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THE EFFECT OF VOLTSAGE AND TIME IN SYNTHESIS OF MANGANESE DIOXIDE FROM MANGANESE SULFATE PRECURSOR

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Abstract

The utilization of manganese dioxide (MnO_2) as a cathode material for lithium-ion batteries has attracted considerable attention due to its high theoretical storage capacity of 615 mAh/g. In this study, the synthesis of MnO_2 was carried out from manganese sulfate ($MnSO_4$) precursor, a pregnant solution from the leaching process of manganese ore from Trenggalek Regency. The electrolysis method has been used in this synthesis of MnO_2 in an electrochemical cell consisting of two graphite electrodes with dimensions of (16 x 5 x 0.3) cm. The purpose of this study is to determine the effect of voltsage and time on particles produced of MnO_2, the phase and crystal structure by MnO_2, and its morphological microstructure. The electrolysis process was carried out in 2,000 ml of $MnSO_4$ solution under constant stirring at 60 °C with DC voltsage varied by 2, 4, 6, and 8 volts and time run by 4, 8, 12, and 16 hours. The precipitates formed at the anode were separated, then the particles were dried at 110°C for 2 hours. The composition of MnO_2 was analyzed by XRF (x-ray fluorescence), the phase and crystal structure were evaluated by XRD (x-ray diffraction), and the morphological microstructure was captured by SEM (scanning electron microscope). The results revealed that the highest mass gain of MnO_2 produced is 31.63 grams which are electrolyzed at 8 voltss for 16 hours. The highest purity of MnO_2 is 89.23% which is electrolyzed at 2 voltss for 16 hours. The particles produced were α-MnO_2 with a tetragonal crystal system and nearly spherical with size particles ranging from 136.01-202.48 and 144-352 nm.

Keywords: *Manganese sulfate, manganese dioxide, electrolysis, crystal structure, polymorphy*

1. INTRODUCTION

Manganese mineral is one of Indonesia's natural resources. The manganese mineral occurs in nature commonly as pyrolusite (MnO_2) and psilomelane ($BaH_2O_2.Mn_5O_{10}$). According to the United States Geological Survey (USGS), about 85-90% of manganese use in the world is applied to the metallurgical industry. In comparison the remaining 10% is applied to the non-metallurgical industry. According to the Geological Agency, in 2015, Indonesia had 61,631,820 tons of manganese ore resources and 87,236,536 tons of manganese ore reserves spread across several regions in Indonesia [1]. Trenggalek Regency in East Java Province has one the best quality of manganese ores [2].

Manganese ore in Trenggalek Regency is found as pyrolusite with a Grade A quality that contains above 40% MnO_2 [3]-[4]. The compositions of manganese ore from the Trenggalek Regency are shown in Table 1, which shows that the MnO_2 level in manganese ore from Trenggalek Regency is about 46.03% [5]. However, the manganese ore from Trenggalek Regency has not been used optimally [2],[4]. Therefore, further research is needed to get the desired product, especially

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using MnO_2 as cathode material for lithium-ion batteries.

Table 1. XRF analysis results of manganese ore from Trenggalek Regency [5]

Compounds	Wt. %
Manganese (MnO_2)	46.03
Silica (SiO_2)	48.73
Iron Oxide (Fe_2O_3)	3.77
Calcium (CaO)	1.10
Barium (BaO)	0.46
Phosphor (P_2O_5)	0.56

Lithium-ion batteries have been widely developed because of their advantages; a high energy efficiency of about 75-90%, long cycle life of about 500-2000 cycles, and low self-discharge of about 5-10% per month [6]. Cobalt has been commonly used in commercial lithium-ion batteries, known as LCO (lithium cobalt oxide). However, the development of LCOs is hampered due to their high cost and environmental issues, which are considered unfriendly to the environment [7]. Various oxides of transition metals have been studied as alternative cathode materials for lithium-ion batteries. From the different transition metal oxide, manganese dioxide (MnO_2) has attracted so much attention to be used as a cathode material for lithium-ion batteries due to its high storage capacity of 615 mAh/g [8], which is expected to fulfill the demands of high performance of lithium-ion batteries. Manganese dioxide is also considered to have the potential to be used as a lithium-ion battery cathode because of its abundant natural resources [9].

Manganese dioxide has various polymorphic crystal structures, including β-, α-, δ-, and γ-MnO_2. The electrochemical properties of manganese dioxide depend on the crystal structure and morphology of the oxide. From the various polymorphic crystal structures of manganese dioxide, α-MnO_2 has special attention as a cathode material for lithium-ion batteries due to the presence of a 2x2 tunnel in its crystal lattice, which is considered to facilitate accommodation and transport for the inclusion of lithium ions [10].

MnO_2 particles can be prepared by the electrolysis method. The electrolysis method was chosen in this study due to its uncomplicated process compared with hydrothermal, sol-gel, sonochemical, and other methods. Widiyastuti et al., [11] reported that α -MnO_2 had been successfully prepared from the $KmnO_4$ solution by electrolysis method using two carbon electrodes with 2 voltss applied. The particles were rod-like in shape with a diameter of 493.22 nm. In this study, the synthesis of MnO_2 by electrolysis method will be developed from manganese sulfate ($MnSO_4$) precursor, which is a pregnant leach solution from the leaching process of manganese ore from Trenggalek Regency. The Electrolysis process was carried out with variations of voltsage and time to determine its effect on the mass gain of obtained MnO_2 and to determine the polymorphic crystal structure and the morphology of obtained MnO_2.

2. MATERIALS AND METHODS

A pregnant leach solution of manganese sulfate ($MnSO_4$) produced by the leaching process of manganese ore from Trenggalek Regency was used as a precursor in this study. This process was carried out in an electrochemical cell consisting of two graphite electrodes with dimensions of (16 x 5 x 0.3) cm. The schematic of the electrolytic cell is shown in Fig.1. The electrodes were set in parallel with the anode connected to (+) and the cathode connected to (-) polar of the DC power supply. The distance between anode and cathode was 5 cm, and both anode and cathode were immersed into $MnSO_4$ solution with a final depth of 8 cm.

The sample was first filtered and then analyzed by ICP-OES (inductively couple plasma-optical emission spectroscopy) to determine the compositions of $MnSO_4$ solution before being processed by the electrolysis method. The electrolysis process was carried out in 2000 ml of $MnSO_4$ solution under constant stirring at 60°C with DC voltsage varied by 2, 4, 6, and 8 voltss and time varied by 4, 8, 12, and 16 hours. The precipitates formed at the anode were separated, then the particles were dried at 110 °C for 2 hours to get a powder of MnO_2. At the end of the experiment, the product was weighed to determine the mass gain of obtained MnO_2.

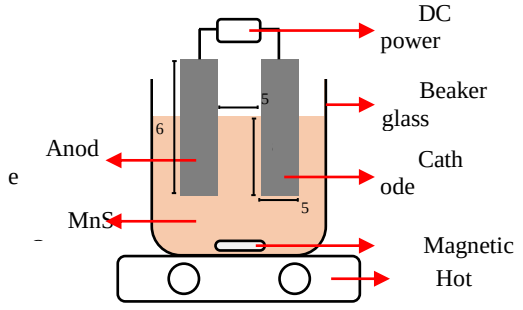


Figure 1. The schematic of electrolytic cells

The compositions of MnO_2 were then analyzed by XRF (x-ray fluorescence), the phase and

crystal structure were also evaluated by XRD (x-ray diffraction), and the morphological microstructure was captured by SEM (scanning electron microscope) for further analysis.

3. RESULT AND DISCUSSION

The ICP-OES (inductively couple plasma-optical emission spectroscopy) results of $MnSO_4$ solution before processed by electrolysis method are shown in Table 2 which shows that the manganese (Mn) level in $MnSO_4$ solution is 384.033 ppm.

Table 2. $MnSO_4$ initial composition analyzed by ICP-OES

Element	ppm	Element	ppm
Ag	0.01178	Fe	0.05516
Al	0.36621	K	0.05516
Ca	3.32535	Mg	1.02671
Co	0.03355	Mn	384.033
Cr	0.08665	Na	0.99584
Cu	0.21774	Ni	0.07297

In a synthesis of MnO_2 prepared by the electrolysis method, electrical energy is converted directly into chemical energy, which is stored in the products of the reaction. When the current is passed through the $MnSO_4$ solution, the reaction will occur as an anodic and cathodic reaction. The anodic reaction would be processed in three steps, as shown in Equations (1)-(3). The cathodic reaction and the overall reaction can be written as shown in Equation (4)-(5) [12]. During the reaction, manganese is deposited at the anode as MnO_2.

$$Mn^{2+} + 2H_2O \rightleftharpoons MnO_2 + 4H^+ + 2e^- \quad (1)$$
$$MnO_2 + Mn^{2+} + 2H_2O \rightleftharpoons 2MnOOH + 2H^+ \quad (2)$$
$$MnOOH \rightleftharpoons MnO_2 + H^+ + e^- \quad (3)$$
$$2H^+ + 2e^- \rightleftharpoons H_2 \quad (4)$$
$$MnSO_4 + 2H_2O \rightleftharpoons MnO_2 + H_2SO_4 + H_2 \quad (5)$$

The color transformation of MnSO4 solution can observe the synthesis of MnO_2. The color of $MnSO_4$ was pink before electrolysis; and then it turned black. It happens due to the decreasing Mn content in $MnSO_4$ solution during the electrolysis process. The most significant color transformation of $MnSO_4$ is in a condition of 8 voltss applied for 16 hours, as shown in Fig. 2. During the electrolysis process, bubbles are also formed at cathode due to the hydrogen that occurs in cathodic reaction as written in Equation 4.

(a) (b)

Figure 2. MnSO4 solution processed by electrolysis method: (a) before processed, (b) after processed

$MnSO_4$ solutions were then analyzed again by ICP-OES to determine the compositions of $MnSO_4$ after being prepared by electrolysis. The ICP-OES results of $MnSO_4$ are shown in Table 3, which indicates that the Mn level in $MnSO_4$ is 142.232 ppm.

Table 3. ICP-OES analysis results of $MnSO_4$ solution after processed by electrolysis method at 2 volts for 16 hours

Element	ppm	Element	ppm
Ag	0.15151	Fe	0.40623
Al	0.59212	K	0.63093
Ca	3.24400	Mg	0.96942
Co	0.03123	Mn	142.232
Cr	0.16532	Na	1.41810
Cu	0.14877	Ni	0.12794

It decreases due to reactions during the electrolysis process, which transform the Mn to MnO_2 deposited, and it also causes the increasing of other elements in solution.

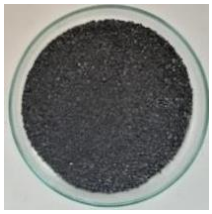


Figure 3. Manganese dioxide prepared by electrolysis method

The precipitates formed at anode were separated, then the particles were dried to get a powder of MnO_2. The obtained MnO_2 prepared by electrolysis is a solid black as shown in Fig. 3.

3.1 Synthesis of MnO_2 in Various Voltsage Prepared by Electrolysis

The electrolysis process was carried out with various voltsages applied by 2, 4, 6, and 8 voltss. The effect of voltsage on the mass gain of MnO_2 produced by electrolysis is shown in Fig. 4. It is expected that increasing the voltsage of electrolysis will lead to an increased mass gain of MnO_2.

According to the results, the mass gain of MnO_2 produced by the electrolysis method is directly proportional to the voltsage applied.

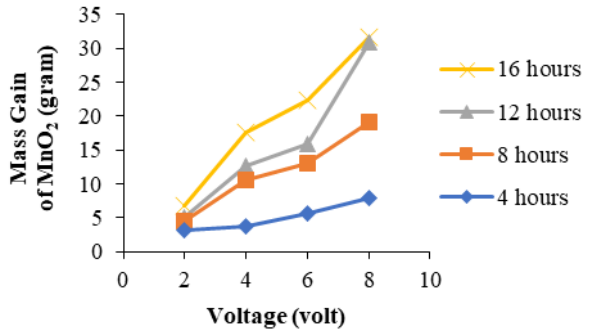


Figure 4. The effect of voltsage on mass gain of MnO_2 prepared by electrolysis

The voltsage used in electrolysis will affect the amount of current, as written in Equation 6.

$$V = i \; x \; r \qquad (6)$$

V is voltsage in volts (V), *i* is current in ampere (A), and *r* is resistance in ohm. The higher voltsage will increase the amount of current passing through the electrolyte, which will also lead to a rise in the rate of particles produced at the anode. It has been well-known, as stated in Faraday's law, that the amount of particles produced is directly proportional to the current passing through the electrolyte, which is written in Equation 7.

$$W = \frac{e \; x \; i \; x \; t}{F} \qquad (7)$$

Where *w* is the mass of species produced at the electrode in gram (g), *e* is equivalent weight in gram/mol, I is the current in ampere (A), and F is Faraday constant which is equal to 96,500 coulombs. 1F is the charge required to dissolve 1g equivalent of the anode.

3.2 Synthesis of MnO_2 in Various Time Prepared by Electrolysis

The electrolysis process was carried out with time varied by 4, 8, 12, and 16 hours. As shown in Fig. 5, the mass gain of MnO_2 produced increases during electrolysis for a longer time. The highest mass gain of MnO_2 is prepared for 16 hours, and the lowest is prepared for 4 hours. It is expected that increasing the time of electrolysis will lead to an increased amount of particles produced.

According to the results, the mass gain of MnO_2 produced by the electrolysis process is directly proportional to the electrolysis time. The longer time of electrolysis will lead to an increase in the rate of particles produced at the anode, and therefore, it will also increase the mass gain of MnO_2. As stated in Faraday's law, it is also suitable that the amount of particles produced in the electrolysis process is directly proportional to the electrolysis time, as written in Equation 7.

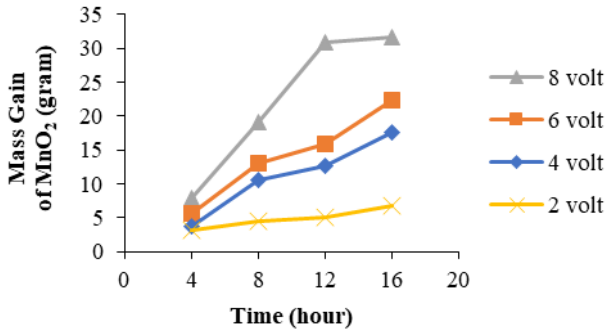


Figure 5. The effect of time on mass gain of MnO_2 prepared by electrolysis

This result is also similar to the previous study, Hidayat et al., [13] reported that electrolysis of MnO_2 from battery waste produces 0.0341 gram MnO_2 at 20 minutes and 0.1045 gram at 60 minutes. Both were electrolyzed at 5 voltss. It means that increasing the time of electrolysis will also increase the mass gain of MnO_2.

3.3 XRF Analysis Results

The compositions of obtained MnO_2 were analyzed by XRF (x-ray fluorescence). The XRF characterization was done on MnO_2 particles prepared at 2 voltss for 16 hours.

Table 4. XRF results of MnO_2 particles prepared by electrolysis at 2 volts for 16 hours

Compounds	%	Compounds	%
K_2O	0.118	NiO	0
MoO_3	0.026	SO_3	1.025
TiO_2	0.014	SiO_2	6.664
MnO_2	89.231	CaO	0.148
Fe_2O_3	2.567	Cr_2O_3	0.155
V_2O_5	0.050		

According to the results, in Table 4, the level of MnO_2 is 89.231%. It indicates that the electrolysis process can potentially increase the MnO_2 level.

The lower MnO_2 level indicated that the impurity level in MnO_2 is still relatively high, and it will decrease the performance of MnO_2 as a cathode material for lithium-ion batteries. Therefore, MnO_2 needed for producing lithium-ion batteries must have high purity. According to the Ministry of Energy and Mineral Resources Republic of Indonesia No. 25 the year 2018, the

minimum purity of MnO_2 processed by the electrolysis method is 90% [14], which has not been achieved in this study of synthesis of MnO_2.

3.4 XRD Analysis Results

The polymorphic crystal structure of obtained MnO_2 was analyzed by XRD (x-ray diffraction). The XRD characterization was done to particles of MnO_2 prepared with various voltsages applied by 2, 4, 6, and 8 voltss for 16 hours. The XRD patterns of MnO_2 particles prepared with multiple conditions are shown in Figure 6. The XRD patterns for all samples are compared to the ICDD (*international center for diffraction data*) database using the PANalytical HighScore Plus application to determine the polymorphic crystal structure. As shown in Figure 6, all the diffraction peaks of particles are in good agreement with ICCD database No. 00-044-0141, which is the standard value of α-MnO_2. According to ICDD database No. 00-044-014, α-MnO_2 has a tetragonal crystal system.

The electrochemical properties of MnO_2 strongly depend on its crystal structure and morphology of the oxide. As stated by Yang et al., [10], α-MnO_2 has the greatest electrochemical properties of other forms due to the presence of a 2x2 tunnel in its crystal lattice, affecting its storage capacity. Therefore, it's great to be used as cathode material for lithium-ion batteries since they require a high storage capacity.

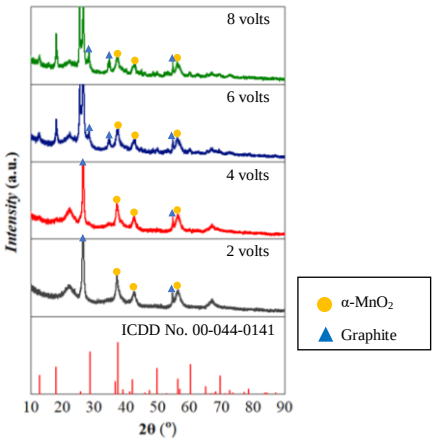


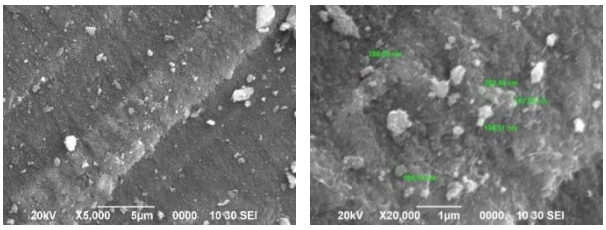
Figure 6. XRD pattern of MnO_2 particles prepared by electrolysis at various voltsages for 16 hours compared to ICDD data base No. 00-044-0141

The patterns for all samples have five characteristic peaks at 2θ= 37°, 42°, 56° which matches with the value of α-MnO_2. However, there are also other peaks which match with the ICDD No. 96-900-0047 database that belongs to graphite. Graphite is an inert electrode, but also a very brittle compound due to its perpendicular planes. Therefore, the existence of graphite in XRD patterns for all samples is expected to come from the electrodes when the deposits at the anode were being separated since graphite is a very brittle compound. As shown in Figure 6, the peaks that belong to impurity increased along with the higher voltsage. It also shows that all the XRD patterns have a different intensity which is the higher intensity is found in the XRD pattern of MnO_2 prepared at 2 voltss for 16 hours, and the lowest one found in the XRD pattern of MnO_2 prepared with 8 voltss applied for 16 hours.

According to the results, the XRD patterns do not exhibit well-defined peaks along with the higher voltsage. Nursiti et al., [15] and Widiyastuti et al., [11] also reported the same result in a previous study of synthesis of MnO_2 prepared by electrolysis from $KMnO_4$ solution; both said that the XRD patterns exhibit well-defined peaks at particles prepared at the lower voltsage. It indicated a poor crystalline of these materials. Increasing the voltsage only lead to increasing the production rate of MnO_2 particles as it has been known that the amount of particles deposited at electrodes in the electrolysis process is directly proportional to the current as stated in Faraday's law. The current, in this case, is also directly proportional to the voltsage.

3.5 SEM Analysis Results

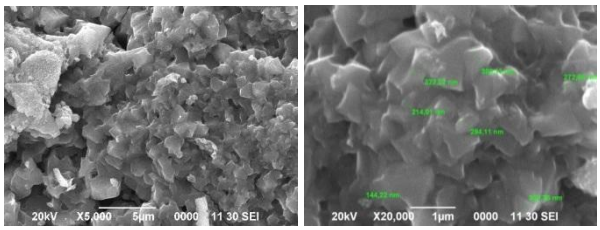
The morphology of obtained MnO_2 was analyzed by SEM (*scanning electron microscope*). The SEM characterization was done to obtain MnO_2 with the highest purity of MnO_2, which is electrolyzed at 2 voltss for 16 hours, and the lowest one, which is electrolyzed at 8 voltss for 16 hours to see the difference. The SEM results of obtained MnO_2 with 2 volts voltsage applied are shown in Fig. 7. At a magnification of 5,000x, it is clearly shown that the particles are not agglomerated. However, the morphology of particles is slightly difficult to be observed. The image likely indicates that the particles may have a nearly spherical morphology. At a magnification of 20,000x, as shown in Fig. 7(b), the particles of MnO_2 have a size ranging from 136.01-202.48 nm.



(a) (b)

Figure 7. SEM image of MnO_2 particles prepared by electrolysis method with 2 volts applied for 16 hours at (a) magnification of 5,000x and (b) magnification of 20,000x

The SEM results of obtained MnO_2 with 2 volts applied for 16 hours are shown in Figure 8. At a magnification of 5,000x, the particles appear as many agglomerates of very nearly spherical. On the other hand, at a magnification of 20,000x as shown in Fig. 8(b), it shows that the particles have a nearly spherical shape morphology with a size ranging from 144-352 nm. According to the results, it is clearly shown that the particles of MnO_2 prepared with 2 volts applied to have a smaller particle size compared to the particle size of MnO_2 equipped with 8 volts applied. This result is similar to the previous study, Viscarini et al., [16] have been reported that the particles prepared by electrolysis of $KMnO_4$ solution at 2 volts have a larger particle size area than the particles prepared at the higher voltage. According to the results, it can be noted that increasing the voltage during electrolysis, in this case, will also increase the particle size of obtained MnO_2. The particle size of obtained MnO_2 will also influence the quality of MnO_2 as cathode material for lithium-ion batteries; the smaller particle size makes a surface area more prominent. A larger surface area will also make the storage capacity of MnO_2 become larger. Therefore, it improves the quality of MnO_2 as cathode material for lithium-ion batteries.



(a) (b)

Figure 8. SEM image of MnO_2 particles prepared by electrolysis method with 8 volts applied for 16 hours at (a) magnification of 5,000x and (b) magnification of 20,000x

4. CONCLUSION

Manganese dioxide has been successfully prepared at various voltage and times by electrolysis of $MnSO_4$ using two graphite electrodes. The highest amount of obtained MnO_2 is 31.63 grams which are electrolyzed at 8 volts for 16 hours. The highest purity of obtained MnO_2 is 89.23% which is electrolyzed at 2 volts for 16 hours. The particles have nearly spherical shape morphology with size ranging from 136.01-202.48 nm which is electrolyzed at 2 volts for 16 hours and 144-352 nm which is electrolyzed at 8 volts for 16 hours. The particles produced were α-MnO_2 with a tetragonal crystal system.

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