MnO₂ Nanoparticles Prepared by Alternating Monopolar Arrangement Electrolysis and Their Electrochemical Performances

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Abstract. Manganese dioxide nanoparticles have been successfully synthesized by the electrolysis method using 4-pairs carbon electrode in the alternating monopolar arrangement. The advantage of the arrangement is a significant increase in the product yield compared to the single pair electrodes. KMnO₄ solution in pH 0.2 and 9 were used as precursor and electrolyzed for thirty minutes at a temperature of 60 °C. The generated particles resulted from electrolysis in pH 0.2 (MnO₂-A) and in pH 9 (MnO₂-B) were characterized using X-ray diffraction (XRD), scanning electron microscope (SEM), and nitrogen adsorption-desorption isotherms to examine their crystallinity, morphology, and the specific surface area. The α-MnO₂ was observed for MnO₂-A particles and amorphous for MnO₂-B particles. The particles size of MnO₂-A was larger than that of MnO₂-B with the specific surface areas of 396 and 98 m²/g, respectively. The higher surface area of MnO₂-A corresponding to the channel pore of short rod-like morphology. On the other hand, MnO₂-B contributed to the spherical particles. The measurements of cyclic voltammetry (CV) were also carried out to measure their specific capacitances and their performance for oxygen reduction reaction (ORR) electrocatalyst. MnO₂-A exhibited higher specific capacitance of 13.57 F/g compared to MnO₂-B that only had 3.62 F/g. In addition, MnO₂-A also gave better performance as ORR electrocatalyst measured in O₂-saturated 0.6 M KOH resulted in 2.69 transferred electron number per oxygen molecule.

Introduction

In recent years, manganese dioxides are still an interesting commodity for application in storage and conversion of energy. For application in energy storage, the device is often called electrochemical capacitors, supercapacitor, electrical double-layer capacitor, or pseudocapacitor. Manganese oxides become a worthy of important as active electrode material for electrochemical capacitor because of the high specific capacitance, the low cost of abundance raw material and environmentally friendly compared to other transition metal oxides (Wei et al., 2011; Zhang et al., 2009). As energy conversion, manganese dioxides have been widely known for the use of dry cell and battery industry since the 1970s (Takahashi, 1981). Nowadays, fuel cell and metal-air battery as electrochemical energy conversion, need an efficient catalyst for oxygen reduction reaction (ORR) electrocatalyst. MnO₂-A exhibited higher specific capacitance of 13.57 F/g compared to MnO₂-B that only had 3.62 F/g. In addition, MnO₂-A also gave better performance as ORR electrocatalyst measured in O₂-saturated 0.6 M KOH resulted in 2.69 transferred electron number per oxygen molecule.

Among the synthesis method that has been developed, the electrochemical method is one of the promising methods for producing functional nanoparticles. The synthesis of manganese oxide using a pair carbon electrode for KMnO₄ electrolysis has been successfully reported (Mahmudi et al., 2018). The particle morphology can be controlled by the acidity of the precursor solution resulting 2-electron reduction pathway. The electrolysis method using multi-electrode design was reported to generate silver
nanoparticles which the yield in unit time is significantly increased with maintaining the characteristics of the nanoparticles (Huang et al., 2015). Multiple electrodes with a monopolar arrangement was carried out to increase the production rate of magnetite particles (Manrique-Julio et al., 2016). However, the produced particles were larger than that of a pair electrodes system, reaching ~500 nm. The modification of multiple electrodes of monopolar arrangement is called an alternating monopolar (AM) arrangement. The AM arrangement brought about the significant increase in production rate up to 30 times higher compared to the production rate of one-pair of electrodes system. The AM arrangement has been applied in the production of Fe₃O₄ nanoparticles without the change in the product particle size and purity (Nurlilasari et al., 2019). The scale method for preparing magnetite nanoparticles through the electrochemical method has been discussed (Setyawan and Widiyastuti, 2019).

In the present study, the multiple electrodes with AM arrangement were applied for the electrolysis production of manganese oxide nanoparticles. The effect of acidity of the precursor solution was studied on the effect of the characteristics of generated particles. In addition, the electrochemical measurement was carried out to determine the specific capacitance as a supercapacitor candidate. Furthermore, the performance of the generated manganese oxide nanoparticles as electrocatalyst for oxygen reduction reaction (ORR) was evaluated.

**Experimental**

**Materials**
The potassium permanganate (KMnO₄, 97.5%, UNI-Chem Indonesia), the potassium hydroxide (KOH, 97.0%, UNI-Chem Indonesia), and the sulfuric acid (H₂SO₄, 98.0%, Merck) were used as received without purification.

**Synthesis of MnO₂**
Eight carbon electrodes were arranged according to the alternating monopolar arrangement, as shown in Figure 1. Each electrode (dimension 5 x 2.5 x 0.3 cm³) was connected to the positive and negative terminal of a DC power supply (GPD X303S, GW Instek). The distance between electrodes was the same as reported in our previous research (Nurlilasari et al., 2019). 400 mL of 0.079 M KMnO₄ solution of pH 0.2 and 9 were prepared for acid and base electrolysis condition. Electrolysis was conducted at a voltage of 3 V at a temperature of 60 °C under constant stirring for 30 minutes. In order to obtain MnO₂ particles, the suspension of electrolysis results was centrifuged, filtered, washed with the deionized water, and dried at 150 °C for four hours.

![Figure 1. Experimental set-up](image)

**Characterization**
X-ray diffraction (XRD, PANalytical X’Pert) was used to analyze the crystal structures of the generated MnO₂ particles using Cu Kα radiation at λ=1.54 Å. To examine the morphology of the generated particles, scanning electron microscope (SEM, Zeiss Evo MA 10) was used. The specific surface area was obtained from the Brunauer-Emmett-Teller (BET) method by measurement of nitrogen adsorption-desorption isotherms (Quantachrome instrument, NOVA1200e).

**Electrochemical measurements**
The specific capacitances of MnO$_2$ electrolyzed in base and acid condition were determined from cyclic voltammetry (CV) at potential applied ranging from -1 to 1 V with a sweep rate of 10 mV/s. The sample was compacted into 15 mm diameter of flakes and then layered into aluminum and filter paper, which soaked in 0.1 M Na$_2$S$_2$O$_3$ that used as an electrolyte. They were configured in symmetric layers of Aluminum-Sample-Electrolyte-Sample-Aluminum. The specific capacitance (C$_s$, F/g) was calculated using the following equation:

$$C_s = \frac{1}{m v (V_c - V_a)} \int_{V_a}^{V_c} I(V) \, dV$$

where $v$ is the potential scan rate (mV/s), $(V_c - V_a)$ is the applied potential range (V), $I$ is the current response per unit area (mA/cm$^2$), and $m$ is the sample mass (g).

In order to investigate the performance of MnO$_2$ as electrocatalyst, the electrochemical measurements were carried out in three-electrode system in which MnO$_2$ was used as working electrode material. MnO$_2$ was formed into a homogeneous solution by mixing with polyvinylidene difluoride (PVdF) and 1-methyl-2-pyrrolidone (NMP) with a mass ratio of 3:1:1 then printed on nickel foam. A platinum foil and Ag/AgCl electrode were used as a counter and reference electrodes, respectively. 0.6 M KOH solution was used as the electrolyte, which was saturated with oxygen gas and maintained under oxygen atmosphere during examining electrocatalyst performance. Manganese oxide loading as catalyst synthesized in acid and base conditions were the same. The CV for ORR measurement were recorded by applying a scan rate of 10 mVs$^{-1}$ from 1.0 to −1.0 V.

To ascertain the number of electrons that get involved in the oxygen reduction reaction, the Koutecky-Levich (K-L) equations was used:

$$\frac{1}{i} = \frac{1}{B \omega^{1/2}} + \frac{1}{i_K}$$

$$B = 0.201 n F C_{O_2} D_{O_2}^{2/3} \nu^{-1/6}$$

where $i$ is the measured current density, $\omega$ is the angular velocity of the disk (rpm), $i_K$ is the kinetic current density, $n$ is the transferred electron number per oxygen molecule, $F$ is Faraday constant, $C_{O_2}$ is the bulk concentration of O$_2$ molecules in the electrolyte solutions, $D_{O_2}$ is the diffusion coefficient, and $\nu$ is the kinematic viscosity of the electrolyte solutions.

### Results and Discussion

XRD patterns of MnO$_2$ electrolyzed in acid and base condition using 4-pairs alternating monopolar electrode arrangement is shown in Figure 2. The distinctive peaks of XRD pattern electrolyzed in acid condition agreed well with JCPDS 44-01410 corresponding to $\alpha$-MnO$_2$. The five highest peaks at 20 values of 18.108°, 28.842°, 37.523°, 49.865°, and 60.276° can be indexed to crystal planes of (200), (310), (211), (411), and (521), respectively. On the other hand, the electrolysis carried out in base condition resulted in the amorphous phase indicating by the broad XRD pattern. The similar patterns were also revealed by KMnO$_4$ electrolysis using a pair electrode that $\alpha$-MnO$_2$ and amorphous phases were produced in the condition of acid and base, respectively (Mahmudi et al., 2018).

![Figure 2. XRD pattern of MnO$_2$ particles electrolysis in a) base and b) acid condition](image-url)
SEM images of base and acid condition in electrolysis process using 4-pairs alternating monopolar electrode arrangement are shown in Figure 3. The size of particles generated in acid condition is larger than that in base condition. Although the particle size in acid condition is larger, their surface area is also larger measured by BET method. The surface area of particles electrolyzed in base and acid condition is 98 and 396 m²/g, respectively. The higher surface area of particles electrolyzed in acid condition corresponding to the channel pore of short rod-like morphology. On the other hand, base condition contributed in the spherical particles.

![SEM images of MnO₂ particles electrolysis in a) base and b) acid condition](image)

Figure 3. SEM images of MnO₂ particles electrolysis in a) base and b) acid condition

Cyclic voltammetry (CV) analysis was used to characterize the MnO₂ particles as electrochemical capacitor. Figure 4 shows the CV curves of MnO₂ electrolyzed in acid and base conditions at scan rate of 10 mV/s. Both graphs shows the rectangular characteristics curves indicating good electrochemical properties of the electrode materials without redox peaks. However, the CV curve area of MnO₂ synthesized in acid condition is larger than that of MnO₂ synthesized in base condition corresponding to the specific capacitance ($C_s$) of 13.57 and 3.62 F/g, respectively, calculating using equation 1. The results were correlated with the higher crystallinity for MnO₂ synthesized in acid condition that contributed in the higher specific capacitance.

![Cyclic voltammetry curves of MnO₂ electrolyzed particles in acid and base condition using 4-pair electrodes alternating monopolar arrangement](image)

Figure 4. Cyclic voltammetry curves of MnO₂ electrolyzed particles in acid and base condition using 4-pair electrodes alternating monopolar arrangement

Further investigation on MnO₂ particles for applied as electrocatalyst for oxygen reduction reaction, the particles was casted in nickel foam for the electrochemical measurement in alkaline solution by maintaining saturated oxygen flow. Figure 5 shows the CV curve of MnO₂ particles electrolyzed in acid and base condition using 4-pair electrode AM arrangement measured under O₂-saturated 0.6 M KOH solution at scan rate of 10 mVs⁻¹. It can be shown that the reduction reaction peak of the three curves are 0.315, 0.217, and 0.154 V vs Ag/AgCl (or 0.525, 0.427, and 0.364 V vs NHE), for samples of nickel
foam only (NF), MnO$_2$-B, and MnO$_2$-A, respectively. The oxygen can be reduced to hydroxyl ion according to the following reactions (Chakkaravarthy et al., 1981):

\[
\begin{align*}
\text{O}_2 + 2\text{H}_2\text{O} + 4e^- & \rightarrow 4\text{OH}^- & E^0 = 0.401 \ \text{V vs. NHE} \quad (4) \\
\text{O}_2 + \text{H}_2\text{O} + 2e^- & \rightarrow \text{HO}_2^- + \text{OH}^- & E^0 = -0.076 \ \text{V vs. NHE} \quad (5)
\end{align*}
\]

A mixed reaction is possible so that the potential of the cathode where the oxygen reduction reaction occurs in alkaline medium will be stable between 0.401 and –0.076 V and the potential of sample MnO$_2$-A lies between the two potential values. In addition, sample MnO$_2$-A exhibits the highest reduction reaction peak current density and then followed by MnO$_2$-B and nickel foam only. The nickel foam only has a lowest reduction reaction peak current that corresponds to the less electrochemical activity.

![Figure 5. Cyclic voltammetry curve of MnO$_2$ particles electrolyzed in acid (MnO$_2$-A) and in base (MnO$_2$-B) measured in an O$_2$-saturated 0.6 M KOH](image)

For further investigation on the kinetics of oxygen reduction reaction of MnO$_2$-A catalyst, the rotating disk linear sweep voltammetry (LSV) was employed. LSV method can examine accurately a kinetically controlled ORR by extinguishing the mass transfer controlled ORR. The measurement of LSV was conducted in 0.6 M KOH solution under saturated oxygen flow that recorded at 5 mV/s. The LSV curves of MnO$_2$-A catalyst is shown in Figure 6 which were recorded at five rotation speeds of rotating electrode. The diffusion-limiting current densities increased with the RDE rotation speed because of the faster oxygen flux to the electrode surface. The diffusion-limiting current density was observed at applied voltage of –0.7 V is 1.98 mA/cm$^2$ observed for 1600 rpm RDE rotation speed. The onset potential which is defined as the potential at which the catalyzed ORR current starts to appear is observed at –0.020 V. The obtained onset potential of MnO$_2$-A catalyst is almost the same value with the nanorod MnO$_2$ catalyst synthesized using a pair electrodes (Mahmudi et al., 2018).
Figure 6. LSV curve of sample MnO$_2$-A, electrocatalyst synthesized by electrolysis in acid condition using 4-pair electrodes alternating monopolar arrangement

Figure 7 shows the K-L plots of MnO$_2$-A catalyst by correlating $i^{-1}$ vs $\omega^{-1}$ at various applied voltages to obtain the number of electron involved in the ORR, $n$. The number of electron transferred for the ORR is used to evaluate the catalyst performance. It can be seen that the K-L plots at the various potentials shows relatively good linearity and parallel lines. From the graph, the average electron number involved in the ORR at five different potentials is 2.69 approaching to the mechanism of the 2-electron reduction reaction of the oxygen molecule. Therefore, the ORR follows a series pathway that is initiated by 2-electron reduction of oxygen to peroxide of Eq. 5 (Gorlin et al., 2012). The reduction reaction might be followed by one of the following reactions:

$$\text{OOH}^- + \text{H}_2\text{O} + 2e^- \rightarrow 3\text{OH}^- \quad (6a)$$

$$\text{OOH}^- \rightarrow \frac{1}{2}\text{O}_2 + \text{OH}^- \quad (6b)$$

Eq. 6a is a 2-electron reduction step of peroxide to water and Eq. 6b is the peroxide disproportionation reaction to produce oxygen in half the original amount through a chemical reaction. Therefore, the manganese oxide synthesized by electrolysis using 4-pairs carbon electrode in the alternating monopolar arrangement under acidic condition is suitable used for ORR catalyst that follows 2-electron reduction reaction mechanism.

Figure 7. Koutecky-Levich plots of oxygen reduction reaction of sample MnO$_2$-A, electrocatalyst synthesized by electrolysis in acid condition using 4-pair electrodes alternating monopolar arrangement
Conclusion
The electrolysis of KMnO₄ solution at two distinct pH using alternating monopolar arrangement of 4-pair carbon electrodes successfully produced manganese dioxide nanoparticles. The selected system increased the production rate of MnO₂ nanoparticles without the change in their characteristics. The \( \alpha \)-MnO₂ was observed for MnO₂ synthesized from precursor pH 0.2 and amorphous for MnO₂ synthesized from precursor pH 9. The specific surface area of \( \alpha \)-MnO₂ nanoparticles was also 4-fold larger than that of amorphous MnO₂. \( \alpha \)-MnO₂ nanoparticles produced from precursor pH 0.2 resulted in specific capacitance of 13.47 F/g and 2.69 transferred electron number per oxygen molecule as ORR electrocatalyst measured in O₂-saturated 0.6 M KOH.

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