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The Effect of Reflux Time from Natural Zeolite on Electrical Conductivity

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Abstract: This study aims to determine the electrical properties, namely the value of the electrical conductivity of natural Zeolite. Natural Zeolite was synthesized using the reflux method with NaOH as an activator with variations of 12, 24, and 36 hours with a molar concentration of 5M NaOH. Tests were carried out using XRF characterization (X-Ray fluorescence), XRD (X-Ray Diffraction), and LCR Meter. The XRD results showed the highest peak value at 36 hours of 85.22 nm. The XRF results of the Zeolite elements formed were 66.087% SiO_2 and 8.45% Al_2O_3 and in the LCR Meter test, the highest conductivity value was obtained at 36 hours of reflux with a conductivity value of $5.5x10^{-2}$ S/m. The value of the electrical conductivity is directly proportional to the particle size where the greater the conductivity value the greater the particle size produced. The electrical conductivity results showed that Zeolites are included in semiconductor materials and have the potential as supercapacitor electrodes

Keywords: Natural Zeolites, reflux time, conductivity, semiconductor materials, supercapacitor electrodes

1. Introduction

The use of batteries as energy storage has been widely used today. Batteries have short life cycles, low power densities, and long charging times. This is because the battery must convert electrical energy into chemical form so that this energy can be stored [1]. Compared to batteries, supercapacitors have many advantages, including having a large power density, very large charge storage capacitance, fast charging, and long lasting. One of the components that determines the performance of a supercapacitor is the electrode [2]. Generally, supercapacitor electrodes use carbon materials because of several superior properties, such as high surface area, high electrical conductivity, but carbon materials also have weaknesses such as being relatively expensive. So alternative materials are needed that can be used as substitutes for carbon as the material for supercapacitor electrodes. The material that can replace carbon as a supercapacitor electrode is zeolite, where zeolite has a fairly high surface area, selectivity in shape, size and charge, and has molecular sized pores. Zeolite is also included in organic membranes which have the property of

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not being easily damaged when exposed to organic solvents or chemicals, so that the lifetime of the membrane can be longer [3]. Zeolite can be used as a support for electronic devices as an alternative semiconductor material so that it can be used as a supercapacitor electrode material [4].

Zeolite is one of the most abundant mineral sources found in Indonesia, the use of which is not yet optimal [5]. Judging from its crystal structure, zeolite has a three-dimensional framework structure with cavities inside, formed by tetrahedral $[SiO_4]^{4-}$ and $[AlO_4]^{5-}$ which are interconnected by oxygen atoms in such a way, thus forming an open three-dimensional framework containing channels [6]. channels and cavities, which are filled with metal ions, usually alkali or alkaline earth metals and water molecules that can move freely [7]. Zeolites as a class of inorganic microporous crystalline materials are widely used in catalysis, adsorption/separation, and ion-exchange. In addition, new applications of zeolitic materials have also been found in luminescence, electricity, magnetism, medicine, and microelectronic [8]. The hollow structure and framework of zeolites means that zeolites have many uses, including as adsorbents, cation exchangers, gas sensors, catalysts and molecular filters. Apart from that, zeolite is also used as a support for electronic devices as an alternative semiconductor material [9].

Zeolites consist of synthetic Zeolites and natural Zeolites. Natural zeolites are zeolites that are formed due to complex chemical and physical processes from rocks that experience various kinds of natural changes [10]. Zeolite consists of natural zeolite and synthetic zeolite. Zeolites occur naturally as well as it can be prepared in the laboratory. Zeolites are usually divided into two main categories: natural (e.g., clinoptilolite, mordenite and garronite), and the synthetic Zeolite [11]. Natural Zeolite is mined directly from nature so it has a much cheaper price compared to synthetic Zeolite [12]. One area that has a lot of natural Zeolite is in West Sumatra. According to the Directorate of Natural Resources of West Sumatra, in the area of Lubuk Selasih, Kenagarian Batang Barus, Gunung Talang District, Solok Regency, minerals of the type Ca-Bentonite were found containing CaO = 9.14%, MgO = 1.01%, LOl = 3.26%, SiO_2 = 65.4%, Al_2O_3 = 8.43%, Fe_2O_3 = 2.96%, K_2O = 3.90%, TiO_2 = 0.19%, P_2O_5 = tt, SO_3 = none. Natural Zeolites have several weaknesses, including containing many impurities such as Na, K, Ca, Mg, and Fe and their crystallinity is not good [13].

Natural Zeolite has a lot of impurities so a method is needed so that these impurities can be reduced so as to increase the electrical conductivity value of the Zeolite [14]. By increasing the electrical conductivity value, it is hoped that good quality supercapacitor electrodes can be obtained. There are several methods that can be used, but in this research the method used is a heating method called the reflux method. Reflux is a method of repeated heating in chemical processes. The reflux method is able to change the alumina and Silica mineral phase into Zeolite where the longer the reflux time causes more Zeolite to be formed. The Reflux method is expected to increase the crystallinity of the synthesized Zeolite by removing a number of impurity oxides Fe_2O_3, CaO, MgO, K_2O. The use of $NaOH$ solution as an activator in dissolving silica salts and alumina will produce Zeolites of different sizes [15]. In this research, to obtain the electrical properties of Zeolites, samples from natural Zeolite rocks in Solok district have been used processed using the Reflux method.

2. Materials and Method

The material for this research is natural rock originating from Solok district. This natural rock contains several chemical elements such as aluminum and silica. With the presence of these compounds, these rocks can be said to be Zeolite rocks. Zeolite rock is the main material for this research. The Zeolite rock is refined by grinding it using using a lump and pestle and filtering it to get a fine powder using a filter. After that the powder from natural Zeolite can be used to carry out the first stage, namely determining the elements. contained in natural Zeolites with XRF characterization. The purpose of testing the value of the compounds formed in the Zeolite using XRF is to find out whether the Zeolite rock can be used or has met the standard value of the Zeolite itself. The value of the Zeolite compound elements formed can be seen in table 1.

Table 1. Content of Zeolite formed

Variation No.	Element Name	Element Precentage (%)
1	Al_2O_3	8,45
2	SiO_2	66,087
3	P_2O_5	4,225
4	Cl	0,035
5	K_2O	3,445
6	CaO	10,959
7	Ti	0,59
8	V	0,009
9	Mn	0,026
10	Fe_2O_3	5,485

Based on table 1 above, the content of aluminum and silica has a high enough content so that it can be said that these rocks are classified as zeolite. In the XRF characterization to determine the elements present in zeolite rocks, the highest percentage values were obtained, namely silica and aluminum, where the values of these elements were 66.087 and 8.45 and also the presence of other impurities that are found in the natural zeolite and where these impurities commonly occur because these are ingredients from nature.

The zeolite synthesis process was carried out by mixing 30 grams of powder from natural zeolite rock with 300 ml of NaOH solution with a solution level of 5 molar. The mixture was stirred in a magnetic stirrer for 24 hours at room temperature.

Figure 1. Stirring with a magnetic stirrer

After stirring for 24 hours, the solution was transferred to a 500 ml flask to carry out the reflux process and the temperature used was 100 Celsius using temperature variations of 12, 24 and 36 hours. The resulting precipitate was washed with distilled water until it reached Neutral pH and dried in an oven at 105 Celsius. The reflux process can be seen in Figure 2.

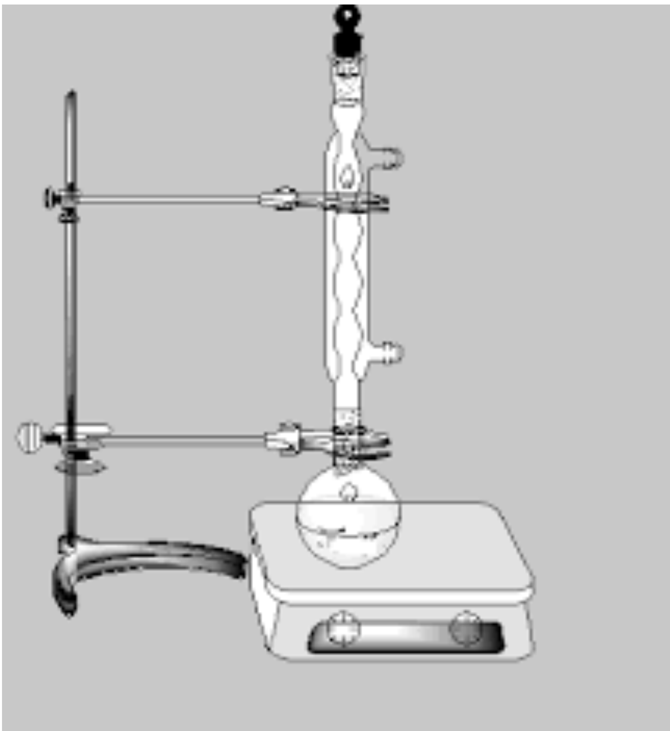


Figure 2. Reflux device

Figure 2 is a tool for the reflux method, this tool functions as a heater used in this study. The use of this tool can increase the value of the electrical conductivity of natural zeolite materials. The components of this reflux tool include a hotplate as a heat source, then a test tube used to place the solution to be used, the condenser is used for cooling where in the condenser there is a flow of water going in and out so that it can stabilize the temperature in the reflux, then there is a thermometer which is useful as a temperature gauge.

The process of characterizing and measuring electrical conductivity is carried out using XRD which is used to measure crystal size and to determine the value of electrical conductivity using an LCR meter. Prior to carrying out the characterization of electrical conductivity, compaction is carried out first after obtaining natural zeolite in the form of powder. Compaction is carried out based on which composition a thin tablet will be formed whose diameter and height are determined. Tablet-shaped samples are measured for resistance by sandwiching it so that the value is easily read by the LCR meter. LCR measurements are carried out by giving resistance to the material. Free electrons will flow in the material if there is a potential difference between the two point then the potential difference will flow from a lower potential to a higher potential so that it will cause a current.

The final stage is the data analysis stage. Data analysis is performed to analyze particle size and measure the value of electrical conductivity using the equation. To determine the particle size, data analysis is performed using the equation:

$$D = K\frac{\lambda}{B\cos\theta} \quad (1)$$

Based on equation 1. D is the particle size, K is a constant with a value of 0.9, λ is the X-ray wavelength (Å) the value is 1.54 Å, B is the width of the half maximum FWHM peak (rad), θ is the Bragg angle .

To determine the value of electrical conductivity, measurements are carried out using the lcr meter, the data obtained with the lcr meter is processed by the equation

$$\sigma = 1/\varrho \quad (2a)$$

where

$$\varrho = R\,(A/L) \quad (2b)$$

Based on equations 2a and 2b. σ is the electrical conductivity, ϱ is the resistivity, R is the resistance obtained, A is the cross-sectional area and L is the height.

3. Results and Discussion

The results of this study consists of 2 characterization tests, namely to determine particle size and electrical conductivity in natural zeolite. The data obtained is included in indirect data, where to determine particle size and electrical conductivity value, it is processed first using the formula. The sample used in the test can be seen in the following Figure 3.

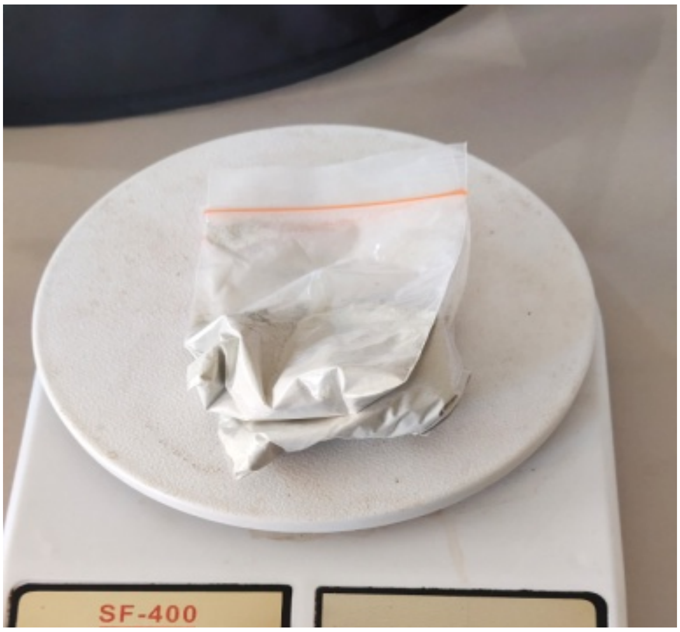


Figure 3. Sample shape of natural zeolite that has been ground

Figure 3 is a sample form that is ready for the test which has carried out the reflux process until drying using an oven. Before carrying out XRD (Particle Size) and LCR Meter (Electrical

Conductivity) characterization, XRF testing is carried out again which is useful to determine whether after the reflux method the impurities in the natural zeolite rock can be reduced or not.

Table 2. Element values contained in the zeolite content after refluxing

Variation No.	Element Name	Element Presentase (%)
1	Al_2O_3	10,79
2	SiO_2	70,035
3	P_2O_5	3,112
4	Cl	0,035
5	K_2O	3,497
6	CaO	9,959
7	Ti	0,57
8	V	0,009
9	Mn	0,026
10	Fe_2O_3	1,485

In the Table 2 above, there are several changes in the elemental values of the zeolite contained in the rock after refluxing for 36 hours, which we can see in the table above. In the table above you can still see the dominant values of the zeolite composition, namely Silica and Aluminum compounds have the highest element percentages, whereas silica has an element value percentage of 70.035% and aluminum is 10.79%. And there are several other impurities that have percentage values, namely the elements P_2O_5, Cl, K_2O, CaO, Ti, V, Mn and Fe_2O_3.

Figure 4 is the result of the XRD characterization to determine the particle size of the zeolite that has been carried out by the reflux method. The X-ray Diffraction pattern produced from natural Zeolite which has been tested using the effect of time from the reflux method which varies the time used in this study, namely at 12, 24, and 36 hours analyzed, there are peaks of 2θ and intensity. From the Figure, it is clear that the influence of long time variations will increase the particle size of the zeolite.

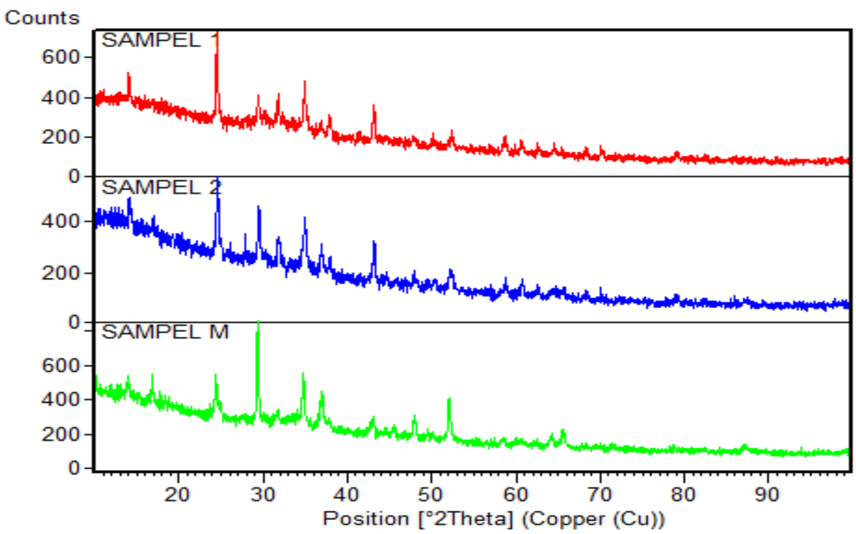


Figure 4. XRD characterization graph

In Figure 4, it can be seen that there are peak variations from the results of the XRD measurements carried out. Where in each variation there is a value of the Zeolite element, namely SiMn. At the 12-hour variation, there are high peaks and not wide, indicating that the sample has a size of the nano order. From these peaks, the diffraction value obtained is 70,780 nm. At the 24-hour variation, there are also several high peaks and non-widening peaks that have a nano order size, which obtains a diffraction value of 76,347 nm. At 36 hours the peak-to-peak value was also obtained which was slightly higher and did not widen, where the size was nano-sized and obtained a higher diffraction value of 85.22 nm of the three time variations used in the reflux method the value of the particle size was always increases with increasing time variation. The measurement process uses LCR beforehand, the zeolite powder which has been refluxed is formed into pellets. The shape of the resulting pellets can be seen in the Figure 5.

Figure 5. The shape of the pellets from zeolite before the LCR meter is carried out

Figure 5 is the form of zeolite which has been compacted so that it is in the form of pellets where the resulting size is 4 mm in diameter and 2 mm in height. Based on the results of the LCR meter characterization, the value of the electrical conductivity was obtained which can be seen in Table 3 . The conductivity value was varied with a frequency of 100,500 and 1000 Hz so that the value of the electrical conductivity was obtained which was in the range of $0.011 x 10^{-2} – 5.5 x 10^{-2}$ S/m which where this value is included in the semiconductor range.

Table 3. Results of electrical conductivity measurements with frequency variations

Frequency	Conductivity (10^{-2})		
(Hz)	12 hours	24 hours	36 hours
100	0,073	3,610	4,693
500	0,011	4,100	5,475
1000	0,101	4,380	5,500

Based on the table above that there is an influence of frequency which results in an increase in the value of the conductivity obtained. The frequency is increased, the value of the resulting conductivity also produces an increased value. Where the highest conductivity value is at the time variation of 36 hours using a NaOH concentration of 5 molar with an electrical conductivity value of 5.50x 10^{-2} S/m.

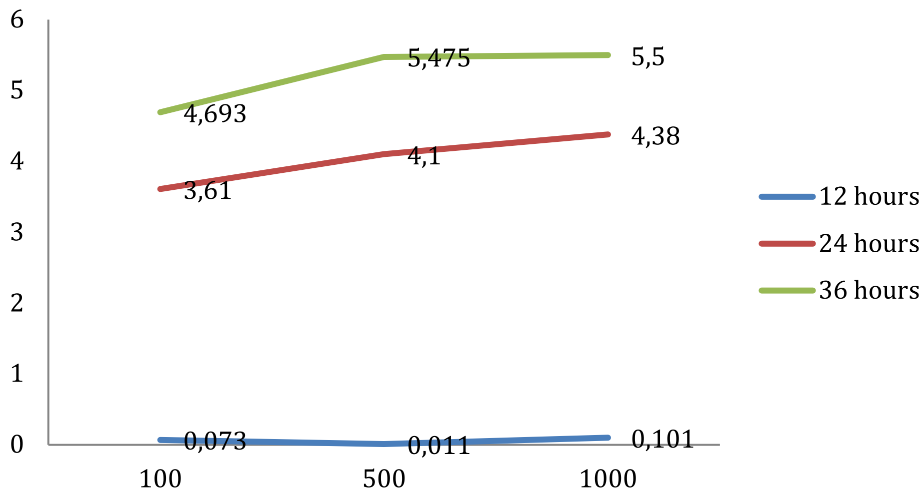


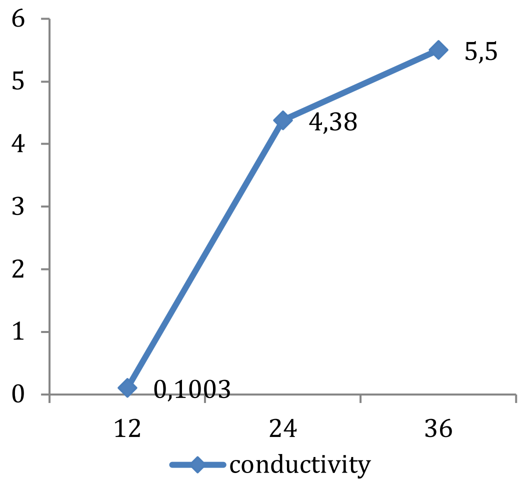
Figure 6. Value of electrical conductivity by varying the frequency

Based on the results of the characterization of the LCR meter, the value of electrical conductivity which has a fairly good value is at a frequency of 1000 Hz which can be a benchmark for good conductivity values in the range of semiconductor values. From these data, capacitance and resistance values can also be obtained, then the data is processed to get the value of electrical conductivity and area capacitance. Table 2 shows the value of the electrical conductivity resistivity obtained at a frequency of 1000Hz.

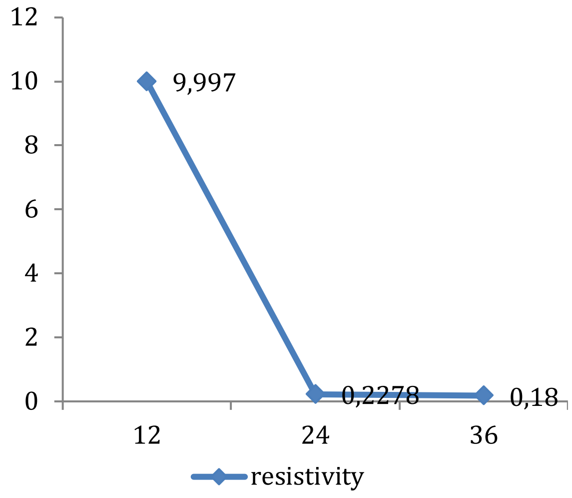
Table 4. Resistivity, conductivity and area capacitance area

No	Sample	Cross Sectional Area	Resistivity	Conductivity	Area Capacitance
1	12 hours	5.024 x 10^{-5} cm	9,997x10^{2} Ωm	1.003x10^{-3} S/m	5,2x10^{-6} C
2	24 hours	5.024 x 10^{-5} cm	2,278x10^{1} Ωm	4,380 x 10^{-2} S/m	4,2x10^{-4} C
3	36 hours	5.024 x 10^{-5} cm	1,800x10^{1} Ωm	0,550x10^{-1} S/m	3,4x10^{-4} C

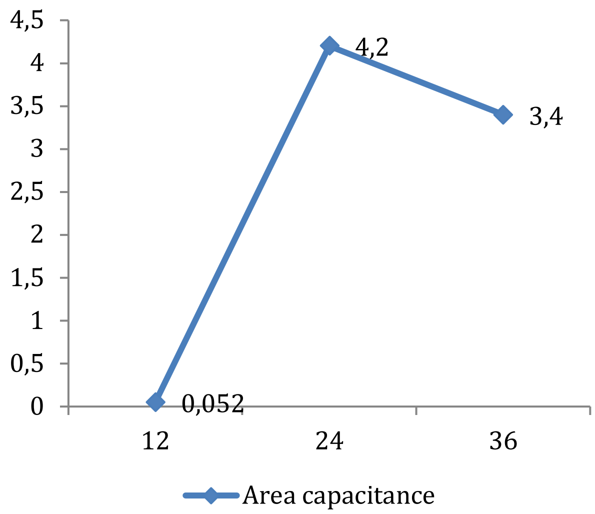
Based on table 4 above, there were 3 variations carried out in this study, namely 12, 24 and 36 hours where each variation had a different resistivity and conductivity value. It can be seen from the table above that the effect of reflux time greatly affects the resistivity value and the electrical conductivity value of natural zeolite where the longer the time used, the resistivity value decreases and the longer the reflux time, the higher the conductivity value. The resistivity value is inversely proportional to the value of reflux. conductivity because basically the conductivity value is 1 resistivity. The comparison of resistivity and conductivity values can be seen in the picture. the graph below. Based on the electrical conductivity value, the electrical conductivity value of mini-style zeolite is included in the value of semiconductor materials, where the value of the semiconductor is between 10^{-7}S/m to 10^{3}S/m. In this study, the electrical conductivity value obtained was at value of $1x10^{-3}$S/m for 12 hours, $4.38x10^{-2}$S/m for 24 hours, $5.5x10^{-2}$S/m for 36 hours.



(a)



(b)



(c)

Figure 7. Comparison of conductivity (a) resistivity (b) and area capacitance (c)

The research results obtained are comparable to the theory that the longer the reflux time, the value of the conductivity also increases. Which in data processing can be seen an increase in the conductivity value from 12, 24 and 36 hours temperature which is caused by an increase in crystal size. With a larger crystal size, the area capacitance and conductivity value will be larger and will decrease if the value of the conductivity has reached the optimum value. Increasing the carbonization temperature time from reflux causes an increase in crystal size. The size of the crystal itself can also be interpreted that there is an increase in the orderliness of the arrangement of atoms.

When viewed in terms of crystallinity, the higher the degree of crystallinity of the sample, the conductivity value will increase [16]. This is indicated by the conductivity values which are in the same range. The sample with a concentration of 5M at a reflux time of 36 hours is a synthetic zeolite with a good level of crystallinity as seen in the highest intensity of the XRD peak compared to other samples.

4. Conclusion

From the LCR results it can be concluded that the value of the electrical conductivity of natural zeolite is directly proportional to the reflux time which is carried out where the longer the reflux time, the greater the value of the electrical conductivity and value of the electrical conductivity is directly proportional to the particle size where the greater the conductivity value the greater the particle size produced Based on the value of the electrical conductivity obtained, the conductivity of natural zeolite is at that of a semiconductor material, which is between 10^{-7} S/m to 10^{3}S/m. And from the results of this study, natural zeolite can or has the potential to be used as a supercapacitor electrode material.

References

[1] W. Lu, R. Hartman, L. Qu, and L. Dai, "Nanocomposite electrodes for high-performance supercapacitors," *J. Phys. Chem. Lett.*, Vol. 2, No. 6, pp. 655–660, 2011, doi: 10.1021/jz200104n.

[2] E. Kocyigit, Microstructural Characteristics and Electrical Conductivity of Zeolite and Its Potential as a Supercapacitor Electrode," Ekp, Vol. 13, No. 3, pp. 1576–1580, 2015.

[3] E. Lisna, "Superkapasitor Berbasis Nanokarbon dari Biomassa," *Kabesak*, Vol. 28, 2018.

[4] I. M. Kalogeras and A. Vassilikou-Dova, "Electrical properties of zeolitic catalysts," *Defect Diffus. Forum*, No. 164, pp. 1–36, 1998, doi: 10.4028/www.scientific.net/ddf.164.1.

[5] P. Auerbach, S., Carrado, K., Dutta, *Zeolite Science and Technology*. 2003.

[6] Sunarti and Nazudin, "SINTESIS ZEOLIT A DARI ABU DASAR BATUBARA (COAL BOTTOM ASH) DENGAN METODE PELEBURAN DAN HIDROTERMAL Sunarti1*," *MJoCE*, Vol. 11, No. 1, pp. 8–16, 2021.

[7] E. Izci and A. Izci, "Dielectric behavior of the catalyst zeolite NaY," *Turkish J. Chem.*, Vol. 31, No. 5, pp. 523–530, 2007.

[8] V. Van Speybroeck, K. Hemelsoet, L. Joos, M. Waroquier, R. G. Bell, and C. R. A. Catlow, "Advances in theory and their application within the field of zeolite chemistry," *Chem. Soc. Rev.*, vol. 44, no. 20, pp. 7044–7111, 2015, doi: 10.1039/c5cs00029g.

[9] M. Ahkam, "Sintesis Dan Karakterisasi Membran Nanozeolit Y Untuk Aplikasi Pemisahan Gas Metanol-Etanol," *Skripsi, Fak. Mat. Dan Ilmu Pengetah. Alam Univ. Indones. Sint.*, 2011.

[10] D. Y. Lestari, "Kajian Modifikasi dan Karakterisasi Zeolit Alam dari Berbagai Negara," *Pros. Semin. Nas. Kim. dan Pendidik. Kim. 2010*, p. 6, 2010.

[11] A. Khaleque *et al.*, "Zeolite synthesis from low-cost materials and environmental applications: A review," *Environ. Adv.*, Vol. 2, No. August, 2020, doi: 10.1016/j.envadv.2020.100019.

[12] Kusdarto, "Potensi Zeolit Di Indonesia," *J. Zeolit Indones.*, Vol. 7, No. 1411–6723, p. 2, 2008.

[13] C. B. Dartt and M. E. Davis, "Chapter 6 Applications of zeolites to fine chemicals synthesis," *Catal. Today*, Vol. 19, No. 1, pp. 151–186, 1994, doi: 10.1016/0920-

5861(94)85006-2.

[14] A. Hartmann *et al.*, "Zeolite Synthesis under Insertion of Silica Rich Filtration Residues from Industrial Wastewater Reconditioning," *Adv. Chem. Eng. Sci.*, Vol. 04, No. 02, pp. 120–134, 2014, doi: 10.4236/aces.2014.42015.

[15] Sunardi, T. Rohman, E. Mikrianto, and R. Rusmayanthi, "Pengaruh Waktu Refluks dengan NaOH (Sunardi dkk)" *Terap. Kim.*, Vol. 1, No. 2, pp. 83–92, 2007.

[16] A. Kusmiran and R. Desiasni, "Analisis Pengaruh Konsentrasi Natrium Hidroksida terhadap Sifat Mekanik Biokomposit Berpenguat Serat Sisal," *J. Fis.*, Vol. 10, No. 2, pp. 11–18, 2020, doi: 10.15294/jf.v10i2.25462.