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THE EFFECT OF VARIATIONS IN ELECTROLYTE TEMPERATURE AND CURRENT ON THE SYNTHESIS OF MANGANESE DIOXIDE FROM MANGANESE SULFATE PRECURSORS BY ELECTROLYSIS METHOD

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Abstrak

Perkembangan ilmu dan teknologi dewasa ini dalam bidang elektronik, khususnya penyimpanan energi meningkatkan permintaan dalam penggunaan baterai sekunder litium. Pengembangan baterai litium difokuskan pada kapasitas penyimpanan energi dengan menggunakan mangan dioksida (MnO_2) sebagai bahan katoda baterai litium. Mangan dioksida dipilih sebagai bahan katoda baterai litium karena memiliki kapasitas penyimpanan yang tinggi yaitu sekitar 615 mAh/g dibandingkan dengan material lain seperti grafit yang memiliki kapasitas penyimpanan 372 mAh/g. Sintesis MnO_2 dilakukan dengan metode elektrolisis dari prekursor mangan sulfat ($MnSO_4$) yang diperoleh dari proses pelindian bijih mangan Kabupaten Trenggalek. Proses elektrolisis dilakukan selama 5 jam dengan menggunakan variasi temperatur elektrolit 30, 40, 50 dan 60ºC serta variasi arus 2, 3, 4 dan 5 A untuk mengetahui pengaruh temperatur elektrolit dan arus terhadap perolehan massa, polimorfi struktur dan morfologi MnO_2 yang terbentuk. Perolehan massa tertinggi diperoleh pada penggunaan temperatur elektrolit 60 ºC dan arus 5 A yaitu sebesar 11,4 gram. Hasil karakterisasi MnO_2 dengan menggunakan XRF (*x-ray fluorescence*) *Thermo type* ARL 9900 menunjukkan kadar mangan dioksida sebesar 85,472% dan hasil analisa dengan menggunakan XRD (*x-ray diffraction*) Shimadzu *type* 7000 diperoleh polimorfi struktur senyawa MnO_2 yang terbentuk adalah polimorfi α-MnO_2. Citra SEM (*scanning electron microscope*) menunjukkan bahwa partikel MnO_2 memiliki bentuk bulat berduri dan cenderung beraglomerasi dengan nilai diameter partikel berkisar antara 50-70 nm.

Kata Kunci: Elektrolisis, MnO_2, $MnSO_4$, temperatur elektrolit, arus

Abstract

The advancement of science and technology in the field of electronics, particularly in the field of energy storage, is increasing the demand for the use of lithium secondary batteries. The use of manganese dioxide (MnO_2) as a lithium battery cathode material is focusing the development of lithium batteries on energy storage capacity. Manganese dioxide was chosen as the cathode material for lithium batteries because it has a high storage capacity of about 615 mAh/g compared to other materials such as graphite which has a storage capacity of 372 mAh/g. MnO_2 was synthesized by the electrolysis method from manganese sulfate ($MnSO_4$) precursor which was obtained from the Trenggalek manganese ore leaching process. The electrolysis process was carried out for 5 hours using variations in electrolyte temperature of 30, 40, 50, and 60 ºC as well as variations in a current of 2, 3, 4, and 5 A to determine the effect of electrolyte temperature and current on mass gain, structural polymorphy, and morphology of MnO_2 formed. The highest mass gain was obtained at the use of an electrolyte temperature of 60 ºC and a current of 5 A, which was 11.4 grams. The characterization of MnO_2 using XRF (x-ray fluorescence) Thermo type ARL 9900 revealed manganese dioxide levels of 85.472%, and the analysis using XRD (x-ray diffraction) Shimadzu type 7000 revealed that the polymorphy structure of the MnO_2 compound formed was α-MnO_2 polymorphy. The MnO_2 particles have a spiny round shape and tend to agglomerate, as shown by the SEM (scanning electron microscope) image, with particle diameter values ranging from 50 to 170 nm.

Keywords: *Electrolysis, MnO_2, $MnSO_4$, electrolyte temperature, current*

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1. INTRODUCTION

Batteries have been the most widely developed electrical energy storage technology as science and technology have progressed, particularly in the field of electronics in energy storage. Lithium battery is a secondary battery that is widely developed today. Lithium batteries have advantages including high storage capacity, no memory effect, and can be recharged [1]. The development of lithium batteries is focused on increasing battery storage capacity and battery charging speed. One of the materials that are widely used as a lithium battery cathode is manganese dioxide (MnO_2). Based on data from the Geological Agency, Ministry of Energy and Mineral Resources, it is stated that manganese resources in Indonesia are about 60,893,820 tons and total manganese reserves are 87,236,536 tons [2]. With the manganese potential in Indonesia, the processing and utilization of manganese ore can be distinguished based on the manganese content in the ore. Manganese ore processing based on grade can be divided into two, pyrometallurgical and hydrometallurgical. Manganese ore with levels above 45% or commonly referred to as metallurgical grade is processed pyrometallurgical into ferromanganese metal as a ferroalloy for the manufacture of iron and steel. Meanwhile, manganese ores with levels below 45% are hydrometallurgically treated and used for the production of non-metallurgical grades which are suitable for use in the dry battery industry as battery electrodes [3].

Manganese dioxide was chosen as the cathode material for lithium batteries because it has a high storage capacity of about 615 mAh/g [4]. Manganese dioxide is an oxide of manganese that can be crystalline or amorphous. The crystalline structure has a polymorphic crystal structure, such as β-MnO_2, α-MnO_2, γ-MnO_2 or δ-MnO_2. The polymorphic structure of MnO_2 can possess a widely varying structural composition, and hence electrochemical activity [5]. Each of these crystalline structures has a tunnel structure with different sizes. β-MnO_2 (pyrolusite), α-MnO_2 (ramsdellite), γ-MnO_2 (nsutite) and δ-MnO_2 (vernadite) have tunnel structures (1x1), (2x2), (1x1)(1x2), and (1x∞) successively [6]. Among the various polymorphies of MnO_2, such as β-MnO_2, α-MnO_2, δ- MnO_2, and γ-MnO_2, the polymorphic structure α-MnO_2 is much more active both chemically and electrochemically [7]. The polymorphic structure α-MnO_2 is the most suitable for battery applications and can be made chemically and electrochemically [8].

2. MATERIALS AND METHODS

2 liters of $MnSO_4$ were filtered for impurities before being poured into a 2000 ml beaker. 5 ml of $MnSO_4$ solution was taken and diluted up to 100 times in a volumetric flask before being analyzed for elemental content using ICP-OES (inductively coupled plasma-optical emission spectrometry). The anode was then wrapped in a screen mesh cloth and two graphite electrodes (16 x 5 x 0.3 cm^3) were prepared. $MnSO_4$ solution was electrolyzed for 5 hours with electrolyte temperature variations of 30, 40, 50, and 60 °C and current variations of 2, 3, 4, and 5 A.

The MnO_2 obtained was then dried in an oven for 2 hours and at a temperature of 110 °C. Furthermore, the MnO_2 formed was weighed using a digital balance and analyzed using XRF (x-ray fluorescence) Thermo type ARL 9900 to determine the levels of compounds contained in the MnO_2 sample. XRD (x-ray diffraction) Shimadzu type 7000 analysis was also carried out to determine the polymorphy formed and SEM analysis to determine the polymorphy of MnO_2 formed.

Manganese ore is obtained from Trenggalek. At first, manganese ore was analyzed using XRF to determine the elements contained in the ore, and the results of XRF testing are shown in Table 1. Manganese ore was then leached using the sulfuric acid solution at a stirring speed of 400 rpm, the acid concentration of 12% H_2SO_4, temperature 75 °C for 180 minutes to produce $MnSO_4$ precursor solution which will be used as raw material for MnO_2 synthesis.

Table 1. XRF analysis of manganese ore from Trenggalek[9]

Oxide Compounds	Wt.%
MnO_2	46.03
SiO_2	48.73
Fe_2O_3	3.77
CaO	1.10
BaO	0.46
MgO	0.00
P_2O_5	0.56

3. RESULTS AND DISCUSSIONS

ICP-OES (inductively coupled plasma-optical emission spectrometry) was used to determine the manganese content of the $MnSO_4$ precursor solution during the initial characterization. Table 2 shows the results of the ICP-OES analysis of the $MnSO_4$ solution, which shows that the manganese content in the precursor is around 387.185 ppm.

Table 2. ICP-OES analysis for $MnSO_4$ solution

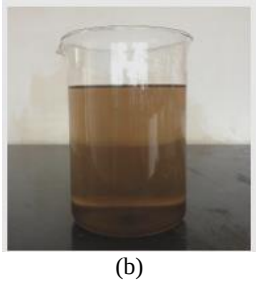
Element	ppm
Aluminum (Al)	0.505078
Gold (Au)	0.012406
Boron (B)	0.085176
Calcium (Ca)	4.18425
Iron (Fe)	0.194278
Potassium (K)	0.324122
Lithium (Li)	0.0204
Magnesium (Mg)	1.05311
Manganese (Mn)	387.185
Sodium (Na)	0.964326

3.1 Electrolysis Process

Electrolysis is a decomposition reaction in an electrolyte by an electric current. When an electric current is passed through an electrolyte solution in an electrolytic cell, a chemical reaction occurs. [10].

The color change that occurs in the $MnSO_4$ precursor during the electrolysis process is directly visible. The solution was pink before the electrolysis process was carried out, as shown in Fig.1(a), and after the electrolysis process was completed for 5 hours, the solution changed color to dark brown, as shown in Fig.1(b), where a very significant change in the color of the solution was obtained at an electrolyte temperature of 60 °C and a current of 5 A.

(a)



(b)

Figure 1. (a) Precursor solution before electrolysis process; (b) Precursor solution after electrolysis process

The $MnSO_4$ solution will decompose into Mn^{2+} and SO_4^{2-} ions during the electrolysis process. Mn^{2+} ions will flow to the anode, causing the reaction described in Eq. (1) to occur [11].

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

Eq. 2 depicts the reaction that occurs at the cathode.

$$2H^+ + 2e^- \rightleftharpoons H_2 \quad (2)$$

While Eq. 3 shows the total electrolysis reaction,

$$MnSO_4 + 2H_2O \rightleftharpoons MnO_2 + H_2SO_4 + H_2 \quad (3)$$

3.2 Electrolysis with Temperature Variation of the Electrolyte

The electrolysis procedure was carried out with electrolyte temperatures ranging from 30 to 40, 50, and 60 °C. According to the findings of the study, the lowest mass gain of MnO_2 was obtained at 30 °C, which was 2.98 grams, and the highest mass gain of MnO_2 was obtained at 60 °C, which was 11.4 grams.

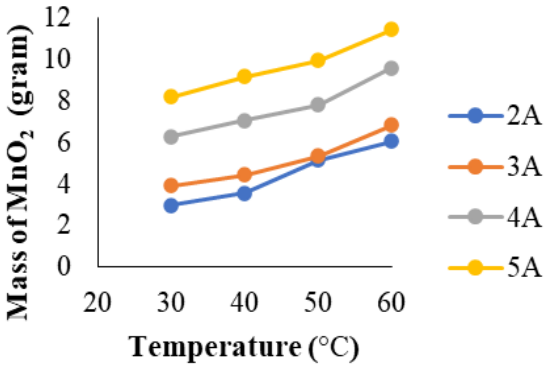


Figure 2. Effect of electrolyte temperature variations on mass gain of MnO_2

The greater the mass of MnO_2 obtained, the higher the temperature of the electrolyte used. Because the mass gain of MnO_2 obtained was greater and the electrolyte temperature tended to be more constant at 60 °C, the optimum condition of the electrolysis process was achieved.

3.3 Electrolysis with Current Variation

The current variations used were 2, 3, 4, and 5 A. According to the findings of the study, the lowest mass gain of MnO_2 was obtained at 2 A current, which was 2.98 grams, and the highest MnO_2 mass was obtained at 5 A current, which was 11.4 grams.

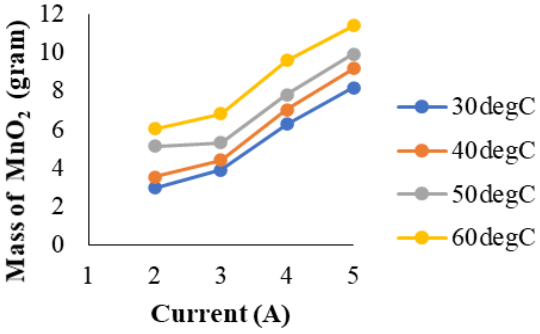


Figure 3. Effect of current variation on mass gain MnO_2

The reaction rate of the electrolysis process can be affected by current. The higher the current user, the more MnO_2 is formed.

3.4 MnO_2 XRF Analysis

The levels of MnO_2 formed after the electrolysis process were determined using XRF (x-ray fluorescence) analysis. Table 3 shows the XRF characterization results, which show MnO_2 levels of 85.472 wt.%.

Table 3. XRF analysis for MnO_2

Compound	Wt.%
K_2O	0.066
MoO_3	0.019
TiO_2	0.044
MnO_2	85.472
Fe_2O_3	2.128
SiO_2	8.377
V_2O_5	0.05
P_2O_5	0
CaO	0.084
Cr_2O_3	0.174
NiO	0
SO_3	3.574
Cl	0
Sc_2O_3	0.009

The increase in MnO_2 levels after the electrolysis process was initially 46.03 wt.% and increased to 85.472 wt.%. This indicates that the electrolysis process used can increase the levels of MnO_2 formed. The higher purity of MnO_2 obtained will improve MnO_2's electrical performance as a lithium battery cathode even more.

3.5 XRD Analysis on MnO_2

The polymorphy of the crystal structure formed in MnO_2 compounds was also determined using XRD (x-ray diffraction). XRD analysis was performed on three samples, the lowest current of 2 A at a temperature of 60 °C, the highest current of 5 A at a temperature of 30 °C, and the highest current of 5 A at a temperature of 60 °C. Using the OriginPro 2021 software, the polymorphs in MnO_2 compounds were identified by comparing the results of the sample x-ray diffraction test with data from the ICDD (international center for diffraction data) standard. Figure 4 shows comparative images of x-ray diffraction for each currency. The comparison image of the experimental MnO_2 sample's x-ray diffraction pattern has similarities with the X-ray diffraction pattern based on ICDD standard No. 00-044-0141, which is a diffraction pattern of α-MnO_2 polymorphy with a tetragonal crystal system. The XRD test was performed with an angle of 2θ between 15° and 90°. Typical peaks of α-MnO_2 were found at 2θ (°) = 26, 29, 37, 42, and 56 in sample 2A; 60 °C, and impurity peaks were found at 2θ (°) = 24, 27, 32, and 55. Typical peaks of α-MnO_2 were found at 2θ (°) = 18, 26, 29, 36, 37, 46, 47, 49, 52, 56, 57, 60, and 73 in sample 5 A; 30 °C, with impurity peaks found at 2θ (°) = 16, 25, 27, 28, 35, 43, and 55. Typical peaks of α-MnO_2 were found at 2θ (°) = 18, 26, 29, 37, 42, 50, and 57 in sample 5A; 60 °C, and impurity peaks were found at 2θ (°) = 27, 35, 38, and 55.

The sample contains approximately 82.7% α-MnO_2 compounds and 17.3% graphite, according to XRD analysis. The presence of other compounds in the MnO_2 sample caused the formation of this impurity peak, with graphite containing the most impurity.

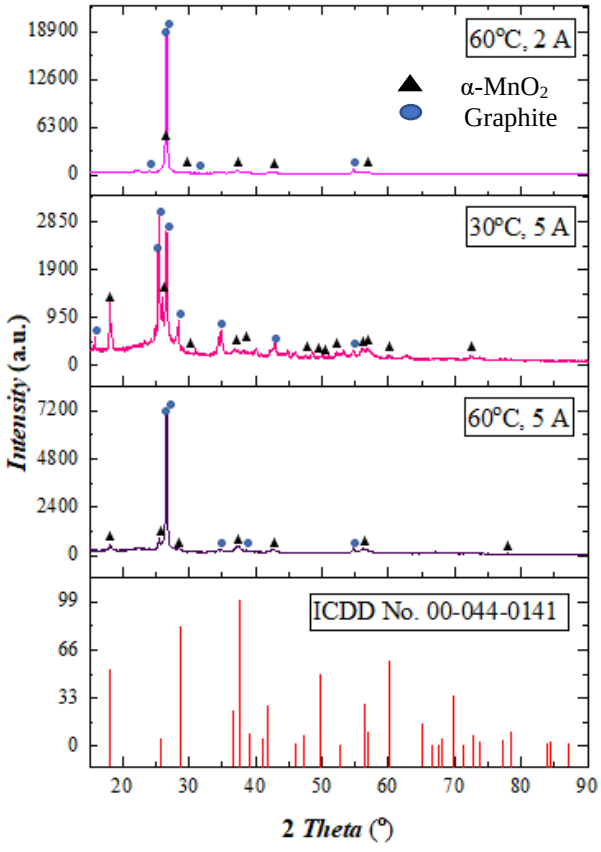


Figure 4. X-ray diffraction pattern for electrolyzed MnO_2 based on ICDD No. 00-044-0141

The brittle nature of the graphite electrode can cause graphite impurities because graphite is easily eroded and mixed with MnO_2. Based on the three XRD images obtained, it is possible to conclude that MnO_2 compounds with α-MnO_2 structural polymorphy are obtained at each temperature and current used. Polymorphy with a

α-MnO_2 structure is best suited for use as a battery cathode material [12]. Because it has a crystal structure large enough to accommodate and decompose oxygen molecules, the structure of α-MnO_2 has the best electrocatalytic ability [6].

3.6 SEM Analysis on MnO_2

SEM (scanning electron microscope) analysis was also performed to determine the morphology of the MnO_2 formed. At a temperature of 60 °C and a current of 5 A, SEM analysis was performed on the sample with the highest mass gain of MnO_2.

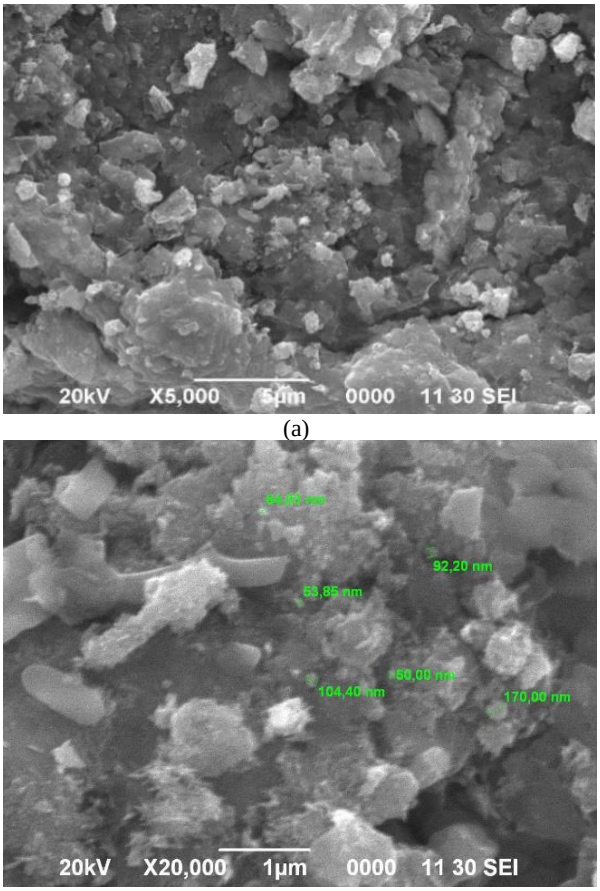


Figure 5. (a) Morphology of MnO_2 using SEM at 60 °C and 5A current, (b) Magnification of (a) which MnO_2 diameter particle size

Figure 5 shows that the particle diameters of the MnO_2 particles produced at a current of 5 A range from 50 to 170 nm at a magnification of 20,000x. The acquisition of a much smaller diameter of the MnO_2 particle increases the surface area of the particle, allowing the MnO_2 particle's electrical storage performance to improve.

4. CONCLUSIONS

The highest mass gain was obtained at the use of an electrolyte temperature of 60 °C and a current of 5 A, which was 11.4 grams. The higher temperature of the electrolyte, the mass gain of MnO_2 will increase, as well as the higher the current used, the mass gain of MnO_2 will be increase. The brittle nature of the graphite electrode can cause graphite to be easily eroded and mixed with MnO_2. The MnO_2 compound has a spiny round shape and tends to agglomerate with particle diameter values ranging from 50-170 nm.

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