Electrolysis Synthesis of MnO$_2$ in Acidic Environment and Its Electrochemical Performance for Supercapacitor

Mahmudi$^{1,2}$, W. Widiyastuti$^2$, Puspita Nurlilasari$^2$, Samsudin Affandi$^2$, Heru Setiawan$^2,*$

$^1$Department of Chemistry, Faculty of Mathematics and Natural Sciences, Universitas Negeri Malang, Jl. Semarang 5 Malang 65145, Indonesia.
$^2$Department of Chemical Engineering, Faculty of Engineering, Institut Teknologi Sepuluh Nopember, Jl. Arif Rahman Hakim Surabaya 60111, Indonesia

*Corresponding author’s email: sheru@chem-eng.its.ac.id

Abstract. Herein, the simple electrolysis synthesis route to produce α-MnO$_2$ is reported. The phase and crystal structure were evaluated by means of X-ray diffraction data collection and analysis. The morphological microstructure of as-prepared samples were captured by scanning electron microscope. The diameter distribution was studied by particle size analyzer. The electrochemical performance was systematically investigated by means of cyclic voltametry test. The produced MnO$_2$ was also prepared to form composite with carbon. The results revealed that the MnO$_2$/C composites perform outstanding characteristics mainly in terms of their maximum specific capacitance of 922.67 mF/g, with maximum power density of 90.150 W/kg, and maximum energy density of 0.063 Wh/kg. Therefore, the MnO$_2$/C composite meets the criteria of the prospective applicability for supercapacitor.

Keywords: MnO$_2$, electrolysis, electrochemistry.

1. Introduction
Among the all diverse crystal morphologies of manganese dioxides (MnO$_2$), α-MnO$_2$ and β-MnO$_2$ have attracted a great deal of attention due to their (2×2) tunnel structure that provide the incorporation of lithium ions [1]. MnO$_2$ is considered as vital component for rechargeable lithium batteries and it is regarded as the most appealing cathodic material for the near future invention of lithium ion-based batteries. As the implication, various methods have been conducted to produce MnO$_2$, such as sonochemical [2], electrostatic self-assembly [3], electrodeposition [4,5], chemical bath deposition [6], hydrothermal [7–9], precipitation [10], microwave-assisted reflux [11], sol-gel, and conventional ceramic or solid state diffusion [12–14]. However, those methods are less effective in terms of cost and time consuming than electrolysis method that is introduced in this present study. Previous works that succeeded in producing MnO$_2$ by electrolysis approach have been reported by [15,16].

The synthesis of MnO$_2$ nanoparticles can be conducted by electrolyzing KMnO$_4$ solution. In this electrolysis process, the oxidation number of MnO$_4^-$ is +7, which is the highest oxidation number for atom. Hence, the Mn atom in MnO$_4^-$ ion cannot be further oxidized, the only possible change must be reduction. The corresponding chemical reactions for MnO$_4^-$ are
\[
\begin{align*}
\text{MnO}_4^- + 3e + 4 \text{H}^+ & \rightarrow \text{MnO}_2 + 2\text{H}_2\text{O} \quad E^0 = +1,67 \text{ Volt} \\
\text{MnO}_4^- + 2\text{H}_2\text{O} + 3e & \rightarrow \text{MnO}_2 + 4\text{OH}^- \quad E^0 = +0,588 \text{ Volt}
\end{align*}
\]

Synthesis of MnO\textsubscript{2} by electrolysis in KMnO\textsubscript{4} solution can be explained as follows: when two carbon-based electrodes are immersed in the mixture of KMnO\textsubscript{4} and H\textsubscript{2}SO\textsubscript{4} solution, and electrical current is given to the electrodes under a DC potential of \( E_{app} = 2 \text{ V}, \text{H}^+ \text{ and } K^+ \text{ ions will move to cathode as well as MnO}_4^- \text{ and SO}_4^{2-} \text{ will move to anode.} \)

The migration of ions occurs during the electrolysis process. An electrolysis will obtain MnO\textsubscript{2} \text{ if MnO}_4^- \text{ ions are controlled on the cathode surface. It is due to the oxidation number of Mn atom (+7) in MnO}_4^- \text{ ions transforms into Mn (+4) in MnO}_2, indicating a reduction process. It requires that the process should take place on the surface of cathode. If MnO}_4^- \text{ is on the anode surface, MnO}_2 \text{ will never be produced. Therefore, to synthesize MnO}_2 \text{ by electrolysis in KMnO}_4 \text{ solution, MnO}_4^- \text{ ions must be controlled on the cathode surface.} \)

There are three ways that KMnO\textsubscript{4} solution in sulfuric acid condition can produce MnO\textsubscript{2}. Firstly, the sulfuric acid solution is electrolyzed (\( E_{app} = 2 \text{ V}, \text{carbon-based electrodes} \) for few seconds and KMnO\textsubscript{4} solution is dropped wisely on the back part of cathode. If the it is done on the front part of cathode, MnO\textsubscript{2} cannot be formed. Secondly, KMnO\textsubscript{4} solution (in a 600 mL glass, completed with the electrodes) is stirred slowly and electrolyzed with \( E_{app} = 2 \text{ V} \) for also few seconds before sulfuric acid is added. Thirdly, electrolysis of KMnO\textsubscript{4} was done with nafion membrane between cathode and anode. The membrane is introduced to make MnO\textsubscript{4} \text{ control in cathode. Electrolytes in cathode region are KMnO}_4 \text{ and sulfuric acid solutions, meanwhile electrolyte in anode region is KMnO}_4 \text{ solution only.} \)

From the preliminary study [17], it is revealed that the synthesis of MnO\textsubscript{2} nanoparticles by electrolyzing KMnO\textsubscript{4} solution in acidic environment leaded to unpure MnO\textsubscript{2} product. To overcome that problem, it is then introduced a modification process during the electrolysis and the modification will be represented in the next section as well as its discussion.

2. Materials and Methods
The materials that were used in this research were KMnO\textsubscript{4} (99.5%, UNI-chem A.R.), H\textsubscript{2}SO\textsubscript{4} (97%, Merck A.R); aquadest; and electrodes (carbon). 5 gram KMnO\textsubscript{4} in 400 mL aquadest was stirred and carbon-based electrodes was immersed into it with DC applied potential of 2 Volt. Electrolysis for 30 mins was done to carbon-based electrodes (with dimension of 5 x 4 x 0.3 cm\textsuperscript{3}). The immersed electrode was 2 cm and the cathode-anode separation was also 2 cm. Depth of the immersed electrode was changed by introducing 100 mL H\textsubscript{2}SO\textsubscript{4} to KMnO\textsubscript{4} solution until the final depth was 2.5 cm. The produced precipitate was well washed and dried at 150 °C. X-ray diffraction (Philips: Expert Pro) measurement was conducted to reveal the phase and crystal structure of the sample. The transmission electron microscope (JEOL JEM TEM 1400) was performed to study the crystalline properties; particle size analyzer was used to characterize the particle size.

3. Results and Discussion
Figure 1 represents the XRD characteristics of the obtained MnO\textsubscript{2} with varying electrolysis potential. It is clearly revealed that the all XRD profiles are in a good agreement with \( \alpha \)-MnO\textsubscript{2} (JCPDS card no. 44-0140) showing the same diffraction peaks at around 12, 37, and 53. An additional peak is found at diffraction angle of 26° which belongs to carbon from the anode.
The particle size of MnO₂ after particle size analyzer (PSA) test is given in Figure 2 (a-b). It is found that the average particle diameter of the synthesized MnO₂ is 493.22 nm. The sample with 2.0 V applied electrolysis potential (voltage) shows uniform distribution of particle size being compared with other potentials; 1.0 V, 1.5 V, or 2.5 V. However, there are two peaks of the particle diameter for MnO₂ with 2 V potential (voltage).

**Figure 1.** XRD Profiles for MnO₂ Produced by Electrolysis in 0.01 M KmnO₄ with H₂SO₄ Addition.

**Figure 2.** (a) Distribution of MnO₂ Particle Diameter and (b) MnO₂ Particle Diameter with Varying Applied Electrolysis Potential (voltage)
The PSA data is supported by SEM photography, in which the electrolysis-synthesized MnO₂ has rod-like uniform morphology and uniform size as depicted in Figure 3.

![Figure 3. SEM Photography of the MnO₂ Produced by Electrolysis in 0.01 M KMnO₄ and Addition of 2 M H₂SO₄ with 2 V Applied Potential.](image)

The PSA data can be compared with the SEM, particularly for sample with 2 V potential. After the comparison, the congruity in terms of particles size characteristic is detected. The rod-like morphology of the MnO₂ imply two kinds of particles size, i.e. (1) the length of the rod and (2) the diameter of the rod. This is what causes the presence of two peaks when PSA test was conducted.

![Figure 4. XRD Patterns for MnO₂ Produced by Electrolysis with and without Nafion Membrane.](image)

Synthesis of MnO₂ from electrolysis in KMnO₄ solution without stirring the electrolyte was completed by placing nafion membrane between the two electrodes. The effect of the use of the nafion membrane can be observed from the XRD data of the produced samples as given in Figure 4.

The addition of the nafion membrane is to increase the productivity of the MnO₂ synthesis. Further analysis by PSA shows the different characteristics MnO₂ particles size due to the nafion membrane. As we can see in Figure 5, the size distribution of the MnO₂ with nafion membrane shows sharper peak than that of without nafion membrane. It indicates the addition of nafion membrane may give rise to particle size uniformity.
The average diameter size of MnO$_2$ with and without addition of nafion membrane are, respectively, (472.5 ± 130.3) and (362.2 ± 105.1) nm. This result also informs that the MnO$_2$ with addition of nafion membrane is bigger than that without nafion membrane and it is probably because of the agglomeration is easier to happen by the presence of the nafion membrane.

Furthermore, cyclic voltametry (CV) test was also employed. CV is regarded as an ideal method to investigate the electrochemical performance of material. The CV test was conducted to the MnO$_2$/C composites as various compositions using scan rate of 10 mV/s and potential range of 0 V to 0.7 V in 0.1 M Na$_2$SO$_3$ electrolyte. 1:2 ratio of MnO$_2$/C is found as the best composition in terms of the electrochemical performance because it has maximum electrical characteristic, see Figure 6.

![Figure 5. PSA Patterns for MnO$_2$ Produced by Electrolysis with and without Nafion Membrane.](image1)

![Figure 6. CV Curves for MnO$_2$/C Composites ratio of 1:1, 1:2, 1:3, and 1:4 at Scan Rate of 10 mV/s in 0.1 M Na$_2$SO$_3$ Electrolyte.](image2)
The specific capacitance of the measured sample was calculated by the following mathematical expression:

\[ C_{sp} = \frac{i}{sm} \]

Where \( i \) is the average cathodic current (mA), \( s \) is the scan rate (V/s), and \( m \) is the total mass of the electrodes (g). \( C_{sp} \) is in unit of mF/g.

The specific capacitances of the samples with MnO\(_2\)/C ratio of 1:1, 1:2, 1:3, and 1:4 are 673.80 mF/g, 922.67 mF/g, 564.78 mF/g, and 702.11 mF/g, respectively. Hence, the maximum specific capacitance is 922.67 mF/g. As a matter of fact, the commercial capacitor has an capacitance of 10 mF and when the same characterization is applied to that commercial capacitor, we would find value of its specific capacitance of 0.0017 mF/g. Therefore, the capacitor with MnO\(_2\)/C would have specific capacitance 500.000 times larger than that of the commercial capacitor. This provides an evidence that the capacitor with MnO\(_2\)/C electrodes are able to store much more electrical charges compared with the commercial capacitor.

Figure 7 shows the impedance plot of MnO\(_2\)/C by means of electrochemical impedance spectra (EIS) test. The test was done at AC amplitude of 10 mV and frequency range of 50 kHz – 10 mHz with 0.1 M Na\(_2\)SO\(_3\) electrolyte.

From Figure 7, the equivalent series resistance (ESR) for samples with MnO\(_2\)/C ratio of 1:1, 1:2, 1:3, and 1:4 are, respectively, 36.17, 45.92, 36.55, and 33.97 Ω. The maximum power density for the samples are 84.678, 65.059, 83.787, and 90.150 W/kg for 1:1, 1:2, 1:3, and 1:4 ratio of MnO\(_2\)/C composites respectively. Meanwhile, the maximum energy are 0.046, 0.063, 0.038, and 0.048 Wh/kg for the samples in the same order.

Based on the Ragone plot, it is found that the MnO\(_2\)/C composite, in particular, with 1:2 ratio is in the chatagory of supercapacitor. The Ragone plot is a graph that can be used to compare the performance of numerous energy storage materials in terms of energy density (Wh/kg) and power density logaritmically.
To end this discussion, the chemical reactions for the formation of MnO$_2$ from KMnO$_4$ in acidic environment are given as follows (Equation 1-2):

$$2\text{KMnO}_4(\text{aq}) + \text{H}_2\text{SO}_4(\text{aq}) \rightarrow 2\text{MnO}_2(\text{s}) + \text{K}_2\text{SO}_4(\text{aq}) + \text{H}_2\text{O}(\text{l})$$

or

$$\text{MnO}_4^- + 4\text{H}^+ + 3\text{e} \rightarrow \text{MnO}_2 + 2\text{H}_2\text{O}$$

The use of KMnO$_4$ solution with high concentration (0.1 M) to synthesize MnO$_2$ nanoparticles by electrolysis is discovered to be effective and efficient.

4. Conclusion

Rod-like α-MnO$_2$ with uniform diameter size was successfully prepared by means of simple electrolysis approach in acidic environment. The α-MnO$_2$ was then proposed as the electrode material in the form of MnO$_2$/C for supercapacitor application. Furthermore, the composite shows excellent electrochemical performance such as large maximum specific capacitance of 922.67 mF/g, with maximum power density of 90.150 W/kg, and maximum energy density of 0.063 Wh/kg.

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