Study on the Electrical Conductivity of Inorganic Conductive Network in Sediments

R Y Zhao\(^1\), Z W Zhao\(^{1,*}\), Z J Weng\(^1\), Y Fang\(^1\) and H L Jiang\(^2\)

\(^1\) School of Electronic Science and Engineering, Southeast University, Nanjing 210096, P. R. China
\(^2\) State Key Laboratory of Lake Science and Environment, Nanjing Institute of Geography and Limnology, Chinese Academy of Sciences, 73 East Beijing Road, Nanjing 210008, P. R. China

E-mail: Zhao_zw@seu.edu.cn

Abstract. The inorganic conductive network provides an essential channel for electron transport and supports the biogeochemical process in sediments, but the conductive mechanism of conductive network is not well understood. In this work, theory of circuit and electronics was applied to build a three-dimensional (3D) resistivity network simulation model for exploring the conductive mechanism and analysing the effect of the particle size on the conductive characteristic of inorganic conductive network. In order to simulate the real sediment environment, inorganic composites with silica (SiO\(_2\)) particles as matrix using magnetite (Fe\(_3\)O\(_4\)) particles as fillers are constructed. The simulation results reveal that the electrical conductivity of these composites rises nonlinearly with the increasing volume fraction of conductive fillers, which is consistent with the percolation theory. Moreover, small-sized conductive particles or large-sized matrix particles are confirmed to exert a positive part in enhancing electrical conductivity of composites.

1. Introduction

It was found that the spatially separated redox process coupled by bioelectric current exists in sediments through the conductive networks composed of complex inorganic and organic components [1]. Compared with organic components, mineral particles, abundant in sediments and considered as the main inorganic conductive components that constitute conductive network in sediments, such as Fe\(_3\)O\(_4\) and FeS\(_2\), not only participate in electron transmission between microbial species, but also significantly enhance the conductivity of sediments [2-4].

In addition, the mechanism of long-distance electron transmission in sediments provides a novel solution and scientific reference for systematically regulating the biogeochemical process of water elements, sediment remediation and developing new energy materials [5-6]. However, in previous work, studies on long-distance electron transport in sediments mainly focus on biological and environmental fields, several researchers have attempted to investigate the construction mechanism and electrical conductivity of conductive network in sediments.

The percolation theory and quantum tunnelling theory [7-8], widely used to investigate polymer composites [9-10], is applied to the study of inorganic conductive networks in sediments in this work. Based on these theories, resistance composition and distribution law of the inorganic conductive network simulated by composite material with inorganic SiO\(_2\) particles as matrix and Fe\(_3\)O\(_4\) particles as conductive fillers are analysed. After that, a 3D simulation model is established to calculate the...
electrical conductivity of conductive composites based on the Kirchhoff's Current Law (KCL) and investigate the effects of particle size on the electrical conductivity of Fe₃O₄/SiO₂ composites.

2. Simulation of conductive network

2.1. Establishment of simulation model

Spheres are used to simulate the SiO₂ particles and Fe₃O₄ particles, and the hard-core model [11-12] is chosen to build a single particle model in that it is more exact when considering tunnelling effect [13]. As shown in figure 1(a), the particle consists of an impenetrable solid core with radius of \( r \) and a penetrable soft shell with thickness of \( t/2 \). The solid core represents the particle entity, while the outer shell represents the effective tunnelling effect area. If the distance \( d \) between two adjacent particles is less than the effective tunnelling effect distance \( t \) [14], particles will be regarded as connected with each other by tunnelling conduction. Otherwise, the path among two particles is an open circuit.

![Figure 1](a) Single particle hard-core model. (b) Adjacent particles model

The length, width and height of the simulation generated domain is defined as \( L \), \( W \) and \( H \) respectively. The spatial location of particle randomly distributing in 3D space is expressed by the equation:

\[
\begin{align*}
    x &= (L \cdot \text{rand}) - \left(\frac{L}{2}\right) \\
    y &= (W \cdot \text{rand}) - \left(\frac{W}{2}\right) \\
    z &= (H \cdot \text{rand}) - \left(\frac{H}{2}\right)
\end{align*}
\]

(1)

Where \( \text{rand} \) is a random number between \([0, 1]\) region, and \((x, y, z)\) is the centre point coordinate of particle. When the distance between two particles is smaller than \( t \), the electrons between two separated particles can pass through the potential barrier to realize electron transmission [12]. In this case, the resistance between two particles consists of the intrinsic bulk resistance of conductive particles and the tunnelling junction resistance [15] between particles caused by electron tunnelling. Beyond this distance, the value of resistance approaches infinity. Therefore, the resistance \( R_{ij} \) between the \( i \)-th particle and \( j \)-th particle depends on the distance \( d_{ij} \) between two particles is written by the equation:

\[
R_{ij} = \begin{cases} 
  R_i + R_t, & 0 < d_{ij} < t \\
  \infty, & d_{ij} \geq t
\end{cases}
\]

(2)

Where \( R_i \) is the intrinsic bulk resistance of particle, \( R_t \) is the tunnelling junction resistance between the \( i \)-th particle and the \( j \)-th particle. The tunnelling junction resistance is calculated by Simmons formula [16-17], which is expressed by the following equation:

\[
R_t = \frac{U_{ij}}{A J} = \frac{p^2 d_{ij}}{A e^2 \sqrt{2m\lambda}} \exp\left(\frac{4\pi d_{ij}}{p \sqrt{2m\lambda}}\right)
\]

(3)

Where \( J \) is the tunnelling current density, \( U_{ij} \) is the electrical potential difference of particles, \( A \) is the cross-sectional area which is assumed to be the same as the cross-sectional area of particles [12,17], \( e \) is the single electron charge, \( m \) is the electron mass, \( P \) is Planck constant, and \( \lambda \) is the barrier height.

The intrinsic bulk resistance of particles calculated by the volume method can be obtained:

\[
R = \frac{1}{\pi \rho} \int_0^r \frac{1}{\rho r^2} e^{\frac{4\pi d_{ij}}{p \sqrt{2m\lambda}}} \frac{\rho}{\pi r} dr
\]

(4)

Where \( \rho \) is the resistivity of the particle and \( r \) is the particle radius.
2.2. Solution of simulation model

Firstly, the centre of each particle is defined as a node, and the node voltage analysis method [18] is used to solve the voltage of any node on the circuit. Selecting one node as a zero-potential reference point, and voltage \( u_i \) at the \( i \)-th node is equal to the potential difference between the \( i \)-th node and the reference point. For the \( i \)-th node, the current flowing into the node can be given as follows:

\[
I_i = u_i \sum_{k=1}^{n} g_{ki} - \sum_{k=1}^{n} u_k g_{ki}, \quad k \neq i
\]

(5)

Where \( g_{ki} \) is the conductance between the \( k \)-th node and the \( i \)-th node. It is assumed that the lower boundary is zero-potential reference point and the upper boundary is observation point, and the node numbers of these boundaries are set to \( n \) and \( 1 \), respectively. The current flowing into the upper boundary is set to 1A, which is equal to the corresponding current flowing out of the lower boundary. Since the other nodes inside the conductive network are not in contact with the outside, the currents flowing through these nodes inside are zero. According to the above analysis, the node current equation set can be obtained:

\[
\begin{bmatrix}
\sum g_{1} & -g_{12} & \ldots & -g_{1(n-1)} \\
-g_{21} & \sum g_{2} & \ldots & -g_{2(n-1)} \\
\vdots & \vdots & \ddots & \vdots \\
-g_{n-1,1} & g_{n-1,2} & \ldots & \sum g_{n-1}
\end{bmatrix}
\begin{bmatrix}
u_1 \\
u_2 \\
\vdots \\
u_{n-1}
\end{bmatrix} =
\begin{bmatrix}
1 \\
0 \\
\vdots \\
0
\end{bmatrix}
\]

(6)

Where \( g_{\theta} = g_{ii} \), and \( \sum g_{n,\ldots} \) is the sum of all the conductance connected with the \( i \)-th node. The minimum norm solution method (using minres function in Matlab software) is applied to solve the linear equations. Subsequently, the equivalent resistance and electrical conductivity of the conductive network can be solved according to Ohm’s law.

3. Results and discussion

3.1. Conductive mechanisms of composites

It has been proved that a classical power law formula [19], i.e., \( \sigma = \sigma_0 (\phi - \phi_c)^t \), can exactly reflect the electrical percolation behaviour of the particle composites. Here exponent \( t \) is a constant, \( \phi \) is the volume fraction of conductive particles and \( \phi_c \) is the percolation threshold which is equal to the critical value of volume fraction of conductive particles at the sharp rise of electrical conductivity. The electrical conductivity of the composites (i.e., \( \sigma \)) is directly proportional to the conductivity of conductive particles (i.e., \( \sigma_0 \)). In table 1, \( \phi_c \) is calculated by fitting the power law formula to the simulation results in figure 2 for the composites with different particle size of Fe3O4 in SiO2 matrix. Herein, similar percolation behaviour is observed in figure 2 for all composites and the electrical conductivity curve shows a steep rise near the expected percolation threshold, which show that the proposed model can predict the percolation behaviour of composites correctly.

| Composites                  | Percolation threshold \( \phi_c \) (vol%) |
|-----------------------------|----------------------------------------|
| Fe3O4 (20nm)/SiO2           | 17.01                                  |
| Fe3O4 (200nm)/SiO2          | 22.13                                  |
| Fe3O4 (2\mu m)/SiO2         | 25.64                                  |

Table 1. Percolation threshold obtained by fitting the power law formula

As shown in figure 2, the volume fraction of conductive fillers significantly affects the electrical properties of composites [12, 17-18]. Taking Fe3O4(20nm)/SiO2 composite as an example, the electrical conductivity curve increases rapidly near the percolation threshold \( \phi_c = 17.01\% \), which is consistent with the percolation formula above. Initially, the electrical conductivity is not influenced by a small quantity of particles. At this time, the average distance between conductive particles is larger than the effective distance of tunnelling effect, and thus the path among the adjacent particles is an open circuit, and the contact resistance between these particles approaches to infinite. Therefore, the composites mainly represent the weak conductivity of the matrix. When the volume fraction of fillers ranges from 17.01\% to 30\%, the trend of electrical conductivity rises dramatically from \( 8 \times 10^{-14} \text{ S/m} \) to
5×10^{-2} S/m. During this process, the electron tunnelling between particles is easier to realize owing to the ever-decreasing average distance of fillers. With the help of electron tunnelling between conductive fillers, conductive paths will be formed between adjacent conductive particles, and the series-parallel action of conductive paths will form a network for transmitting electrons, which makes the composites show electrical conductivity. Once the volume fraction of fillers arrives at 30%, the electronic conduction network established by the electron tunnelling mechanism tends to be perfect, and the continuous increase of conductive fillers will not have distinct effects on the improvement of the electrical conductivity.

![Figure 2](image2.png)  
**Figure 2.** The effect of conductive particle size on the electrical conductivity of composites.

![Figure 3](image3.png)  
**Figure 3.** The effect of matrix particle size on the electrical conductivity of composites.

### 3.2. Electrical conductivity of composites

The effect of the particle size on the electrical conductivity of composites simultaneously consisted of Fe₃O₄ and SiO₂ was not fully investigate. Moreover, it is difficult to achieve particles with identical sizes. Under these circumstances, the influences of particle size on electrical conductivity are analysed by means of 3D simulation model.

The trend of the electrical conductivity of composites shown in figure 2 is obviously related to conductive particle size. Although the composites consisting of small-sized conductive particles present higher electrical conductivity under low volume fraction, the conductivity tends to change more slowly with the volume fraction and the maximum conductivity is lower than that of composites consisting of large-sized conductive particles. The series-parallel channels based on tunnelling theory are sensitive to the distance between the particles and the number of particles involved in the establishment of the conductive paths. The average distance between small-sized particles is large, which makes it difficult to form conductive paths between conductive particles. However, the number of small-sized particles participating in the formation of conductive paths increases faster than that of large-sized particles. It can be concluded that the number of conductive paths generated in composites with small-sized conductive particles is naturally larger than that in composites with large-sized conductive particles.

Additionally, the effects of different matrix particle sizes on electrical conductivity are studied. It can be seen from figure 3 that the electrical conductivity of the composite based on micron-sized SiO₂ is obviously higher than that of the composite based on nano-sized SiO₂. The difference in electrical properties of Fe₃O₄/SiO₂ composites with varying size SiO₂ as matrix is attributed to the effect of matrix size on electron tunnelling and the establishment of conductive paths. It is obvious that the pores of micron-sized SiO₂ matrix are bigger than those in nano-sized SiO₂ matrix. Therefore, the conductive nanoparticles distributed in the pores of micron-sized matrix will be more easily concentrated, so the probability of conductive particles conducting with each other is higher, hence the electrical conductivity will show a higher level. Furthermore, since nano-sized SiO₂ is closer to the
size of fillers, nano-sized matrix particles evenly distributing around the fillers act as a “wall” that prevents the electron transfer.

4. Conclusions
By establishing the 3D simulation model of inorganic conductive network, the conductive mechanisms and the electrical conductivity of Fe₃O₄/SiO₂ composites are studied. The electrical conductivity of composites is found positively relevant to conductive particle content. Micron-sized matrix particles are more conducive to the electrical conductivity of composites, and the electrical conductivity of composites based on micron-sized SiO₂ can reach a higher level by adding a small quantity of conductive fillers. On the contrary, small size conductive particles contribute to improving the conductivity of composites. This non-linear trend of electrical conductivity is consistent with the percolation theory, which further verifies that the established model is effective. The conductive mechanism of inorganic conductive network is the basis of the further study on organic conductive network in sediments, and the 3D simulation model of inorganic conductive network proposed in this work also provides a fresh idea for further study on long-distance electron transport and biogeochemical process in sediments.

Acknowledgments
This work was financially supported by the National Natural Science Foundation of China (51879042, 51839011); Postgraduate Research & Practice Innovation Program of Jiangsu Province, the Fundamental Research Funds for the Central Universities (KYCX20_0105); State Key Laboratory of Nuclear Power Safety Monitoring Technology and Equipment (K-A2020.415); National Key Research and Development Program of China (2018YFE0125500).

5. References
[1] Nielsen LP, Risgaard-Petersen N, Fossing H, Christensen PB and Sayama M 2010 Nature. 463(25) 1071-4
[2] Hermans M, Lenstra W K, Hidalgo-Martinez S, Helmond N V, Witbaard R, Meysman F, Gonzalez S and Slomp C P 2019 Environmental Science & Technology. 53(13) 7494-503
[3] Bo B J, Findlay A J, Pellerin A 2019 Frontiers in Microbiology. 24(10) 849
[4] Kato S, Hashimoto K, Watanabe K 2012 Proceedings of the National Academy of Sciences. 109(25) 10042-6
[5] Malvankar N S, King G M and Lovley D R 2015 The ISME Journal. 9(2) 527-31
[6] Liu F, Rotaru A, Shrestha P, Malvankar N, Nevin K and Lovley D 2015 Environmental Microbiology. 17(3) 648-55
[7] Shinde Mahesh A and Kim Haekyoung 2021 Materials Today Communications. 26
[8] Judd J 2004 Fire Prevention & Fire Engineers Journal. 381 36
[9] Simmons J G 1963 Journal of Applied Physics. 34(9) 2581-90
[10] Irzhak V I 2021 Colloid Journal. 83(1) 64-9
[11] Ying H, Wang W, Xiao Z, Guo X, and Zhang Y 2018 Journal of Applied Polymer Science. 135(32) 46517
[12] Wang G, Wang C, Zhang F and Yu X 2018 Computational Materials Science. 150 102-6
[13] Guanda Yang, Dirk W Schubert, Fritjof Nilsson, Muchao Qu and Michael Redel 2020 Macromolecular Theory and Simulations. 29(5)
[14] Balberg I 2009 Journal of Physics D Applied Physics. 42(6) 64003-18
[15] Chen X, Alian A R and Meguid S A 2020 European Journal of Mechanics - A/Solids. 84 104053
[16] Simmons J G 1963 Journal of Applied Physics. 34(6) 1793-803
[17] Dongjia Kim and Jaewook Nam 2020 Phys. Chem. C. 124(1) 986-96
[18] Ning H, Karube Y, Cheng Y, Masuda Z and Fukunaga H 2008 Acta Materialia. 56(13) 2929-36
[19] Milind Jagota and Isaac Scheinfeld 2020 Phys. Rev. E. 101 012304