Synthesis of Aluminium Nanoparticles Using Electrochemical Method

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Abstract. Aluminium nanoparticles (Al NPs) have been synthesized using electrochemical method. The synthesis was conducted by electrolysis of aluminium metal in a sodium citrate solution as an electrolyte solution. Formation of Al NPs was investigated on the variation of potential (5-50 V), concentration of electrolyte solution (0.02-0.42 M), and electrolysis time (15-75 minutes). The obtained product was characterized by X-ray Diffraction (XRD), Transmission Electron Microscopy (TEM), Energy Dispersive X-Ray (EDX), and UV-Vis Spectrophotometer. XRD pattern indicate that the obtained product was aluminium nanoparticles. The result show that the size of Al NPs were 56-63 nm with the Al compositions of 7.08%. The optimum condition was reached at 40 V with 0.18 M sodium citrate solution during 45 minutes electrolysis process. The plasmon band peak was found at 234 nm. In this condition Al NPs is more stable.

1. Introduction
Nano size and nano dimensional material has attracted many scientist in various fields. The structure of nanomaterials can significantly improve physical, chemical and biological properties [1]. It is due to the main characteristics of nanoparticles, e.g. the small size, surface, quantum size and quanta tunnel effect [2]. Metallic nanoparticles also have potential application in sensing [3,4], photonics catalysis and device fabrication. Aluminium (Al) is one of the metals that can be used as a based material for nanoparticles synthesis. Al has an unusual properties, e.g. light weight, high strength, corrosion resistance and high electrical and thermal conductivity [5]. Al nanoparticles (Al NPs) are considered as an innovative material, which can be used in the application of advanced energetic materials. In addition, Al NPs can be used in optoelectronic applications [6]. Al NPs can be synthesized using solid-phase techniques, liquid-phase techniques and gas-phase processes [2,7]. Electrochemical method included in liquid-phase technique has more advantageous in simplicity, not time consuming, relatively low temperature and cheaper [8,9]. This method has been used to synthesize gold [9], nickel hydroxide [10,11], aluminium oxide [12], silver [13] and tin dioxide nanoparticles [14]. In previous work, the aluminium oxide nanoparticles has been fabricated by Kolo via electrolysis using NaCl as an electrolyte solution. Unfortunately, the nanoparticles obtained has a relatively large size, which were around 96-211 nm [12]. In this study Al NPs were synthesized by electrolysis using sodium citrate as
an electrolyte solution. It is because sodium citrate can be used as a reducing agent and stabilizer to prevent aggregate formation [13]. The effect of potential, electrolyte concentration and electrolysis time were also investigated. The obtained products were characterized using X-ray Diffraction (XRD), Transmission Electron Microscopy (TEM), Energy Dispersive X-ray Analysis (EDX) and UV-Vis Spectrophotometer.

2. Experimental

2.1. Materials
Aluminium (Al) metal sheet (95.96%) with 1 mm thickness was bought from PT. Panca Logam, Indonesia. The metal sheet then cut into a dimension of 90 × 4 mm. The surface were abraded using emery paper. Furthermore, the metal was cleaned using deionized water and acetone consecutively. The metal is wrapped with heat shrink tube. Sodium citrate was purchased from MERCK which is used directly without any purification. The deionized water was obtained from PT. Brataco Chemicals, Indonesia.

2.2. Methods
Al NPs was synthesized by electolysis method as from our previous study [12,14]. Al metals were prepared as described in section 2.1 that used as both cathode and anode. Sodium citrate solution was used as an electrolyte. The electrolysis cell used can be found at previous work [12,14]. The effect of potential, electrolyte concentration and electrolysis time on Al NPs formation was investigated. Potential effect was performed at 5-50 V with an electrolyte concentration of 0.02 M for 15 minutes. Electrolyte concentration effect was carried out at variation of 0.02-0.042 M with potential of 40 V for 15 minutes. The effect of electrolysis time was studied under 15-75 minutes in electrolyte concentration of 0.18 M at 40 V. All measurement was conducted at 95°C accompanied by 50 rpm stirring process. The Al NPs crystalline structure was observed using Philips X’Pert MPD (Multi-Purpose Diffractometer) XRD with Cu Kα1 (λ = 1.540598 nm) and Kα2 (λ = 1.544426 nm). The morphology and size of Al NPs was monitored by HITACHI H–9500 TEM. The element composition was measured by AMETEK EDAX EDX. The plasmon band peak was observed using GENESYS 10S UV-Vis Spectrophotometer.

3. Result and discussion

3.1. XRD analysis
Diffraction pattern of the Al NPs can be seen in figure 1. The diffractogram showed that several peaks were similar with Al₂O₃ standart according to JCPDS 046-1212 for α-Al₂O₃, JCPDS 023-1009 for θ-Al₂O₃ and JCPDS 046-1131 for δ-Al₂O₃. It can be seen that the typical peak for α-Al₂O₃ was appeared on the data, while the typical peaks for θ-Al₂O₃ and δ-Al₂O₃ were not found. This indicates that the α-Al₂O₃ phase is more dominant in the product than the other two phase. The high peaks on diffractogram may resulted from the phase accumulation with sodium citrate as an impurities (JCPDS 043-1526 for C₆H₇NaO₇).
3.2. **TEM-EDX analysis**

The result of TEM analysis is shown in figure 2. The size of Al NPs were around of 56.85-63.65 nm with slightly rounded and almost similar shape. The EDX analysis results identify the presence of aluminium (Al) signal from Al NPs, where the Al element is shown in the third peak at 1.47 KeV with composition of 7.08% (figure 3). The first peak at 0.52 KeV signifies the presence of oxygen (O) that involved in the product with composition of 82.65%. The second peak at 1.04 KeV signifies the presence of sodium (Na) from the electrolyte solution with composition of 10.27%.

![Figure 1. Diffractogram of Al NPs](image)

![Figure 2. TEM image of Al NPs](image)

![Figure 3. EDX analysis of Al NPs](image)

3.3. **UV-Vis Analysis**

3.3.1. **The Effect of Potential.** The optimum condition in this variation was obtained in a potential of 40 V with a maximum absorbance value of 0.290 at 223 nm (figure 4). It can be seen that the potential
did not significantly affected on the shift of wavelength. The wavelength provides information about the particle size. It can be assumed that the size of the Al NPs obtained at this various potential were similar. The absorbance value give information about the number of particles produced [9,10,12–15]. The Al NPs spectrum has shown different absorbance values for each given potential, which mean the higher absorbance value produced more nanoparticles.

3.3.2. The Effect of Electrolyte Concentration. Best result in this variation was obtained in 0.18 M electrolyte concentration with maximum absorbance value of 0.414 at 233 nm (figure 5). This result shows that the addition of electrolyte concentration causing a wavelength shift. The higher concentration give the greater wavelength. So it can be assumed that the size of the particles increased in the addition of electrolyte concentration. The highest absorbance value indicate the largest number of nanoparticles obtained. Decreasing of absorbance values at subsequent concentrations can be caused by precipitation of big particles [15].

Figure 4. The effect of potential on Al NPs formation

Figure 5. The effect of electrolyte concentration on Al NPs formation
3.3.3. The Effect of Electrolysis Time. Electrolysis time slightly affected in wavelength shift. It can be found at figure 6. The optimum condition in this variation was obtained at 45 minutes with maximum absorbance value of 0.525 at 234 nm. However, the obtained absorbance values also getting higher. It is indicate that the number of the nanoparticles obtained were greater. The optimum condition were determined based on the stability of the product. The electrolysis process more than 45 minutes can caused precipitation and produced white precipitate. The result show that the product has big particle size and unstable. Increasing of absorbance values in the range of 60-75 minutes can be caused by a lot of particles formed, but the distribution of the particle sizes are heterogen. It can be assumed that the precipitation was caused by the bigger particles and the increasing of the absorbance values was caused by smaller particle sizes contribution.

![Figure 6. The effect of electrolysis time on Al NPs formation](image)

4. Conclusion
Al NPs can be prepared using electrochemical method in sodium citrate solution. The result show that the product was Al₂O₃ nanoparticles with sizes of 56-63 nm and Al composition of 7.08%. Electrolysis at 40 V in 0.18 M sodium citrate solution during 45 minutes synthesis process can produces a more stable product.

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