and can efficiently generate models highly similar to the real foam-like microstructure. It is widely used in fields such as simulating crystalline aggregates[9], concrete mesoscopic structures[10], and biological tissue repair[11]. The Voronoialgorithm not only has high computational efficiency and low cost, but also can flexibly control porosity and connectivity, providing an economical and reliable numerical simulation basis for analyzingthe influence of the pore structure of cement-based electrolytes on ionic conductivity.

To sum up, existing research has made certain progress in the pore structure and ionic conductivity of cement-based electrolytes, but there are stilldeficiencies: Firstly, traditional microstructure analysis relieson high-cost three-dimensional measurement techniques such as X-ray CT, with complex data processing and high costs, which limits its wideapplication in numerical simulation; Secondly, the existing studies lack systematic simulation and optimization of pore connectivity and distribution, making it difficult to efficiently guide the improvement of electrolyte performance. Furthermore, due to the lack of systematic exploration of the relationship between porosity and ionic conductivity, the application of artificial microstructure generation methods in the field of cement-based electrolytes is still relatively limited.

The introduction of the Voronoi algorithm significantly reduced the modeling cost, determined the functional relationship between the pore structureand the ion conduction efficiency, provided a theoretical basis and technical support for the design ofhigh-performance cement-based electrolytes,and further promoted the application potential of cement-based batteries in the field of energy storage and structural integration.

2 Test and simulation methods

2.1 Materials and molds

In this paper, ordinary Portland cement (PO42.5), pure water and nine kinds of analytical grade inorganic ionic salts (KOH, KCl, K_2SO_4, NaOH, NaCl, Na_2SO_4, $Ni(OH)_2$, $NiCl_2$, NiSO4) are selectedas ionic conductive phases. The water-cement ratiois set at 0.4, and the addition amount of inorganicionic salts is 5wt% of the cement mass. First, dissolve the ionic salt in 40g of pure water and stir thoroughly at room temperature until uniform. Subsequently, the obtained solution was mixed with 100gof cement powder, and a uniform slurrywas prepared using the standard cement slurry stirring process. The slurry is injectedinto a cubic silicone moldwith a side lengthof 1cm (the mold temperature iscontrolledat 20℃), and stainless steel electrodesheetsare inserted on both sides of the mold. Allsamples were placed in a standardcuring box and curedat constant temperature and humidity for 28 days to ensure that the hydration reaction proceeded fully.

2.2 EIS

The impedance characteristics of cement-basedelectrolytes were tested in the experiment using the VSP-300 electrochemical workstation of Bio-Logic Company in France. The experiment adopted thealternating current impedance method (EIS). A sinusoidal wave disturbance signal with an amplitude of 500 μV was applied at the electrode interface, and the test frequency range was 7 mHz-1 Hz. By analyzing the response signals of the material toalternating current, the impedance spectrum of the system was obtained, which was used to study theion conduction mechanism and interface characteristics of the electrolyte. The test adopts a two-electrode system, as shown in Figure 1. The stainless steel sheet serves as the counter electrode (CE) andthe working electrode (WE) respectively. The ionicconductivity of the cement-based electrolyte is determined by Equation:

$$\sigma = d \Big/ \left(S \times R_b \right)$$

In the formula: σrepresents the ionic conductivity, $d$represents the thickness of the cement-basedelectrolyte sample, Srepresents the contact area between the cement-based electrolyte and the blocking electrode, and$R_b$represents the bulk resistance of the cement-based electrolyte, which is determined by the test results of electrochemical impedance spectroscopy (EIS).

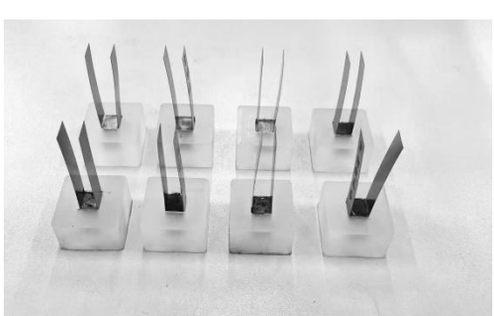

Figure 1 Sample of cement-based electrolyte

2.3 Simulation

COMSOL simulation is mainly based on electrochemical modules and mass transfer modules, and is used to simulate the transport characteristics of ions in cement-based electrolytes. The simulationmodel represents the pore structure of the cement-based electrolyte in three-dimensional geometry, and the geometric dimensions are set at 10mm × 10mm × 10mm according to the sample size measured experimentally. The physical field Settings include the electric field and the coupling of ion diffusion/migration. The Nernst-Planck equation is adopted to describe the ion transport behavior, and the diffusion term is considered. The boundary condition was set to a constant potential difference of 1V to simulate the electrochemical test environmentin the experiment, and the porosity was defined bythe proportion of pores in the geometry. The grid division adopts non-uniform adaptive grids, and the grid fineness in the pore area is higher to capture the local changes of ion concentration. The simulation process is a steady-state analysis. The output voltage distribution, current density, and surface-integration of the cement-based electrolyte are carried out to obtain the equivalent conductivity.

In the simulation analysis, the microscopic pore structure of cement-based electrolytes is generated through the three-dimensional Voronoi algorithm,but it is more illustrative to explain it using two-dimensional images, as shown in Figure 2 below; The two-dimensional Voronoi algorithm is based on-the user-defined n seed points {p1,... pn} divides the two-dimensional domain into convex polygonal elements. Specifically, each unit is a group of points, defined as follows：

$$V_i = \left\{ X \in \Omega \;\middle|\; d\left(x, p_i\right) \le d\left(x, p_j\right) \quad \forall i \ne j \right\}$$

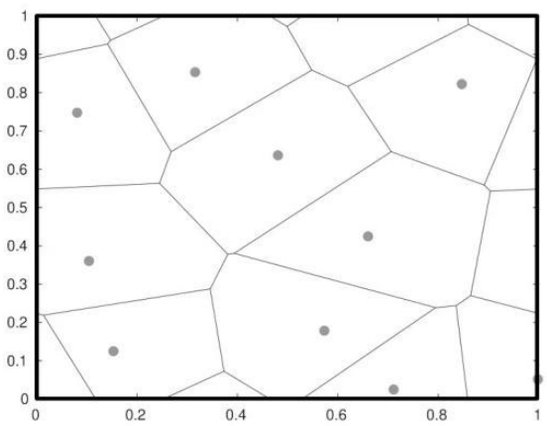

Figure 2 Voronoi algorithm division area

3 Results and discussion

3.1 Research on the ionic conductivity of inorganic salt cement-based electrolytes

The four graphs in Figure 3 show the EIS curves of 5wt% inorganic salt-cement electrolyte. The four graphs indicate that the curves of ordinary Portland cement and nine kinds of 5wt% inorganicsalt-cement electrolyte present a straight line in thelow-frequency region and a small semi-circle in the high-frequency region. The straight line part represents the diffusion and migration of ions in the pore channels. The intersection point of the high-frequency region and the X-axis is the bulk resistance Rbof the cement electrolyte. Figure 3a indicates that the resistance R_b of the ordinary Portland cement body is 1135.4Ω; Figures 3b- 3d show that after the addition of 5wt% inorganic salts, the volume resistances of the 9 groups of cement-based electrolytes all shifted to the left to varying degrees, indicating that the addition of inorganic salts reduced the volume resistance of ordinary Portland cement. The volume resistance range of the 9 groups of cement electrolytes was 252.46Ω-521.34Ω. Among them, the volume resistance Rb of the alkali-salt group was the smallest, followed by the chloride salt and then the sulfate. In the alkali-salt group,the volume resistance of the KOH cement-based electrolyte was the smallest at 252.46Ω. The ionic conductivityof the 5wt% KOH cement-based electrolyte was calculated to be 3.96mS/cm. Compared with the ionic conductivity of 0.88mS/cm of the pure cement-based electrolyte, it is 3.5 times higher than that of the purecement system。

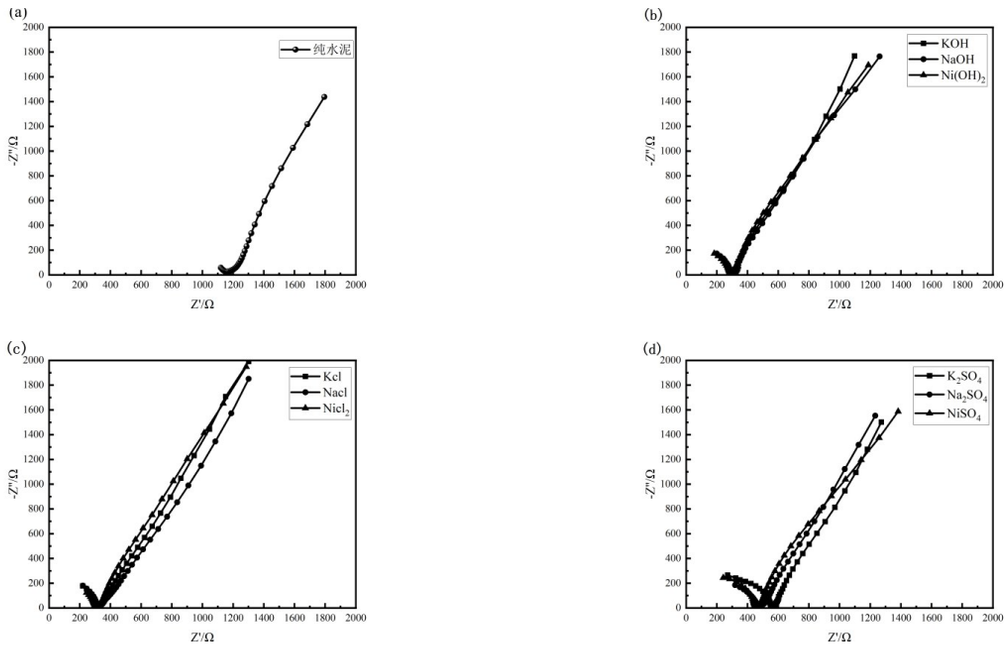

Figure 3 EIS curves of 5wt% inorganic salt-cement electrolytes:(a) pure cement,(b) KOH、NaOH、$Ni(OH)_2$,(c)Kcl、Nacl、$Nicl_2$,(d)K_2SO_4、NA_2SO_4、$NiSO_4$

3.2 Generation and simulation of microstructure of cement electrolyte

As shown in Figure 4 below, a microscopic pore structure with a porosity of 28.4% was generated through the Voronoi algorithm。

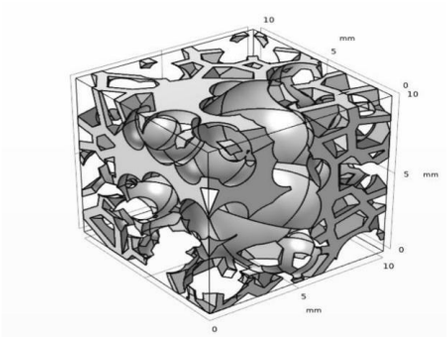

Figure 4 28.4% electrolyte phase

Material parameters: Ionic phase: Ionic conductivity of 5wt% KOH solution 1.3S/m, relative dielectric constant 80；The ionic conductivity of the cement phase is 0.088S/m, and the relative dielectric constant is8；

Surface integral：$I_X = \int_s ecJxdA$

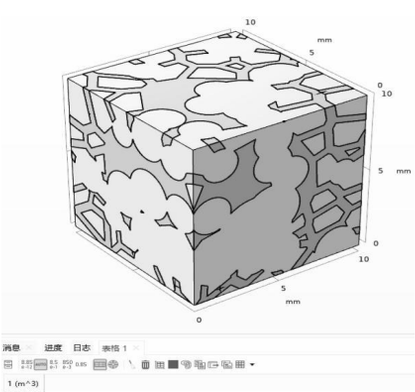

Figure 5 shows a porosity verification of 28.4%

Figure 6 shows the integral result of the current density in the X direction. The calculated equivalent ionic conductivity is 3.87 mS/cm, which is in good agreement with the experimental measurement value of 3.96 mS/cm (relative error 2.3%), indicating the accuracy and reliability of the Voronoi algorithm.

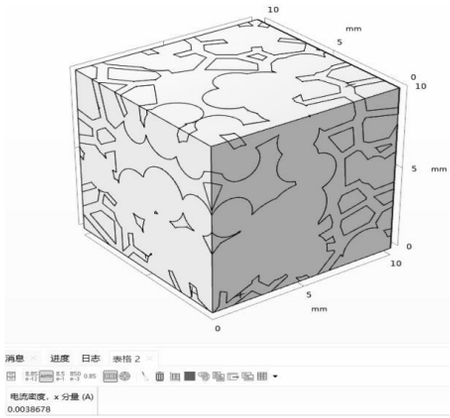

Figure 6 The result after integrating the current density in the X direction

In order to systematically study the influence of porosity on the ionic conductivity of cement-based electrolytes, under the condition that KOH accounted for 5wt% of the cement mass, a series of numerical simulations were conducted by adjusting-the microstructure porosity (ranging from 20% to 70%, with a step size of 1%) through Comsol to analyze the variation law of its conductivity.

Figure 7 shows the quantitative relationship between the ionic conductivity and porosity obtained through simulation. Under the doping condition of 5wt% KOH, the ionic conductivity of the cement-based electrolyte significantly increases with the-increase of porosity. The quantitative relationship between porosity (X) and ionic conductivity (y) canbe expressed by the equation:$y = 0.129x + 0.394$；R^2=0.995，It shows excellent goodness of fit.

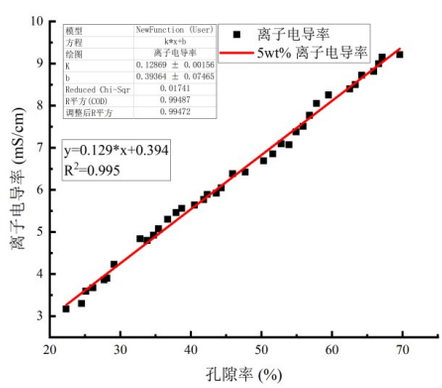

Figure 7 Relationship between porosity and ionic conductivity of 5wt% KOH cement-based electrolyte

4 Conclusion

In this paper, a combination of experimental testing and COMSOL numerical simulation was adopted to systematically study the structure-activity relationship between the ionic conductivity and porosity of cement-based electrolytes. The reliability of the model was verified through the comparative analysis of experimental data and simulation results.

(1) By comparing the effects of three types of electrolyte systems, namely sulfate, chloride and alkali salt, on the ionic conductivity of cement matrix, it was found that the alkali salt system modified by 5wt% KOH had the best performance, withan ionic conductivity of 3.96 S/m, which was significantly better than other systems；

(2) The microstructure model of cement-based electrolytes was constructed by using the Voronoi algorithm, and the equivalent relationship between porosity (20%-70%) and ionic conductivity was established. Under the modification of 5wt% KOH, the linear regression equation is:$y = 0.129x + 0.394$。

The porosity-ionic conductivity relationship model of KOH cement-based electrolyte established inthis paper, and the microstructure model constructed by the Voronoi generation algorithm adopted, can be further extended and applied to the study of the mechanical properties of cement-based electrolytes and their interface effects with battery electrodes in the future.

About the Author

* Corresponding Author: Yining Yang, 231421015@stu.xpu.edu.cn

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