Synthesis and Size Control of Aluminum Nanoparticles using Solution Plasma Process

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Abstract. This research was conducted to investigate the various control techniques to vary the size of aluminum nanoparticles through solution plasma process, specifically the submerged glow-discharge plasma process. Aluminum nanoparticles have received many attention due to their unique combustion, resistance and superhydrophobic properties. A lab-scale based submerged glow-discharge setup has been constructed to produce the nanoparticles. Different concentration of potassium carbonate electrolyte (0.1M – 0.5M) and cathode submerged length (50 mm – 100mm) were used in this study. The results were viewed and analyzed using scanning electron microscopy. As the major results showed that the diameter size distribution ranges from 80nm to 2 µm. Higher concentrations have shown to produce smaller nanoparticles due to the overlapping of electron beams on the cathode surface. Also, shorter cathode submerged lengths have resulted in larger-sized nanoparticles.

1. Introduction
The field of nanotechnology deals with matters in the range of 10⁻⁹ m scale. Although small, this field is of high importance as many large applications that span through all discipline of knowledge depends on it. The main component that this field deals with are nanoparticles. Generally, nanoparticles exhibit unique physicochemical properties that are absent in their bulk (>500 nm) counterparts [1]. Due to their high surface area to volume ratio, it is able to enhance the overall outcomes of many applications. This is seen especially in the case of aluminum nanoparticles.

Aluminum nanoparticles especially its oxide counterpart, which is alumina, has high demands in the global market. Figure 1 shows these demands in different application fields in recent years.

![Figure 1. Market demand for aluminum nanoparticles [2].](image)
nanoparticles. The production rate is dependent on the parameters which are supplied, for example, the temperature or voltage supplied. Even with these existing methods, studies to control the size of aluminum nanoparticles is still on the verge of development. Current situation conveys that the aluminum nanoparticles which are used in the different field of applications are not size specific. Hence, the main purpose of this report is to further develop the current state of size control for the synthesis of aluminum nanoparticles.

Among all of the available methods, the submerged glow-discharge plasma via solution plasma method was the chosen method to be used in this research study. There are many advantages of using this method in the synthesis of aluminum nanoparticles, such as requiring a shorter processing time, lower energy and cost to run the experiments [3]. Other than that, it has a simple experimental setup and it does not emit any harmful gases nor require any chemical addition. It can also be conducted under atmospheric pressure in an open system [3]. Size control can be managed easily by controlling the experimental parameters.

The rationale of this research is to develop a viable size control technique for the synthesis of aluminum nanoparticle. Being able to do so would enhance many applicable outcomes of these nanoparticles. This paper discussion the generation mechanism of glow discharge plasma for the synthesis of aluminum nanoparticles. The parameters which were manipulated were the concentration and cathode submerged length.

2.0 Literature Review

2.1 Stages of Submerged Glow Discharge Plasma

The process of a complete submerged glow-discharge plasma can be summarized in four main stages. The first stage is the electrolysis stage. This is the stage where Ohm’s Law is obeyed. When there is an increase in voltage, current rises as well. The current flow in the electrolytic cell in this stage slowly heats up the cathode. As the voltage is continually increased over time and the cathode’s temperature eventually reaches the electrolyte’s temperature, a thin film of water vapor starts to surround the cathode surface. This stage is known as the vaporization point [4].

The supply of more voltage passed the vaporization point causes the film of water vapor to cover more surface area on the cathode. When this film grows wider and thicker, some of the free radical flow in the electrolyte gets hindered. As an implication, the current of the cell drops. This stage is called the transition stage. As this progresses, the gas film eventually covers the entire cathode and the gases starts to continuously ionize with respect to increasing voltage. From here, due to continuous discharge, light emissions can be seen. This is the localized plasma stage [4]. These four stages can be seen in Figure 2. In this figure, Region 1 shows the electrolysis stage. Point 2 is the vaporization point. Region 3 is the transition stage. Region 4 and 5 are the localized plasma stage but in Region 4 indicates where the initiation of the plasma will start and Region 5 indicates where the glow-discharge plasma covers the entire cathode [5].

The formation of nanoparticles through SGDP method occurs during the localized plasma stage. When it is viewed microscopically, current concentration spots forms randomly at the cathode’s surface. At these spots, a rise in temperature induces more current to flow in those spots and this causes the temperature to rise even more. When this temperature exceeds the melting point of the material, the cathode starts to melt and hence, forming the nanoparticles. From here, the temperature at this emission point drops until an even temperature diction exist in the area due to heat diffusion. As a consequence, the current concentration spot disappears. While this is happening, new spots starts to form the previous emission point because it has a higher surface temperature than the surrounding. This even is illustrated in Figure 3[6].
2.2 Breakdown Voltage, $V_B$, Mid-point Voltage, $V_D$ & plasma intensity.

Based on Figure 2, the voltage which corresponds to Point 2 is known as the breakdown voltage, $V_B$. This voltage is where a gaseous film forms around the cathode. Also, the current at this point is at the maximum. Any increase in voltage would cause a steep drop in the current, indicating that the experiment has moved into the transition stage [7]. The voltage which corresponds to the point between Region 4 and 5 is called the discharge voltage or mid-point voltage, $V_D$. In most experiments, when the voltage surpasses $V_B$, the current starts to rise gradually and this is an indicator that full glow-discharge plasma is about to form. The region in between $V_B$ and $V_D$ is where the initiation of the glow-discharge plasma would happen.

Plasma intensity correlates to the excitation temperature, which is the temperature of the plasma at the cathode surface. There is a close relationship between $V_D$, plasma intensity and the size of the nanoparticles produced. If $V_D$ is low, the plasma intensity decreases and thus, the average nanoparticle size would be small [8].

2.3 Effects of Electrolyte Concentration & Cathode Submerged Length on the Nanoparticle Size

The electrolyte concentration is proportional to the size of the nanoparticles produced [9]. A higher concentration means that the electrolytes are able to dissociate into more free radicals per unit volume. As an implication, the I-V curve which corresponds to the concentration skews to the left. Due to a higher conductivity of the electrolytic cell, a small $V_D$ is adequate enough to initiate the glow-discharge plasma. Subsequently, since $V_D$ is small, the plasma intensity decreases and the resulting nanoparticle size form are small [3]. This is illustrated in Figure 4.

In terms of cathode submerged length, when the cathode is submerged deeper, the I-V curve which corresponds to the submerge length skews slightly to the right. With this, the amount of $V_D$ required to initiate the plasma is slightly more. The plasma intensity with regards to $V_D$ becomes a little bit higher as well [3]. However, this small change in $V_D$ may not be large enough to observe a significant change in the size of the nanoparticles. To obtain a size difference for the nanoparticles, the difference in each

![Figure 2](image.png)

**Figure 2.** Stages of SGDP Method with Respect to the Current-Voltage Graph [4].

![Figure 3](image.png)

**Figure 3.** The formation of nanoparticles [6].
cathode submerged lengths in the experiments must be more than one centimeter. This is illustrated in Figure 5.

![Figure 4](image1.png)

**Figure 4.** I-V curve for varying electrolyte concentration [3].

![Figure 5](image2.png)

**Figure 5.** I-V curve for varying cathode submerged length [3].

### 2.4 Amount of Electric Power to Initiate & Sustain Glow-Discharge Plasma

There are two important terms which are involved in the initiation of the glow-discharge plasma and there are the electric power density for vapor formation, $W_V$ and the power density, $W_m$ required to sustain the plasma. To start the initiation process, $W_m$ has to be greater than $W_V$, otherwise higher electric power and current are required to start the formation of plasma. $W_V$ can be determined from the maximum current at the vaporization point on an I-V curve. $W_v$ decreases when the temperature of the electrolyte increases. This is due to a decrease in the electrolyte’s conductivity at higher temperatures [10]. $W_m$ is determined by calculating the product of the average current and voltage during electrolysis:

$$W_m(W/cm^2) = \frac{Average \ current (A) \times Voltage (V)}{Surface \ area (cm^2)} \quad (1)$$

### 2.5 Characteristics of Aluminum & Alumina Nanoparticles

Aluminum nanoparticles have a greyish-black appearance and are typically spherical in shape. The nanoparticles vary in different sizes. Commonly, these nanoparticles would range from 10 to 30 nm with a specific surface area of 30 to 70 m²/g. Those that range from 70 to 100 nm posses a specific area of 5 to 10 m²/g (Aluminum Nanoparticles 2018). Due to these large specific surface areas combined with its high reactivity, Aluminum have very combustibility. As a consequence, Aluminum nanoparticles are normally used as additives in propellants formulations to generate higher and faster energy release [12]. Aluminum and alumina nanoparticles are resistant against corrosion, scratch and wear. Also, these nanoparticles possess high thermal barrier and superhydrophobic properties. Due to these characteristics, they are highly used in the coating sector [2]. Besides that, their application in
composites have resulted in improvements in durability, fire retardancy, stiffness, thermal fatigue resistance, fracture toughness, creep resistance and were resistance [2].

3. Materials & Methodology

3.1 Precursor Preparation

Aluminum rods of 5 mm in diameter were cut into 8 cm long pieces using a hacksaw. The oxide layers were removed using a sandpaper and rinsed with water to remove any unwanted bits. Potassium carbonate electrolytes were diluted into 0.1 M, 0.2 M, 0.3 M, 0.4 M and 0.5 M concentration. This is done by adding 4.15 g, 8.29 g, 12.44 g, 16.58 g and 20.73 g of potassium carbonate power into a 400 mL beaker and subsequently filling them up with distilled water up to 300 mL. From here, the electrolytes were placed on a heater plate and stirred until all of the potassium carbonate powders have dissolved.

3.2 Experimental Setup

Figure 6 shows the schematic diagram of the experimental setup. Two different experiments are ran based on varying electrolyte concentration and cathode submerged length. For the varying concentration experiments, the cathode was submerged at a fixed length of 1 cm. On the other hand, for the varying cathode submerged length experiments, the electrolyte concentration was kept at 0.1 M. Table 1 shows the summary of the experimental setups.

![Schematic diagram for the experimental setup](image)

**Figure 6.** Schematic diagram for the experimental setup.

| Varying Parameter                      | Electrolyte concentration (M) | 0.1 | 0.2 | 0.3 | 0.4 | 0.5 |
|---------------------------------------|------------------------------|-----|-----|-----|-----|-----|
| Cathode Submerged Length (cm)         |                              | 0.50| 0.75| 1.00| -   |   - |

3.3 Experimental Procedure

After setting up the experiment as based on Figure 6 and Table 1, the DC power supply was switched on and the initial current reading was recorded. Then the voltage was increased by 5 V/30 seconds and
the current reading was recorded for at every increment. This was continually repeated until the glow-discharge plasma has been fully formed. When this happens, the voltage was reduced by 30 V to prevent the melting of the aluminum cathode and the experiment was left to run for 30 minutes to allow the synthesis of the nanoparticles. Distilled water was added regularly to maintain the volume of the electrolyte at 300 mL. When the experiment was completed, the beaker was stored in a box and left overnight to ensure that the nanoparticles were sedimented to the bottom of the beaker. Then, some of the excess electrolyte was removed from each beaker and the samples were transferred into large centrifuge tubes.

3.4 Centrifuging of the Samples
Using a dropper, the remaining electrolyte was removed in each sample until the respective volume is less than 100 ml. The samples were then mixed properly by swirling the dropper around. Subsequently, all of the mixture of each sample was transferred into 4 smaller centrifuge tubes where the volumes is filled up to 12ml. The caps of each tubes were closed, tighten and the samples were shaken. These tubes were then placed into the slots in the centrifuge machine. The speed of the machine was set to 6,000 rpm and the duration of the centrifuge at 15 mins. The centrifuge is then started. After the first cycle is done, a dropper is used to remove the remaining electrolyte in each tube. Next, the tubes were refilled with distilled water up to 12ml and the centrifuge is repeated. After this second cycle, the entire process is repeated for another time.

3.5 Results Reviewing
The size of the aluminum nanoparticles were analyzed through a scanning electron microscope and SEM images were obtained for each samples. Using ImageJ, the images were processed and the sizes of the nanoparticles were measured.

4. Results

4.1 I-V Curves of Submerged Glow-Discharge Plasma

Graph 1. I-V curve for various electrolyte concentration.
Graph 2. I-V curve for various cathode submerged length.

Figure 7. SEM micrograph of aluminum nanoparticles produced from varying submerged length of (a) 50mm, (b) 75mm, (c) 100mm and varying electrolyte concentration of (d) 0.1M, (e) 0.2M, (f) 0.3M, (g) 0.4M and (h) 0.5M.

Table 2. Experimental results for varying electrolyte concentrations.

| Electrolyte Concentration (M) | Glow Discharge Voltage ($V_D$) | Power to initiate glow discharge plasma (W) | Average Size of aluminum nanoparticles (nm) | Standard deviation of aluminum nanoparticles (nm) |
|-------------------------------|--------------------------------|--------------------------------------------|--------------------------------------|-----------------------------------------------|
| 0.1                           | 170                            | 229.50                                     | 140.00                                | 15.09                                         |
| 0.2                           | 165                            | 198.00                                     | 131.90                                | 9.93                                          |
| 0.3                           | 155                            | 229.40                                     | 119.00                                | 9.38                                          |
| 0.4                           | 145                            | 174.00                                     | 105.60                                | 14.62                                         |
| 0.5                           | -                              | -                                          | 167.60                                | 32.30                                         |
Table 3. Experimental results for varying cathode submerged lengths

| Cathode Submerged Length (mm) | Glow Discharge Voltage ($V_D$) | Power to initiate glow discharge plasma (W) | Average Size of aluminum nanoparticles (nm) | Standard deviation of aluminum nanoparticles (nm) |
|-------------------------------|-------------------------------|------------------------------------------|-------------------------------------------|-----------------------------------------------|
| 50                            | 170                           | 229.50                                   | 154.90                                    | 29.30                                         |
| 75                            | 170                           | 153.00                                   | 144.50                                    | 9.61                                          |
| 100                           | 170                           | 131.75                                   | 140.00                                    | 15.09                                         |

Graph 3. Relationship of electrolyte concentration and the average size of aluminum nanoparticles.

Graph 4. Relationship of cathode submerged length and the average size of aluminum nanoparticles.
Table 4. Relationship between $W_r$ and $W_m$ for varying electrolyte concentrations

| Electrolyte Concentration (M) | Total submerged surface area (cm$^2$) | Power density for vapor formation ($W_r$/cm$^2$) | Power density to sustain plasma ($W_m$/cm$^2$) |
|-------------------------------|--------------------------------------|------------------------------------------|------------------------------------------|
| 0.1                           | 2.36                                 | 97.36                                    | 99.02                                    |
| 0.2                           | 2.36                                 | 84.00                                    | 89.39                                    |
| 0.3                           | 2.36                                 | 97.32                                    | 107.59                                   |
| 0.4                           | 2.36                                 | 73.82                                    | 99.72                                    |
| 0.5                           | 2.36                                 | 12.73                                    | 11.83                                    |

Table 5. Relationship between $W_r$ and $W_m$ for varying cathode submerged length

| Cathode Submerged Length (mm) | Total submerged surface area (cm$^2$) | Power density for vapor formation ($W_r$/cm$^2$) | Power density to sustain plasma ($W_m$/cm$^2$) |
|-------------------------------|--------------------------------------|------------------------------------------|------------------------------------------|
| 50                            | 0.98                                 | 134.15                                   | 135.62                                   |
| 75                            | 1.62                                 | 94.41                                    | 98.17                                    |
| 100                           | 2.36                                 | 97.36                                    | 99.02                                    |

5. Discussion

5.1 Relationship between glow discharge plasma intensity on the nanoparticles size

The relationship between the glow discharge plasma intensity and the nanoparticle size is seen in this research. A low plasma intensity indicates that the glow discharge is able to be reached faster due to a high conductivity in the electrolytic cell. Subsequently, more current concentration spots are formed on the cathode surface [6]. These spots may overlap with one another to form smaller nanoparticles. At low plasma intensity, the number of spots is not sufficient enough to overlap with one another. As an implication, the size of the nanoparticles formed is larger.

5.2 Influence of electrolyte concentration on the nanoparticles size

Based on Table 2, the discharge voltage drops as the electrolyte concentration increases. This indicates that at a higher concentration, there are more free moving radicals in the electrolyte, thus making the electrolytic cell more conductive. As a result, glow-discharge plasma was seen at a low plasma intensity [3]. Subsequently, when the gaseous sheath forms around the cathode, it is exposed to a higher density of electron bombardments [6]. This implies that more electron beams are targeted towards the cathode. Hence, overlapping of the current concentration spots do occur in this research and the overall size of the aluminum nanoparticles formed are smaller in size with increasing electrolyte concentration [8]. This here is illustrated in Graph 3. In short, at higher electrolyte concentrations, the resulting aluminum nanoparticle size formed is smaller.

In the experiments conducted under varying concentration, it was noticed that the experiment based on 0.5M of potassium carbonate was the upper limit. At any upper limit, the initiation of the plasma is difficult to achieved. As discussed in the literature review, in order to initiate and sustain the plasma, $W_m$ has to be greater than $W_r$. However, the $W_r$ for the experiment conducted with 0.5M of potassium carbonate, was found to be larger than its corresponding $W_m$ as seen in Table 4. Although no plasma was initiated, some nanoparticles were still formed as a result. This indicates that the temperature on the cathode surface was higher than the aluminum cathode’s melting temperature especially when the voltage is increased over time. As a result, nanoparticles were formed in the electrolysis stage but the overall size are larger.
5.3 Influence of cathode submerged length on the nanoparticle size

According to Table 3, the discharge voltage remains the same for all three experiments. However, the resulting size becomes smaller as the cathode submerged length decreases as seen in Graph 4. At a shorter submerged length, the total submerged surface area exposed to the overlapping of electron beams decreases [3]. Hence, for the 50 mm cathode submerged length experiment, it is inferred that more large-sized nanoparticles were produced than smaller-sized ones. When averaging for the size was done for this sample, the resulting average size was larger than the other two samples. An upper limit was found at 125mm of cathode submerged length. This can be seen at 100mm as its W_m approaches closer to W, based on Table 5. Overall, a longer cathode submerged length results in smaller-sized aluminum nanoparticles.

6. Conclusion

This research aims to create a size control method for the aluminum nanoparticles by varying the electrolyte concentration and the cathode submerged length. Five different electrolyte concentrations were used and experimented to investigate its impact on the average size of the nanoparticles produced. Due to the presence of more electron beams on the cathode surface at higher concentrations, the plasma intensity decreases. Correspondingly, the electron beams tend to overlap more and thus resulting in smaller-sized nanoparticles. Three different cathode submerged lengths were used to study the impact on the nanoparticle size. A shorter submerged length has a smaller total submerged surface area. This reduces the chance of electron beams to overlap on the cathode surface. Hence, the average nanoparticle size formed is larger.

The size control of aluminum nanoparticle enables them to be used in various applications. These nanoparticles can be used as an additive to biodiesel blends for diesel engines as its required size ranges from 60nm to 160nm. The implementation of this nanoparticles reduces the brake specific fuel consumption by 6% as well as reducing NOx and COx emissions by 6% and 19% respectively. Other application includes being a catalyst for rocket fuels due to its unique combustion properties. Since there are many factors that controls the size of aluminum nanoparticles, the research topic can be extended further such as using different cathode shapes or varying the distance between the cathode and the anode. Besides that, the study on the effects of different materials’ melting temperature on the size should be investigated as well since it was noticed that aluminum nanoparticles were still formed even at the electrolysis stage. Therefore, the effects of various electrolyte concentration and cathode submerged lengths reported here can be applied in the field of nanotechnology and nanomaterials.

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