Testing of Electrical Properties and Synthesis of MnO_2-Graphene Composites from Leaching Results of Manganese Rocks

ABSTRACT

This study aims to synthesize and test the electrical properties of the MnO_2-graphene composite from the leaching of manganese rock. The test method is carried out by testing the electrical properties with the parameters, namely capacitance (C), current (I), voltage (V), resistance (R), and conductometer. Each tested three concentration variations, 0.25: 0.75, 0.5: 0.05, and 0.75: 0.5. Supporting parameters for testing use X-Ray Diffraction (XRD) and Fourier Transform Infrared (FTIR). The results showed that the effect of varying the mass ratio of the MnO_2-Graphene composite on the capacitance value was 192.3μF in the variation of 0.25 gr: 0.75, meaning that the higher the concentration of the graphene carbon ratio, the higher the absorption capacity to store charge and electrical energy. For the variation of the voltage obtained by 353 mV at 0.25 gr: 0.75 variations, the current testing variation obtained a value of 13.6 mA at 0.25 gr: 0.75 variations, the variation on resistance obtained the lowest resistance value of 1.6 kΩ in the 0.25 gr variation: 0.75. The X-Ray Diffraction (XRD) test produces α manganese and graphene ranging from 6.8% to 93.2%. The Fourier Transform Infrared (FTIR) test produces Mn-O, CO, and OH bonds. Mn-O with wave numbers 479.44 cm^{-1}, 1.618.35 cm-1, 1.877.47 cm-1, and 992.07 cm^{-1}. CO with wave numbers 1104.27 cm^{-1}, 1190.69 cm^{-1}, and 1384.21 cm^{-1}. OH with wave numbers 1438.44 cm^{-1} and 1627.70 cm^{-1} electrical storage medium.

Keywords: *FTIR, MnO_2-Graphene, Resistance, XRD*

1. INTRODUCTION

The population of world is increasing, one of which is Indonesia. It causes the use of electrical energy to increase because it is included in the basic needs of life. Electrical energy innovations have been carried out from year to year, so it becomes a hot issue every year. One of the innovations is the battery which is used as a material for storing electrical energy. Batteries are a flexible energy source that can be applied to electronic devices such as power supplies and cell phones. Initially, the battery was only used once, or called a conventional battery.

Along with the development of science and technology, the battery can be recharged. Technological developments in electronics also demand quality in terms of power, namely batteries. It spurred the existence of innovations to balance the rapidly growing technology. Research in the field of battery energy is currently more emphasis on using more efficient energy, such as developing energy storage systems, namely metal-air batteries.

Metal-water batteries are an alternative that attracts much attention because they have a higher density than rechargeable batteries. This metal-air battery has the characteristic of being an open cell structure because its use requires oxygen gas to be accessed directly from the air. This battery has strong potential as an alternative energy storage alternative. In addition, it has several advantages in the form of relatively low cost, environmental friendliness, abundant materials, low balance potential, average voltage discharge, and long shelf life (Rahkmad & Rakhma, 2018).

In manufacturing metal-air batteries, the electrode material requires graphene, which is included in a family of carbon elements. According to chemists, physicists, and scientists, the material is now focusing on applied graphene in research and industry because it has good properties, namely having relatively high mobility, better conductivity, and heat than others. Graphene is a material that is known to be very strong today. Technological developments to date show that materials from graphene have a significant impact on chemical sensors, electronic devices, optoelectronics, energy storage, and nanocomposites. Graphene can be applied in various ways, namely in energy sources used as supercapacitor batteries and in solar cells (Rath, 2018).

One of the main challenges in metal-air batteries is the Oxygen Reduction Reaction (ORR) which is hampered when the electrodes are discharged from the battery. The inhibited ORR causes a high overpotential, resulting in a loss of energy efficiency. Therefore, a catalyst such as manganese dioxide (MnO_2) is needed. It is known that manganese oxide exhibits high ORR activity, similar to noble metal catalysts such as Pt, Ru, and Ir, and also manganese oxide is known as a material that is abundant in nature, inexpensive, and environmentally friendly (Rahkmad & Rakhma, 2018).

Manganese oxide is a manganese oxide that can be either crystalline or amorphous. The crystalline structure has a polymorphic crystal structure, such as β-, α-, γ- or δ-MnO_2. Each of these crystalline structures has tunnels of different sizes. β-MnO_2 (pyrolusite), α-MnO_2 (ramsdellite), γ -MnO_2 (nsutite) and δ-MnO_2 (vernadite) have tunnel structures (1x1), (1x2), (1x1) (1x2), and (1x∞) successively. With the tunnel structure possessed by the manganese oxide material, manganese oxide is widely used as a selective catalyst, ion exchanger, and molecule exchanger. Among those crystal structures, α-MnO_2 showed the best electrochemical performance. However, manganese oxide has the feature of low electrical conductivity. Therefore,

Manganese is one of the most abundant elements in the earth's crust. Manganese ore is black-gray, like iron. The investigation results show that the color of the manganese ore varies according to the type of each mineral. Manganese ore has the potential for development as the primary material for the battery industry, along with current technological advances (Juwandari, 2015). Indonesia has not optimally utilized the processing of manganese minerals. Many industries in Indonesia still have to import raw materials, including chemicals, to meet their needs because the raw materials produced domestically are still limited. This condition occurs due to the weak technological ability in Indonesia to increase the added value of these mineral resources. Efforts have been made to increase the added value of Indonesian minerals, namely through research activities and government policies related to regulations regarding Indonesian mineral mining businesses. The business of exploiting manganese mineral resources can have a positive impact on the Indonesian economy because manganese is used in various industries such as the manufacture of steel, paint, fertilizer, livestock,

Manganese ore processing is divided into two parts: pyrometallurgy and hydrometallurgy. Manganese ore with content above 40%, commonly known as a metallurgical grade, is processed pyrometallurgical to become ferromanganese metal. Meanwhile, manganese ore with below 40% is used to produce chemical compounds such as potassium permanganate, MnO_2, and others. This pyrolusite manganese ore can be selectively dissolved in an acidic environment, and this manganese leaching is reductive. In practice, it requires certain compounds to reduce the oxidation number of Mn from Mn (IV) to Mn (II) so that it can be dissolved using acidic compounds.

Sumardi et al. (2012) also carried out manganese rock leaching using molasses as a reducing agent in an acidic environment to obtain the highest percentage of manganese extraction, 95.33% MnO_2. Arita et al. (2015) in their research, extracted manganese dioxide from manganese rock using a reducing agent of empty palm fruit bunches as a reducing agent with H_2SO_4 reagent and obtained an Mn content of 81.99%. As for research on the synthesis of MnO_2-graphene from Zhang et al. (2019), who synthesized it MnO_2-graphene using the one-step hydrothermal method, obtained an energy density of 33.33 Wh/kg, which has the potential as a material for supercapacitor applications. Rakhmad and Rakhma's research (2018) synthesized Manganese Oxide-graphene as a cathode material in the Zn-Air Battery. The results of their research had a conductivity of 39.809 S/m.

Based on the description above, related to the problem of increasing electricity demand, new research and methods are needed to create an electricity storage medium with a high energy density. They can capture sufficient oxygen to provide greater power and utilize natural resources like mineral rocks across Indonesia.

2. MATERIALS AND METHODS

2.1 Tools and Materials

The tools used in this research are a Scanning Electron Microscope (SEM), X-Ray Diffraction (XRD), Fourier Transform Infrared (FTIR), Digital Multimeter, Conductometer, Graphene carbon materials, Acetthyleene blac, polyvinylidene fluoride (PVDF), aluminum foil, distilled water (H_2O), sulfuric acid (H_2SO_4) 2 M, ethanol, sodium sulfate, pH paper, filter paper, molasses, sodium hydroxide (NaOH) 10% pa, sodium carbonate ($NaCO_3$) pa

2.2 Procedure Preparation

The manganese rock samples used were taken from the Paludda area of Barru Regency. The manganese rock was washed with distilled water and dried in an oven at 60 – 90ºC for 2 hours. Then the sample was ground until smooth and sieved using a 150-mesh sieve. It was then stored in a closed container.

2.3 Leaching of Manganese Ore

As much125g of the prepared sample was added to 500 mL of 2 M H_2SO_4, stirred at 90°C, and added 50% molasses as a reducing agent. Leaching time was carried out for 6 hours and stirred using a magnetic stirrer at 300 rpm. Then the mixture was filtered, the leaching solution was heated at 70 ºC, and 10% NaOH was added until the pH reached 5–6 to precipitate metal impurities. Then the solution was filtered and then heated to a temperature of 50ºC and added with sodium carbonate to a pH of 9 to obtain a manganese carbonate precipitate (Arita et al., 2015).

2.4 Manganese Carbonate Calcination

The manganese carbonate obtained from the leaching process is then calcined in a tube furnace at 600ºC for 2 hours to obtain MnO_2 composite.

1. Testing Using FTIR

Fourier Transform Infrared (FTIR) testing was carried out to determine the functional groups formed during the synthesis process with a ratio of 0.5 gr MnO_2. This test was carried out with a wavelength of 500-4000 cm-1.

2. Materials Characterization

0.25 gr of MnO_2 and 0.75 gr of graphene were weighed. The MnO_2-graphene composite sample made was tested for material by X-Ray Diffraction (XRD) This measurement used a Cu-K target anode (λ=1.540600 Å) is carried out at an angle of 2θ (5º–90º). The characterization of the phase content begins with a qualitative analysis of the resulting pattern on XRD which works by utilizing Bragg's Law.

2.5 Testing the Value of Capacitance, Voltage, and Current

Weigh the MnO_2: Graphene composite with each ratio (0.25 gr: 0.75 gr), (0.5 gr: 0.5 gr), and (0.75 gr: 0.25 gr), then add one water and PVA glue to form a slurry. Then the slurry that has been stirred evenly is smeared with two sheets of aluminum foil electrodes with a plate size of 4 x 4 cm^2. Furthermore, the electrode sheet that has been smeared is heated in an oven with a temperature of 105 ºC until dry. Furthermore, the two electrode sheets are faced and given a paper membrane dissolved in sodium sulfate electrolyte solution. The series of electrode sheets that have been completed are then tested using a multimeter to determine the values of capacitance (C), voltage (V), current (I), and resistance (R) (Aripin & Priatna, 2017).

2.6 Conductivity Testing on Manganese-Graphene

Weighed MnO_2 : Graphene Comparison (0.5 gr: 0.5 gr) was added to 50 mL of ethanol and stirred for 2 hours. In the same way for the ratio of MnO_2- Graphene (0.25 gr: 0.75 gr), (0.75 gr: 0.25 gr), 50 mL of ethanol was added and stirred for 2 hours. The results of the Manganese-Graphene solution in various comparisons (0.5 gr: 0.5 gr), (0.3 gr: 0.7 gr), and (0.7 gr: 0.3 gr) were tested for conductivity using a conductometer.

3. RESULTS

4.1 Fourier Transform Infrared Test (FTIR)

Table 1. FTIR Absorption

MnO_2 0.5 gr – Graphene 0.5 gr	Functional groups	Absorption Area (cm-1)
479,44	Mn-O	450-950
618.35	Mn-O	450-950
877,47	Mn-O	450-950
992.07	Mn-O	450-950
1104,27	CO	1080-1390
1190.69	CO	1080-1390
1384,21	CO	1080-1390
1438,44	OH Bends	1528-1700
1627,70	OH Bends	1528-1700
3398,29	Oh Stretching	3550-3200

4.2 X-Ray Diffraction Test (XRD)

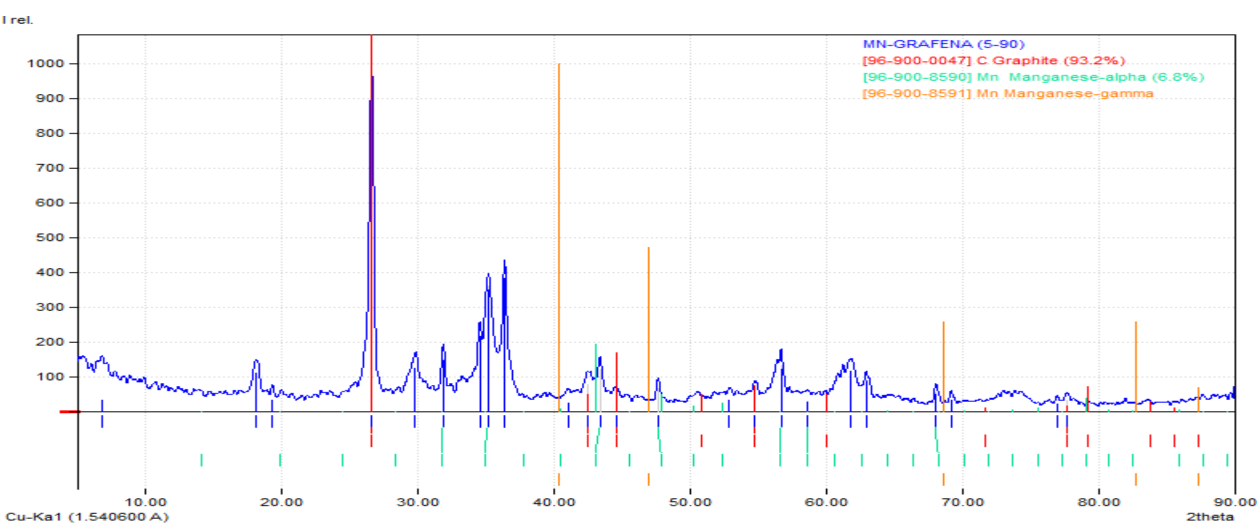

Figure 1. Diffraction pattern XRD analysis of MnO_2-Graphene composites

4.3 Electrical Properties Test

4.3.1 Capacitance Test

Table 2. MnO_2-Graphene Composite Capacitance Test

Sample	Concentration Comparison	The result of measuring the value of capacitance (C) (μF)			
		Simplo	Duplo	triplo	Average
Manganese: Graphene	0.25 gr: 0.75 gr	195	190	192	192.3
Manganese: Graphene	0.5 gr: 0.5 gr	144	143	144	143
Manganese: Graphene	0.75 gr: 0.25 gr	126	127	125	126

4.3.2 Voltage Test

Table 3. Stress Test of MnO_2-Graphene Composite

Sample	Concentration Comparison	Voltage value measurement results (V) (mV)			
		Simplo	Duplo	triplo	Average
Manganese: Graphene	0.25 gr : 0.75 gr	362	376	321	353
Manganese: Graphene	0.5 gr : 0.5 gr	361,1	353,1	321.7	345,3
Manganese: Graphene	0.75 gr : 0.25 gr	359.4	372	238.7	323,3

4.3.3 Strong Current Test

Table 4. Current Test of MnO_2-Graphene Composite

Sample	Concentration Comparison	Current value measurement results (I) (mA)			
		Simplo	Duplo	triplo	Average
Manganese: Graphene	0.25 gr : 0.75 gr	14,3	11,7	13.5	13,16
Manganese: Graphene	0.5 gr : 0.5 gr	8,4	6,2	7,4	7,33
Manganese: Graphene	0.75 gr : 0.25 gr	5,4	5,2	4,8	5,13

4.3.4 Resistance Test

Table 5. MnO_2-Graphene Composite Resistance Test

Sample	Concentration Comparison	Resistance value measurement results (R) (cΩ)			
		Simplo	Duplo	triplo	Average
Manganese: Graphene	0.25 gr : 0.75 gr	1,653	1,433	1,720	1,602
Manganese: Graphene	0.5 gr : 0.5 gr	1.74	2.74	1.78	2.08
Manganese: Graphene	0.75 gr : 0.25 gr	1.73	4.95	8,17	4.95

4.3.5 Conductivity Test

Table 6. Conductivity Test of MnO_2-Graphene Composite

Sample	Concentration Comparison	Results of measurements of Electrical Conductivity (μS cm-1)			
		Simplo	Duplo	triplo	Average

Graphene	1 gr	36,7	36.0	36,9	36,53
Manganese	1 gr	54,4	55.5	55,7	55,2
Manganese: Graphene	0.25 gr : 0.75 gr	94.0	96.0	96.4	95.47
Manganese: Graphene	0.5 gr : 0.5 gr	99.3	98.9	99.6	99.27
Manganese: Graphene	0.75 gr : 0.25 gr	123.0	119,2	119.5	120.57

4. DISCUSSION

Manganese dioxide (MnO_2) is a manganese oxide that can be either crystalline or amorphous. Among the types of MnO_2, namely α-MnO_2, β-MnO_2, γ-MnO_2, and δ-MnO_2, the crystal structure of α-MnO_2 showed the best electrochemical performance. However, MnO_2 has the feature of low electrical conductivity. Therefore, to improve the electrical conductivity of α-MnO_2, it is composited with graphene carbon powder. In this case, the MnO_2-Graphene composite prevents the passivation layer from forming in the primary battery. To find out the performance of the MnO_2-Graphene, the research steps were carried out, namely: Manganese seed sample preparation, MnO_2 synthesis in an acidic environment, Calcination of manganese carbonate, MnO_2-Graphene composite, FTIR and XRD characteristic tests, Multimeter test,

The first stage of sample preparation is grinding rock into powder to crush large and complex materials into small particles. Manganese seed sample preparation was carried out manually using a rock crusher. The manganese seeds are crushed using a rock crusher with a size of 10 mm so that they can be evenly dried using a drying oven. Furthermore, the manganese seed sample was in the oven for 18 hours at 105°C. The sample that was finished in the oven was removed and then milled so that the manganese seed sample was smaller. Furthermore, the sample that has gone through the grinding process is sieved using a filter with a size of 150 mesh. The sieving is used for filtering fine particle/powder material. For the manual method, The preparation is done using traditional tools. The manganese seeds were pounded using a mortar and pestle, after the samples were smooth, the manganese seeds were then placed in the oven for 30 minutes at 105°C. After the manganese seed samples were dried, they were sieved using a shave shaker with a size of 150 mesh.

In the second stage, manganese dioxide synthesis is carried out in an acidic environment. Leaching is done by weighing as much as 125 g of the prepared sample, was added 50%, and 500 mL of 2 M H_2SO_4 was added. The leaching time was carried out for 6 hours and stirred using a magnetic stirrer at 300 rpm at a temperature of 90°C. Then, the mixture was filtered using filter paper. The filtered solution is taken, and the residue is discarded because it contains impurities (Amalia et al., 2016).

The addition of molasses to the leaching of manganese seeds is a reducing agent, previous research (Amalia et al., 2016) proved that molasses is a suitable reducing agent, with manganese extraction yields increasing with increasing concentration. The high concentration of molasses is 50%, with the extraction of manganese seeds around 97.58% produced. The results showed that the extraction presentation was poor without adding molasses compared to other concentrations. The addition of H_2SO_4 serves to create an acidic atmosphere. The acidic atmosphere is created, so a perfect precipitate of MnO_2 is formed. The reduction reaction equation supports this at the cathode involving the transfer of H^+ ions due to the addition of H_2SO_4:

$$MnO_{4^-} + 4H^+ + 3e^- \longrightarrow MnO_2 + 2H_2O$$
$$E^0 = +1.67\ V$$

where it takes 4 moles of H^+ to react with 1 mole of MnO_{4^-} to form 1 mole of MnO_2 precipitate. So that excess acid (H^+) is needed to produce optimum MnO_2 deposits (Rakhmad & Rakhma, 2018).

The next step is to heat the filtered solution at 70ºC using a magnetic stirrer and add 10% NaOH until the pH reaches 5-6. The aim is to precipitate metal impurities such as Fe. It is known that iron dissolves easily in acidic solutions, so the addition of NaOH can purify manganese-rich solutions. The filtered solution is taken, and the residue containing metal impurities is discarded. Then the filtered solution was heated to 50°C using a magnetic stirrer and added with sodium carbonate to pH 9 to obtain a manganese carbonate precipitate. Then the solution was filtered using Whosstman filter paper so that the filter results were maximum to produce manganese carbonate. After the manganese carbonate precipitate is obtained, the manganese carbonate precipitate is dried using an oven at 105ºC.

4.1 Characteristic Fourier Transform Infra-Red (FTIR)

Functional group analysis of the electrodes is needed to determine the molecular bonds present in the powder—functional group analysis using the Fourier Transform Infra-Red (FTIR) tool. From the FTIR measurement results, the resulting spectrum will be obtained as shown in Figure 4.7, the transmittance spectrum of the sample can be seen, and there are four functional group peaks. Three peaks with moderate transmittance are visible at wavelengths of 3192.2 cm^{-1}, 1614.61 cm^{-1}, and 1012.19 cm^{-1}. Meanwhile, there is a low transmittance peak at a wavelength of 479.44 cm^{-1}

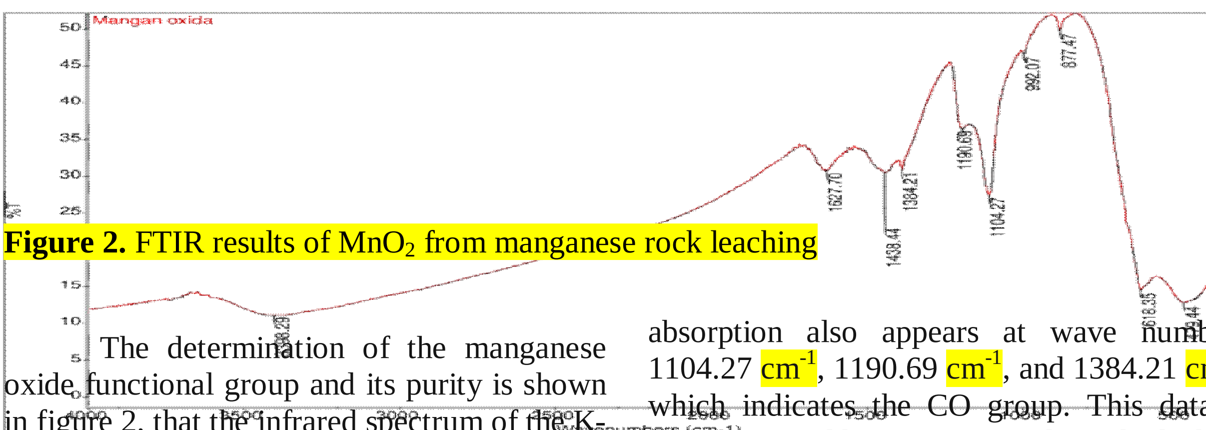

Figure 2. FTIR results of MnO_2 from manganese rock leaching

The determination of the manganese oxide functional group and its purity is shown in figure 2, that the infrared spectrum of the K-type manganese oxide *birnessite* shows peak Typical wave numbers are 479.44 cm^{-1}, 618.35 cm^{-1}, 877.47 cm^{-1}, and 992.07 cm^{-1}. This matter indicates the stretching of the Mn-O bonds in the octahedral layers of the structure *birnessite*. This result is also supported by the results of previous studies, which explain that wave numbers 413 cm^{-1} to 993 cm^{-1} are specific for the Mn-O bond. Tape absorption also appears at wave numbers 1104.27 cm^{-1}, 1190.69 cm^{-1}, and 1384.21 cm^{-1}, which indicates the CO group. This data is also supported by previous studies which show the existence of stretching CO (hydroxyl, ether, ester, or carboxylic acid) at wave numbers 1100- 1400 cm^{-1}. The absorption bands are at wave numbers 1438.44 cm^{-1} and 1627.70 cm^{-1} showing vibration *bending* from the OH group. The absorption band is at wave number 3398.29 cm^{-1} is vibration stretching. This OH vibration describes the absorption band at wave number 3398.29 cm-1 and shows the presence of OH groups from the K-Br pellets, which bonded to metals in the interlayer.

4.2 X-Ray Diffraction Test (XRD)

MnO_2 is a particle with an amorphous or low crystallinity structure crystalline. In this study, α-MnO_2 is the crystallinity structure chosen as the best crystallinity parameter. The conditions used affect the crystallinity obtained from the MnO_2 nanoparticles. It is becauseα formation-MnO_2, β-MnO_2, γ-MnO_2, and δ-MnO_2 can be stable under certain conditions only. In this test, using XRD with an angle of 2θ from *range* 5^o–90^o.

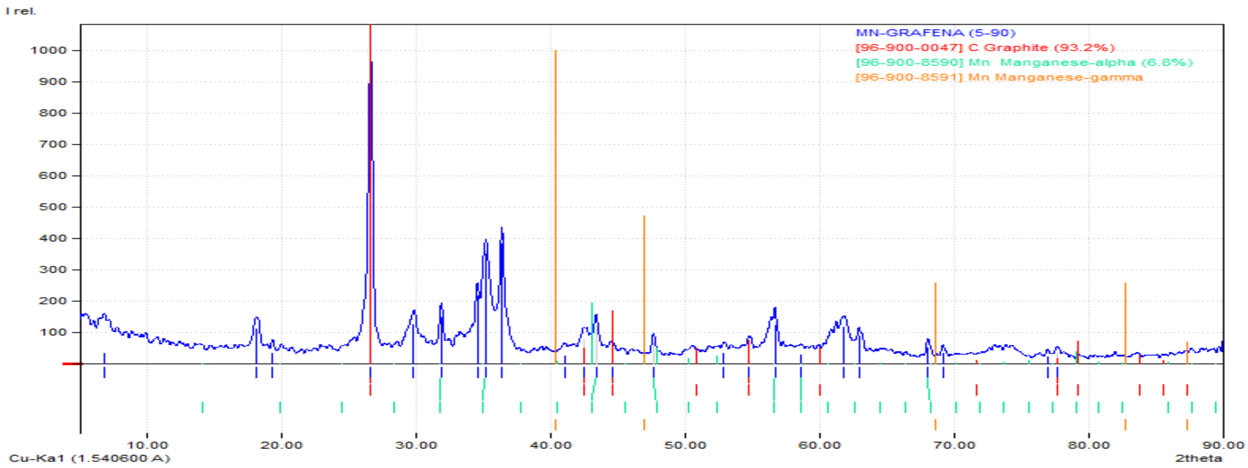

Figure 3. XRD Results of the MnO_2-Graphene Composite

Based on figure 3, the percentage (Mnα) and graphene are around 6.8% and 93.2%, respectively. The initial concentration composition difference between 0.25 g manganese and 0.75 g graphene is relatively high. These data indicate a significant shift in composition between MnO_2 and graphene. This difference is due to the temperature/temperature factor and the air component (CO_2). It resulted in MnO_2 undergoing oxidation due to CO_2 (environmental) factors, in which the element carbon (C) predominated. At the same time, graphene will experience an increase in composition due to the addition of carbon elements that dominate graphene. Based on the results of the XRD data, the purity of the composition of MnO_2 and graphene is about 6.8% manganese (Mn) and 93.2% carbon.

XRD data from the absorption peak$2\theta$from the MnO_2 and graphene composite was obtained at the peak of 26.64^o with a peak of 1000.00. at the top, it reads the crystal lattice of graphene. Meanwhile, the second highest peak is at angle $2\theta 35,20^o$with a peak of 385.02. At the peak, the crystal lattice of MnO_2 is read. Corner 2θ produced by each composite between graphene and MnO_2 has different characteristics. The crystal structure produced by graphene is in the form of an Orthorhombic cube with rectangular cubic specifications.

Meanwhile, the crystal lattice produced by MnO_2 is a face-centered cubic (cubic). The two crystals of the MnO_2-graphene composite have the characteristic of being amorphous. More specifically, the MnO_2 crystal has a stable angular inclination due to the distance between the lattice in the crystal being relatively the same, so it has a tendency best crystallinity (Rakhmad & Rakhma, 2018).

4.3 Electrical Properties Test Results

The characterization of electrical properties was carried out using a multimeter to measure the values of capacitance (C), resistance (R), voltage (V), and current (I) of the MnO_2- graphene composite. In this test, the MnO_2-graphene composite samples with a ratio of 0.75 gr : 0.25 gr, 0.5 gr : 0.5 gr, and 0.25 gr : 0.75 gr were prepared by adding water and PVA glue. -each variation to form a slurry. Then the thickened slurry is smeared on the two electrode sheets that have been prepared. Then the electrode sheets are heated at 105ºC until dry. Furthermore, the electrode sheet is affixed with a sheet of paper that has been dipped in an electrolyte solution. The clamped electrode sheet is then tested using a multimeter.

1. Capacitance Test

This test is carried out by measuring the capacitance (C) to determine the capacity of the stored electric charge. Measurements were made with a plate size of 4 x 4 cm^2 with a series thickness of 1 mm. The area of the electrode plate is directly proportional to the capacitance value. It is because more manganese-graphene composite causes more charge to be stored in the pores of the MnO_2-graphene composite, and more electrical double layers are formed (Yang et al., 2015).

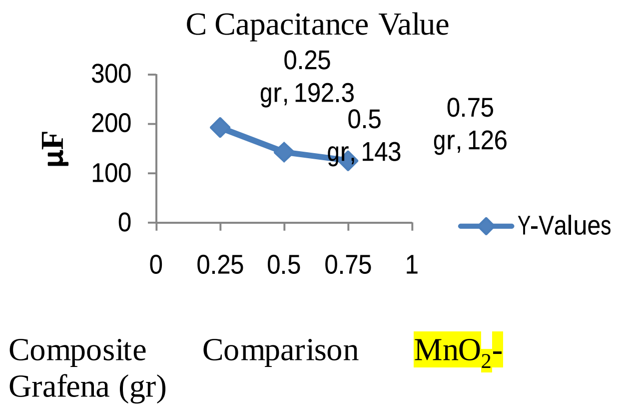

Figure 4. MnO_2-Graphene Composite Capacitance test graph

The result of the capacitance value in figure 4 is that the highest value for the MnO_2-graphene composite ratio is 0.25 g : 0.75 g with a capacitance value of 192.3 µF. From the graph, it can be seen that the difference is huge with the comparison of the MnO_2-graphene composite 0.5 g : 0.5 g with a capacitance value of 143 µF, and the lowest capacitance value is the MnO_2-graphene composite 0.75 g : 0.25 g with a capacitance value of 126 µF. It means that the higher the concentration of graphene carbon ratio can increase the high absorption power to store charge and electrical energy (Sari, 2012). Compared to research on supercapacitor electrodes using coconut shell rGO as the base material composited with ZnO previously carried out by Siregar et al. (2018), there is an increase in capacitance values. It is due to the difference in adding composites to graphene in this study by adding MnO_2 elements. Previous research showed that the capacitance value was only around 7 µF, but in this study, it increased to 192.3 µF. So it can be assumed that the addition of the MnO_2 composite used is quite effective and increases the capacitance value, but further development is needed.

2. Voltage Test

This test determines the voltage value in the MnO_2-graphene composite electrode sheet at various comparisons. Measurements were made with a plate size of 4 x 4 cm^2 with a series thickness of 1 mm.

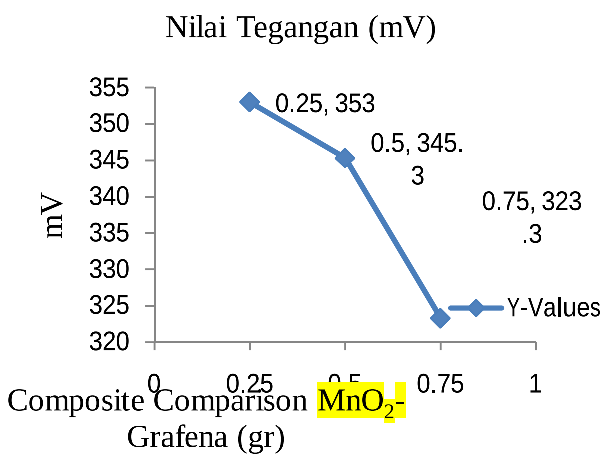

Figure 5. Graph of MnO_2-Graphene Composite Stress test

The Voltage test results in figure 5 shows that the highest value for the MnO_2-graphene composite ratio is 0.25 gr: 0.75 with a resulting voltage value of 353 mV. The graph shows that the difference is almost the same as the comparison of the MnO_2-graphene composite 0.5 gr : 0.5 with a voltage value of 345 mV, and the lowest voltage value is in the MnO_2-graphene composite 0.75 gr : 0.25 with a value capacitance of 323 mV.

1. Current Strength Test

This test determines how much current is generated in the MnO_2-graphene composite electrode sheet at various comparisons. Measurements were made with a plate size of 4 x 4 cm^2 with a series thickness of 1 mm.

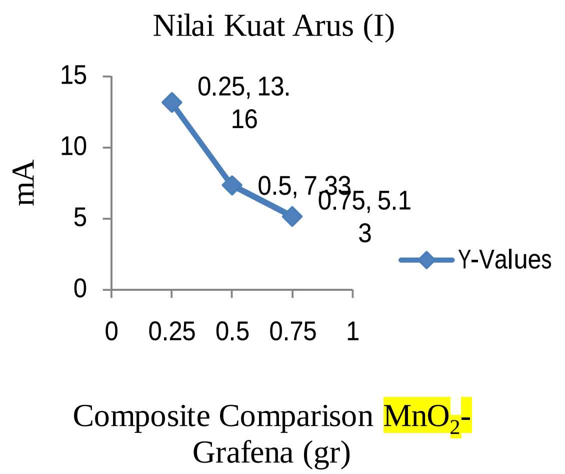

Figure 6. Graph of MnO_2-Graphene Composite Flow Test

The current test results in figure 6 show that the highest value for the MnO_2-graphene composite ratio is 0.25 g: 0.75 g, with a resulting current value of 13.6 mA. From the graph, it can be seen that the difference is huge with the comparison of the MnO_2-graphene composite 0.5 gr : 0.5 with a voltage value of 7.33 mA, and the lowest voltage value is the MnO_2-graphene composite 0.75 gr : 0.25 with a capacitance value of 5.13 mA.

2. Resistance Test

This test determines the resistance value generated in the MnO_2-graphene composite electrode sheet at various comparisons. Measurements were made with a plate size of 4 x 4 cm^2 with a series thickness of 1 mm.

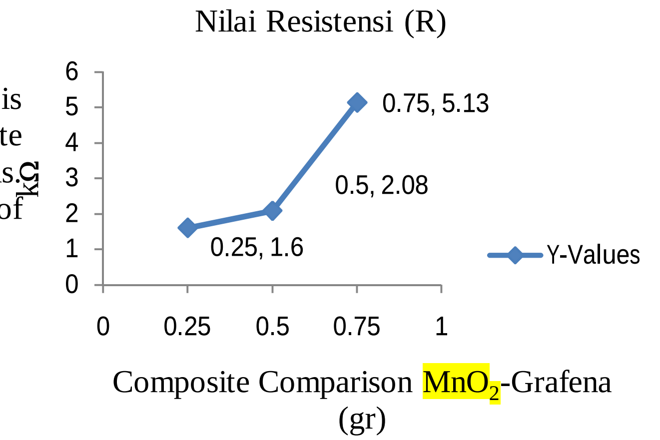

Figure 7. MnO_2-Graphene Composite Capacitance test graph

The results of the resistance test in figure 7, the lowest resistance value produced is the comparison of the MnO_2-graphene composite 0.25 gr: 0.75 with the resulting resistance value of 1.6 kΩ. From the graph, it can be seen that the difference is almost the same as the comparison of the MnO_2-graphene composite 0.5 gr : 0.5 with a resistance value of 2.08 kΩ, and the lowest resistance value on the composite MnO_2-graphene 0.75 gr : 0.25 with a resistance value of 5.13 kΩ.

5. Conductivity Test

Conductivity analysis on a variety of samples of 1 gr graphene, 1 gr manganese, and manganese-graphene composite with variations in the ratio of 0.25 gr : 0.75 gr, 0.5 gr : 0.5 gr and 0.75 : 0.25 by using conductometer at room temperature with the addition of 50 mL pa of ethanol solution to a variety of samples.

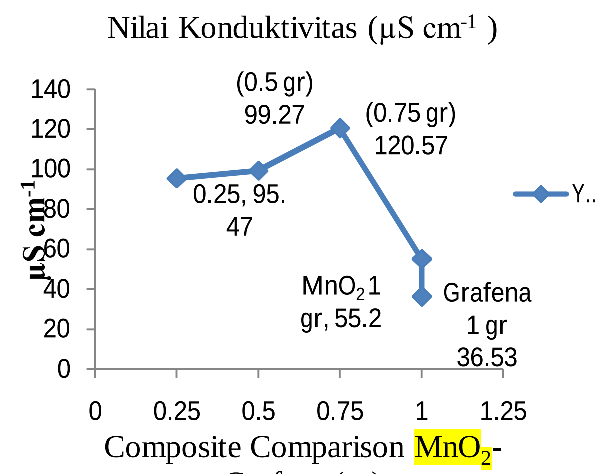

Figure 8. MnO_2-Graphene Composite Capacitance test graph

Based on the results of conductivity analysis using a conductometer from the data in figure 8, it was obtained that the MnO_2-graphene composite 0.75 g : 0.25 g had a high conductivity value of 120.57 µS cm-1. The results of the conductivity test on the comparison of variations The sample in Figure 8 shows that the conductivity value of MnO_2 has increased with the addition of graphene carbon. In accordance with previous studies, the comparison of manganese-carbon composites with manganese-graphene composites produced high conductivity values in the presence of carbon graphene, resulting in a conductivity of 31.847/Ωm and 39, 809/Ωm (Rakhmad & Rakhma, 2018).

The variation in the ratio of MnO_2-graphene 0.50 gr : 0.50 gr has an electrical conductivity of 99.27 µS cm-1, and the variation of MnO_2-graphene 0.25 gr : 0.75 gr has an electrical conductivity value of 95.47 µS cm-1, the difference in conductivity values is not much different. In the variation ratio, 1 g MnO_2 has a conductivity of 55.2 µS cm-1, and graphene has a conductivity value of 36.53 µS cm-1. Following previous studies, it can conduct electricity well by adding graphene. Graphene has better electron mobility than ordinary carbon because the structure and spacing between layers in graphene are minor and do not have many oxygen functional groups that prevent electrons from flowing smoothly.

5. CONCLUSION

The physical properties of manganese MnO_2-graphene can be seen from the FTIR characteristics, which indicate the presence of the Mn-O functional group at wave numbers 479.44 cm^{-1}, 618.35 cm-1, 877.47 cm-1, and 992.07 cm^{-1}. This matter indicates the stretching of the Mn-O bonds in the octahedral layers of the structure *birnessite*. While the characterization with XRD showed an absorption peak of 20 from the MnO_2 composite obtained a face-centered cubic crystal lattice, graphene obtained the highest peak at the peak of 26.64▪ obtained an Orthohombic cubic crystal structure with rectangular cubic specifications.

The effect of varying the mass ratio of the MnO_2-Graphene composite on the capacitance value was 192.3▪F in the variation of 0.25 gr : 0.75 where the higher the concentration of the graphene carbon ratio, the higher the absorption capacity can increase to store charge and electrical energy. The effect of variations on the voltage obtained a voltage value of 353 mV at a variation of 0.25 gr: 0.75. The effect of variations on the current obtained a value of 13.6 mA at a variation of 0.25 gr: 0.75. The effect of variation on resistance obtained the lowest resistance value of 1.6 kΩ at 0.25 gr variation: 0.75.

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