

RESEARCH ARTICLE

Changes in conductivity of illite modified with cationic surfactant

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Illite is a kind of clay mineral widely used in the ceramic industry, chemical fertilizer industry, and other fields. It needs to be modified to improve its surface hydrophobicity before it can be used as filler of organic polymer and other materials. In this study, the conductivity changes of illite modified by cationic surfactant were investigated. Dimethyldioctadecylammonium bromide was selected as the cationic surfactant to modify illite by microwave activation. The conductivity change of illite was studied by X-ray diffraction, scanning electron microscopy (SEM), and ionic conductivity test. The results of X-ray diffraction showed that there was no obvious insertion effect on the surface of illite after treatment and only the surface of illite presented with the cationic surfactant, which proved that the surface modification of illite was successful. The results of SEM showed that the illite layer was loose after the modification. The ionic conductivity of illite increased with the increase of the content of cationic surfactant. There was a significant negative correlation between the change of pH value and conductivity, while the stirring operation had a significant effect on the pH value and conductivity.

Keywords: cation; surfactant; modification; illite; conductivity variation.

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Introduction

Illite is the general name for mica sediments, a layered mineral containing structural water and large amounts of adsorbed water. Illite is a common mineral on the earth's surface. Illite constitutes the four most important clay minerals in clay sedimentary rocks together with kaolinite, chlorite, and montmorillonite [1]. In 1973, scientists found illite in the markokita shale in Calhoun, Illinois, USA, which was named after the origin. Illite is a kind of mineral clay, which is an intermediate mineral among mica, kaolinite, and montmorillonite [2]. Illite is widely distributed in sedimentary rocks. The main reasons for illite formation are weathering and decomposition of feldspar and mica, hydrothermal alteration, and

recrystallization of sedimentary colloid. Illite belongs to the monoclinic system, whose chemical formula is $KAl_2[(Al, Si)Si_3O_{10}(OH)_2 \cdot nH_2O]$. Illite is mostly flakes like blocks with gray-white color. The hardness of fresh ore is 1. Most of the hardness after mining becomes 1.5 - 2. The crystal structure of illite is a tetrahedra-octahedra-tetrahedra (TOT) type unit layer structure like a sandwich formed by two tetrahedrons corresponding to the top oxygen sandwiched with an octahedral layer. The crystal structure of illite is similar to that of mica minerals with the structure of layer charge of 2:1 [3]. Illite is a clay grade mineral, which has many similarities with muscovite, but it is also different. The difference is that illite is rich in SiO_2 and H_2O , while there is a small amount of K_2O . Therefore,

illite is closer to polysilicate muscovite. Although illite contains more H₂O than mica, and the content of H₂O is inversely proportional to that of K₂O, the illite interlayer is mainly K⁺, which is not expansive. Illite grows in a low-temperature and low-pressure environment, which usually occurs in buried rock, low-temperature area, and hydrothermal process. Illite is also the weathering product of muscovite and feldspar. However, it is not easy to be weathered on the surface. When the geological temperature rises, illite is unstable and transformed into other materials. Illite is the main mineral component of modern mudstone and ancient shale [4], which is an important diagenetic and clastic mineral in low-temperature sedimentary rock. According to the current geological survey results, there are 6 illite deposits in China, mainly distributed in Jilin, Henan, Zhejiang, and other provinces. With the rapid development of industries, the use of illite becomes more widespread. The demand for illite will gradually increase. In agriculture, illite can be used to produce potassium fertilizer, providing essential potassium elements for crops. Illite can also be used to manufacture industrial fillers for rubber and plastics. Illite can endow these materials with characteristics such as low-temperature resistance, high thermal stability, flame retardancy, and good mechanical strength. In addition, illite plays an important role in environmental protection. It can purify water quality and is used as a cosmetic raw material due to the soft and smooth texture, good dispersibility, and ability to reflect ultraviolet rays.

The study of illite is beneficial for sustainable development in different fields and has important practical significance. At present, a large number of researchers have studied the microstructure of illite. Further, the adsorption performance, electrochemical performance, modification, and filler of illite were also studied [5]. In addition, the formation, structure, particle size distribution, thermodynamic properties, and optical properties of illite were analyzed. Xia *et al.* combined Gemini surfactant and traditional cationic surfactant to investigate illite,

pyrophyllite, and kaolinite, respectively [6]. Norman *et al.* found that Gemini aggregators showed stronger aggregation ability to illite and other powders compared with similar monomer molecules. The physical electrostatic effect and hydrogen bond effect were mainly used to explain the excitation of the interaction between these two cationic activators and minerals. The different aggregation capacity was related to its unique structure and basic performance. The study of micropolarity and contact angle showed that the critical angle concentration of dimer surfactant in mineral slurries such as illite was relatively lower than that of monomolecular surfactant [7]. Illite led to the better hydrophobicity of dimer surfactant at the mineral-solution interface. Godwinm *et al.* studied the electrochemical properties of illite by analyzing two different illites and found that both illites had similar surface chemical properties [8]. Potentiometric titration of clay mineral suspension found that the surface charge concentration was very sensitive to surface treatment. Although the adsorption and desorption of hydrogen ions and hydroxyl could explain the development of surface charge, the cation of electrolyte exerted a certain influence. At present, the exploration of illite has achieved excellent results. For example, X-ray diffraction was used to study the crystallinity of illite. The crystallinity index of illite was used to distinguish the types of rocks, which classified the transitional rock types between epimetamorphic rocks and sedimentary rocks. In addition, some K-Ar dating analyses using authigenic illite is also carried out.

The intercalation modification method is to combine the cation surface exchange theory and insert the cationic surfactant into the middle of illite clay layer to improve the microstructure of illite interlayer [9]. Cationic surfactant includes organic ammonium salt and phosphonium salt. Montmorillonite, graphene, and mica are mainly modified by intercalation. As a typical layered silicate clay, intercalation treatment also has good modification results on illite. With the gradual improvement of intercalation

modification research, intercalation modification has shortcomings in polymer addition. The stability of organic clay at high temperature decreases, especially after the organic intercalation modification of clay. In the blending clay and polymer to make composite materials, organic ammonium cationic surfactant was easy to decompose at high temperature due to the high melting temperature and shear stress of polymer [10]. The decomposition of modifier would lead to the loss of supporting material flow of clay micro lamellae and collapse. The decomposition affected the performance of composite materials and greatly limited the application of modified clay in polymer composite materials in the field of fillers.

The modification scheme of illite clay is not limited to the methods such as completely wrapped of particle surface and plasma modification. With the development of specialized research on illite clay, the modification scheme becomes more mature [11]. The application field of illite will be broader. However, the source of high-quality illite has decreased with the continuous mining of illite currently. Most illite has complex components and the possibility of direct use is small. This feature greatly limits the application scope of illite, which is not conducive to the rational and full development and utilization of mineral resources. Illite can be applied in more fields by studying its conductivity changes. Therefore, this research aimed to study the conductivity changes of illite modified by cationic surfactant to solve the depletion of high-quality illite resources under years of mining and improve the technology for developing illite resources. Meanwhile, the research studied the modification and performance of illite to broaden the application field of illite. The surface modification of purified and intercalated illite powder was investigated using microwave activation method. The changes in conductivity were studied through X-ray diffraction, scanning electron microscopy (SEM), and ion conductivity testing. By studying various directions to improve and enhance the ore mining and selection

process, targeted downstream projects for developing illite would be launched. Then, the economic value of illite can be fully tapped into, environmental resources can be protected, and the application areas of illite can be expanded.

Materials and methods

Original soil of illite

Illite raw materials used in this study were from Antu County, Jilin, China. The original soil of illite contained quartz impurities, which needed to be purified [12]. The raw ore of illite was ground and crushed (< 100 mesh) into pulp and was kept stand still for 24 hours before stirring with a B13-3 Intelligent Constant Temperature Digital Magnetic Stirrer (Shanghai Sile Instrument Co., Ltd., Shanghai, China). After stand still again, the suspension was extracted and separated by centrifugation using Avanti JXN-30/26 Intelligent and Efficient Centrifuge (Beckman Coulter, Brea, California, USA) [13]. The supernatant was collected and dried using a GZX-9140MBE Electric Constant Temperature Blast Drying Oven (Shanghai Boxun Industrial Co., Ltd., Shanghai, China). The same steps were repeated 2-3 times to obtain the purified illite.

Determination of modifier

Dimethyldioctadecylammonium bromide (DODAB) (Henan Daochun Chemical Technology Co., Ltd., Zhengzhou, Henan, China) is a kind of cationic surfactant. Compared with the traditional modifier, DODAB is more easily absorbed at the two-phase interface, therefore, has better effect in reducing surface tension, foaming, emulsification, and other aspects [14]. The critical micelle concentration (CMC) is low with less irritation, strong solubilization effect, and low cost. DODAB is white powder and can be dissolved in isopropanol when heated. It can be dissolved in water too. DODAB has good coordination with cationic, non-ionic, and surfactant with good chemical stability, heat resistance, pressure resistance, strong acid and alkali resistance [15].

Modification process of illite

The microwave activation method was selected to modify illite by using the cationic surfactant DODAB as modifier [16]. The change of conductivity of illite after modification was studied. Briefly, 5 g of detached illite flakes were added to 107.5 mL of 50% (V/V) isopropanol aqueous solution to result a 5% illite suspension. The suspension was stirred at high speed for 30 minutes and expanded for 24 hours before transferred into the MAS-IIPLUS microwave synthesis/extraction reaction workstation (Xinyi Microwave Chemical Technology Co., Ltd., Shanghai, China) with the reaction power of 800 W, the reaction temperature of 30 - 80°C. The cationic surfactant was dissolved in 10 mL of 50% (V/V) isopropanol aqueous solution and added to the illite suspension before 100 minutes of microwave reaction. The reaction site was washed with 50% (V/V) isopropanol and centrifuged until no Cl^- and Br^- were detected in the silver nitrate solution. The final dosage of modifier was 0.5 time and 1.0 time of illite cation-exchange capacity (CEC), respectively.

Thermal activation and acidification of illite

The illite layer has high charge and strong interlayer binding force, which is not easy to absorb water and expand. Thermal activation and acidification pretreatment of illite can realize organic molecular intercalation and weak interlayer bonding force to promote the preparation of lamellar exfoliation type separation and realize lamellar exfoliation of illite [17]. The purified illite was calcined in muffle furnace at 600°C for 1 hour to complete the thermal activation before mixed with 2 mol/L nitric acid solution for acidification. After stirring for 3 hours at 95°C, the reaction mixture was centrifuged for separation and then washed to neutral with distilled water. The sample was dried at 60°C to obtain the acidified illite.

Intercalation and stripping of illite

2 g of each purified, thermal activated, and acidified illite was added to 5 mL of water and 50 mL of DMSO and mixed for 1 h. The mixture was heated in a 500 W microwave reactor for 50 mins

before filtering and washing with absolute ethanol to remove the unreacted DMSO [18]. After drying at 60°C, illite/DMSO intercalation complex was obtained and was treated in JP-020S Ultrasonic Cleaner (Baite Instrument Co., Ltd., Dandong, Liaoning, China) at 70°C for 1 hour to remove the organic molecules between the intercalation complex layers, peel off the illite flake layer, and modify the peeled illite flake layer.

Determination of cation exchange capacity of illite

0.2 g of the sample was mixed with 25 mL of 1 mol/L NH_4Cl solution. After being heated at 90°C for 35 mins, the sample was filtered with filter paper with all the residues being transferred into the filter paper. The wall of the container and filter paper were washed continuously until no Cl^- was detected in the filtered solution. The residue and filter paper were then washed with 1 mol/L KCl solution and poured back to the original container. 2.0 mL neutral formaldehyde solution (2+1) and 2 drops of phenolphthalein were added, and then titrated with 0.1 mol/L NaOH . The reaction was stopped when pH reached 9.0. The cation exchange capacity (C_{CEC}) of illite was calculated as follows.

$$C_{\text{CEC}} = c \times V / G \times 100 \quad (1)$$

where c was the concentration of NaOH solution (mol/L). V was the volume of NaOH solution consumed (mL). G was the mass of sample (g). C_{CEC} was the cation exchange capacity (mmol/100g).

X-ray diffraction analysis (XRD)

The XRD patterns of modified and unmodified illite were measured by DX-2700 X-ray diffractometer (Dandong Fangyuan Instrument Factory, Dandong, Liaoning, China) with the tube voltage of 35 kV, the scanning range of 5° - 70°, the scanning step width of 0.05. The powder sample was ground to below 200 mesh and spread to the sample table. The film was pressed on a specific tablet and spread to the sample

table. The mineral composition contained in illite and the size of the crystal interlayer spacing were analyzed according to the diffraction peak position in the pattern to provide the basis for the study of modified illite conductivity.

Scanning electron microscope (SEM)

The microstructure of illite was analyzed by JSM-7800F Schottky Field Emission Scanning Electron Microscope (JEOL, Akishima, Tokyo, Japan). The sample was dispersed into ethanol, dropped onto silicon steel sheet, and fixed with conductive adhesive. The sample was then observed at different times. The particle distribution on the sample surface and the effect of illite intercalation and stripping were visualized by observing the micro-morphology of the sample surface [19]. The specific reasons for the change of conductivity were further analyzed.

Ion conductivity test

The ionic conductivity of the composite was measured based on the AC impedance test using CHI604 Electrochemical workstation (Shanghai Chenhua Instrument Co., Ltd., Shanghai, China). The composite film to be tested was clamped between two stainless steel electrodes for AC impedance test [20]. The frequency scanning range was 1 Hz – 100 kHz. The AC excitation signal was 5 mV. ZView software (Ametek, Berwyn, PA, USA) was used to perform equivalent circuit fitting on the impedance curve to obtain the bulk resistance of the composite polymer. The ionic conductivity of illite was then calculated below.

$$\sigma = \frac{d}{RS} \quad (2)$$

where σ was the ionic conductivity. d was the thickness of the composite film. R was the bulk resistance of the composite film. S was the area of the composite film.

Results and discussion

Analysis of illite composition

The chemical composition of illite showed that the main components of the original illite were SiO_2 and Al_2O_3 . There was also a small amount of K_2O , Fe_2O_3 , and FeO (Table 1).

Table 1. Chemical composition of illite ($\omega_B=10^{-2}$)

Ingredient	Original soil (%)
SiO_2	71.52
Al_2O_3	17.26
TiO_2	0.41
CaO	1.12
MgO	0.72
Fe_2O_3	1.14
FeO	1.04
K_2O	5.26
Na_2O	0.04
LOI	3.61

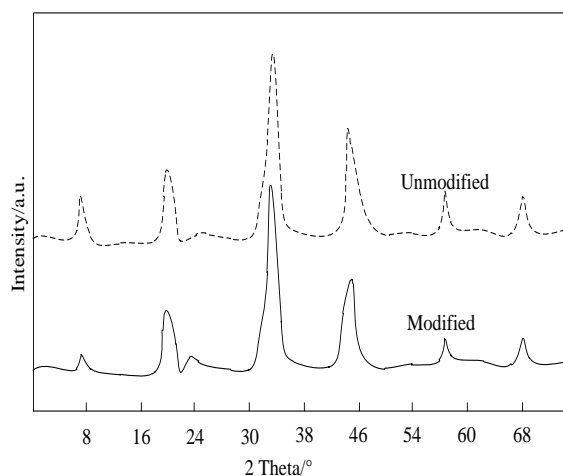


Figure 1. Illite XRD results before and after modification.

The results of X-ray diffraction analysis

The XRD results of illite before and after modification confirmed that illite belonged to monoclinic system according to the position of diffraction peak in XRD experiment with three obvious diffraction peaks being observed (Figure 1). Compared with unmodified illite, the modified illite was different except for the strength of the peaks. The position of the peaks was almost unchanged, which suggested that illite had no obvious insertion effect after surface treatment.

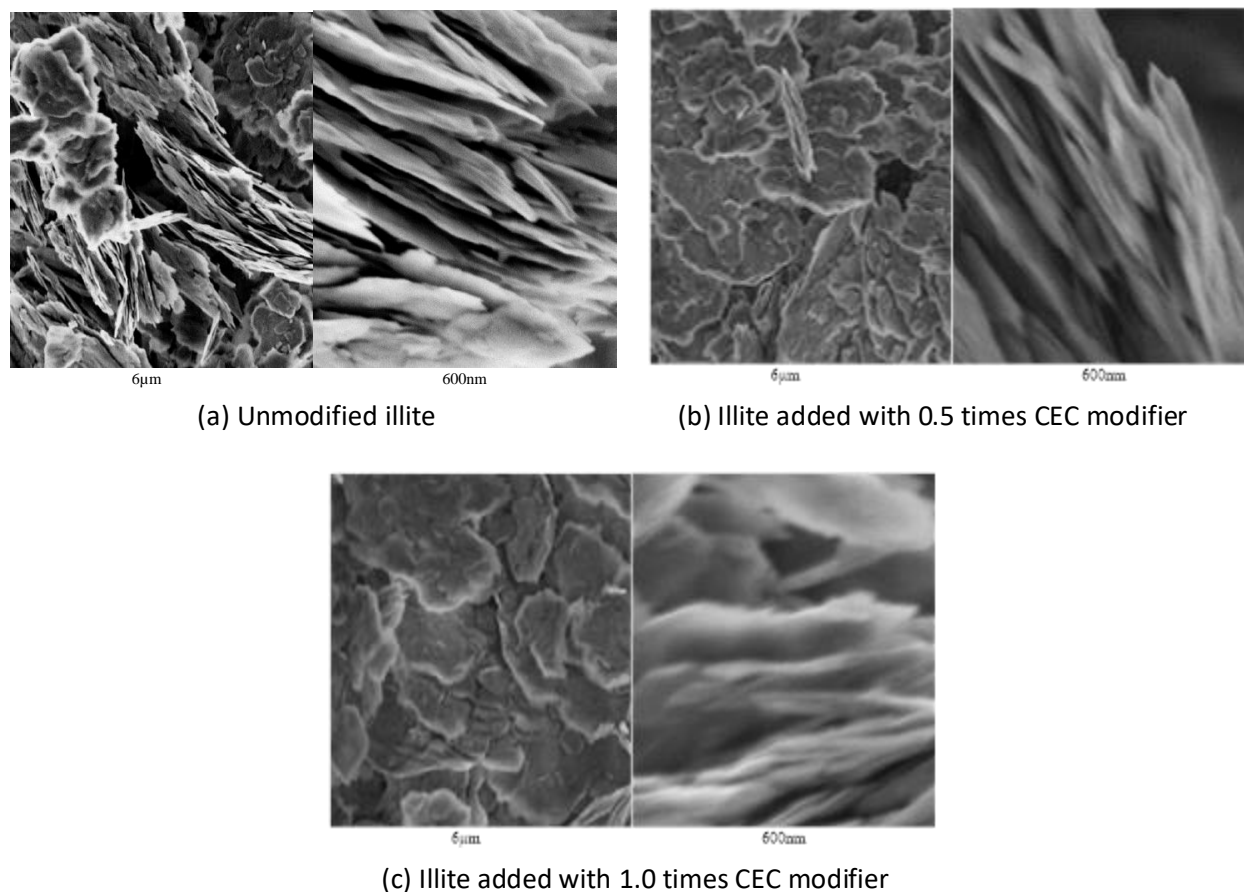


Figure 2. SEM images of illite before and after modification.

Only illite was found after treating with DODAB, indicating that the surface modification of illite was successful. The XRD results also confirmed that illite had a good crystallinity, which was verified by the effectiveness of using DODAB surfactant as modifier to modify illite.

Scanning electron microscope analysis

The morphology of illite before and after modification was shown in Figure 2. The unmodified illite demonstrated sheet structure with each sheet composed of several sub-sheets (Figure 2a). The sheet thickness was about 73 nm. The morphologies of illite with 0.5 and 1.0 times CEC of cationic surfactant were compared to unmodified illite (Figures 2b and 2c). The modified illite showed the same lamellar structure but kept the original morphology. The thickness of the modified illite lamellae was 38

nm, which was thinner than that of unmodified illite. The illite layer was loose after modification, proving the success of illite modification.

The conductivity of illite

The ionic conductivity of modified illite increased gradually with the increase of cationic surfactant content (Figure 3). When the concentration of cationic surfactant reached 20 wt%, the conductivity of modified illite reached the maximum. When the cationic surfactant was more than 4 wt%, the ionic conductivity increased rapidly. However, when the cationic surfactant was more than 14 wt%, the increasing trend of the ionic conductivity became mild. The results showed that the increase of ionic conductivity was due to the decrease of crystallinity of modified illite by adding cationic surfactant. With the addition of cationic

surfactant, the crystalline phase of the modified illite decreased gradually, which hindered the orderly arrangement of the molecular chain of the modified illite. Meanwhile, the growth and extension of the crystalline phase were inhibited by cationic surfactant.

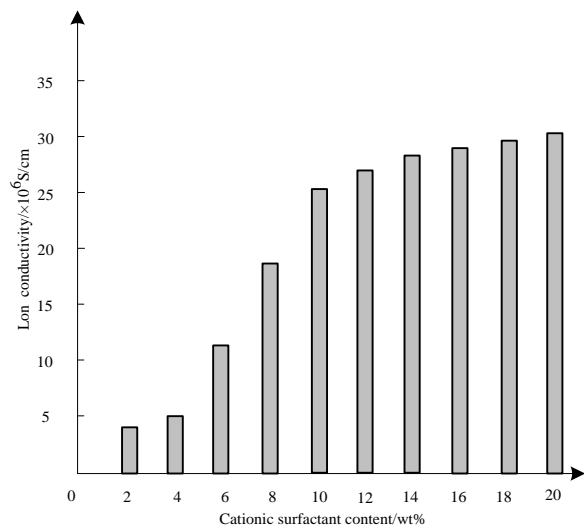


Figure 3. Illite conductivity test for different cationic surfactant contents.

A certain thickness of amorphous phase was formed around illite after the addition of cationic surfactant, forming a capsule like structure. The core of the capsule was the exfoliated illite sheet layer. The outer layer of the capsule was an amorphous region. The lithium-ion transfer rate in the amorphous region was much faster than that in the crystalline region. When Li^+ moved from one layer of illite film to the other side, the conduction velocity of Li^+ became faster when it passed through the amorphous area of the capsule. When it passed through the crystal free area outside the capsule, the conduction velocity decreased or even stopped. Therefore, the addition of a small amount of 5 wt% cationic surfactant made the conductivity of modified illite increased compared with the modified illite system. However, the increase of the ionic conductivity was not obvious. When the concentration of cationic surfactant reached 10 wt%, the separated capsules were connected to

each other to form an interrelated transport network, which facilitated the transport of lithium ions and increased ionic conductivity. Under the same filling amount, the stripped illite had more silicate layer than that in the purified illite, providing more ways for lithium-ion transport.

pH value and conductivity

The pH value of illite modified by cationic surfactant was large when it was stirred stably and decreased rapidly when it stopped stirring. When the stirring time was less than 20 mins, the pH value changed greatly. With the increase of stirring time, the pH value tended to be stable gradually at 7.6-7.8 (Figure 4). The conductivity fluctuated greatly when the stirring time was less than 15 mins and relatively stable when the stirring time was 15 - 100 mins. It slightly increased when the stirring stopped (Figure 5).

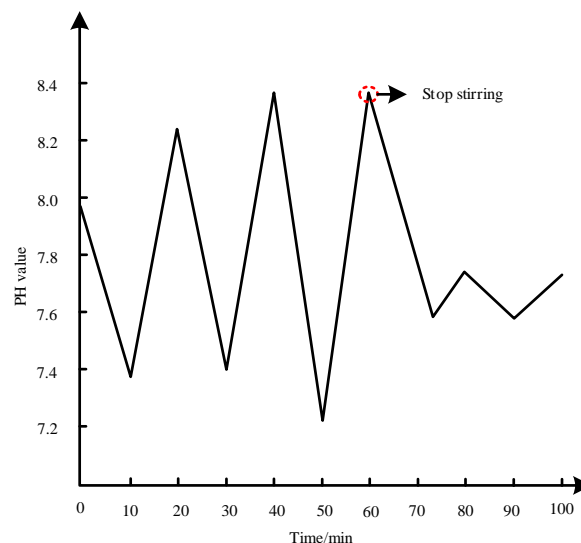


Figure 4. pH value versus time curve.

The results showed that the overall change in pH value during the action of cationic surfactant was significantly negatively correlated with conductivity. Stirring had a significant impact on pH and conductivity. When stirring was stable, there was no significant change in pH value and conductivity. The higher the pH value, the lower

the conductivity. When the action time was short, the pH value rapidly decreased and the conductivity rapidly increased after stopping stirring.

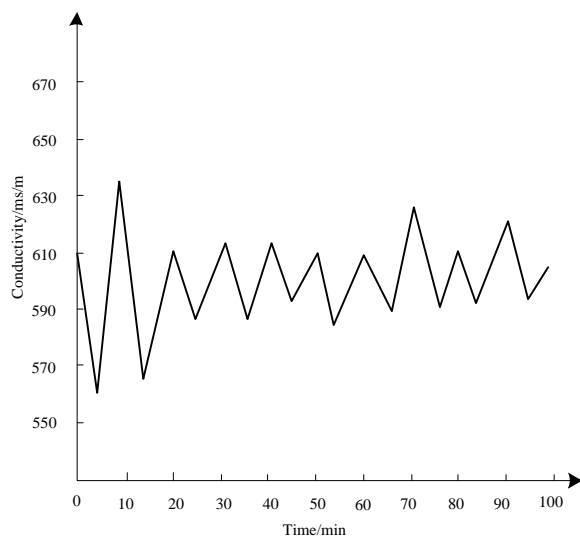


Figure 5. Conductivity versus time curve.

The research on illite in China began in the 1970s and started relatively late with few mineral deposits. Illite clay is one of the common layered aluminosilicate clay minerals. Illite is widely used in many fields due to its excellent physical and chemical properties including high potassium aluminum content, low iron content, delicate texture, corrosion resistance, wear resistance, flowability, absorption, and heat resistance. After being treated with modifiers, illite powder can be mixed with most polymers and illite clay can be widely used as a modification and filling material for polymer materials. The results of this study would benefit the applications of illite in different fields and would be greatly helpful to promote the exploitation of illite economic value and effectively protect the resources.

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