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## THE CONCENTRATION EFFECT OF $K_2SO_4$ ELECTROLYTE SOLUTION ON GLOW DISCHARGE PLASMA ELECTROLYSIS

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### Abstract

*Plasma electrolysis is currently an environmentally friendly technology that is used as an alternative to nitrogen fixation, clean water treatment, batik waste degradation and the synthesis of other compounds. The success indicator of plasma electrolysis technology is seen from the formation of glow discharge. One of the factors that influence the formation of plasma in this method is the electrolyte solution. The electrolyte solution used in this study is  $K_2SO_4$  because its conductivity causes electron jumps. This study aims to determine the effect of various concentrations of  $K_2SO_4$  electrolyte solution on glow discharge plasma at the anode. In the plasma electrolysis reactor with stainless steel cathode and tungsten anode and 0.01 M electrolyte solution; 0.02 M; and 0.03 M  $K_2SO_4$ . The formation of glow discharge plasma occurs at the anode. Changes in concentration affect the critical voltage ( $V_D$ ) where the higher the concentration (0.03 M), glow discharge occurs at a lower voltage (600 V). This is due to the presence of high dielectric strength in the solution causing lower discharge strength to occur in solutions with lower electrolyte concentrations.*

**Keywords:** anode, plasma electrolysis,  $K_2SO_4$  electrolyte, glow discharge

### 1. INTRODUCTION

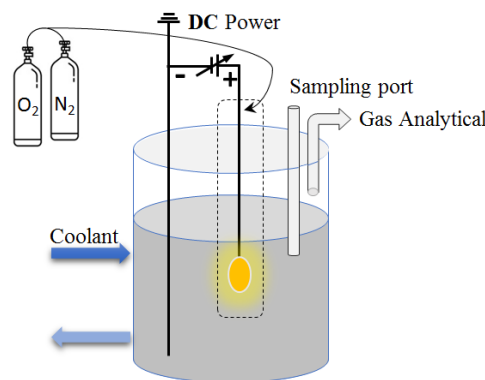
Technologies used for nitrogen fixation, waste degradation or other wastewater treatment produce emissions that cause environmental pollution. This encourages the use of environmentally friendly plasma electrolysis technology. Plasma electrolysis is a combination of electrolysis and plasma formation in the gas phase. This process is carried out at a high voltage which results in the excitation of electrons to form a plasma flame (Farisah et al., 2021). The process of plasma formation in an electrolyte solution produces a large number of reactive species. The reactive species formed break down water and nitrogen molecules and oxygen from the injected air (Sukreni et al., 2019). Direct current (DC) will flow between the electrodes (cathode and anode) and the surface of the electrolyte solution with a high voltage (Karamah et al., 2021). When direct current flows, three zones are identified, namely: (1) ohmic zone, in this zone an increasing current will increase the voltage. This is in accordance with Ohm's law in Faraday's electrolysis (conventional electrolysis), that the current is directly proportional to the voltage (Yang et al., 2017). Plasma formation begins with the presence of gas bubbles around the anode. The voltage formed is called the breakdown voltage ( $V_B$ ) (Farawan et al., 2021). (2) The transition zone, the current flowing decreases and is inversely proportional to the increase in voltage. This is due to the formation of a thin layer and gas envelope around the anode which causes current to oscillate until the gas envelope breaks. The critical voltage ( $V_D$ ) is reached at the transition zone (Salsabila et al., 2020). (3) glow discharge zone, there is a discharge of electrons and the current is directly proportional to the increase in voltage. Plasma stability begins to form and more heat is generated causing joule heating (Wahono et al., 2020). The sheath is re-formed due to evaporation of the electrolyte solution around the cathode (Karamah et al., 2021). Plasma flame is generated continuously between the electrolyte surface and the anode at high voltage, Faraday electrolysis changes to plasma electrolysis (Gupta, 2017). The factor that influences the formation of plasma in the glow discharge zone is the electrolyte solution. Electrolyte solutions that are often used are NaCl,  $Na_2SO_4$ ,  $KHPO_4$ , and  $K_2SO_4$ . The purpose of this study was to determine the effect of  $K_2SO_4$  electrolyte solution on plasma formation due to its higher conductivity (up to 3.4 mS) than other electrolytes (below 3 mS). Because the higher the conductivity, the stronger the electron jump

so that the plasma formed is brighter and more stable so that it can produce a more conducive process.

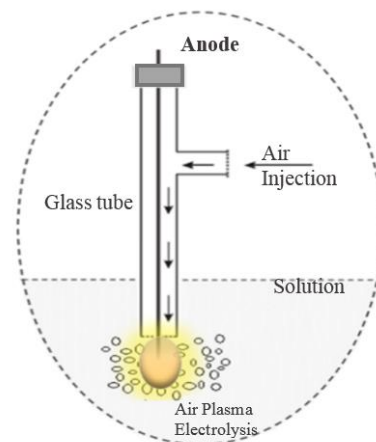
## 2. METHODS

### 2.1. Plasma electrolysis reactor design

In this study, a tubular batch reactor made of glass was used with a diameter of 14 cm. The cover is provided with tubes for electrodes (stainlesssteel cathode and tungsten anode), sampling port and temperature sensor as shown in Figure 1. SS-316 stainless steel cathode is a solid cylinder with a diameter of 6 mm. The anode is a tungsten Rhino-Ground EWTH with a size of 1.6 x 175 mm which is placed in a glass case and only 5 mm is in direct contact with the  $K_2SO_4$  electrolyte solution. The anode glass casing is given a special channel to inject air which is then flowed into the electrolyte solution as shown in Figure 2.



**Figure 1. Plasma Electrolysis Reactor**



**Figure 2. Illustration of air injection into tungsten (anode)**

DC electric current is sourced from PLN, flowing through a transformer connected to a bridge diode. For setting the voltage and current a power analyzer is used.

### 2.2. Plasma Glow Discharge Formation Test

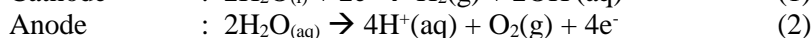
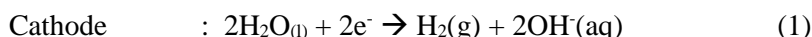
To determine the plasma formation zone, a current-voltage (I-V) characterization test was carried out. For every 20V increase in voltage, current and power are measured. When the breakdown voltage is reached, the current strength will decrease, and when it reaches the critical voltage, the current will increase again, and when passing the critical point, a plasma glow discharge zone is formed. The current-voltage curve is drawn so that it can be seen at the condition that the effective plasma voltage begins to form. This was carried out

at electrolyte concentrations of 0.01 M, 0.02 M and 0.03 M K<sub>2</sub>SO<sub>4</sub>. Other operating variables include the temperature being kept constant at 60°C and the initial pH 6.

### 3. RESULT AND DISCUSSION

In this study, the plasma electrolysis process using K<sub>2</sub>SO<sub>4</sub> as an electrolyte solution resulted in three zones. First, the ohmic zone (0<V<V<sub>B</sub>) where the plasma electrolysis process formed is still conventional. Direct current flows in contact with the anode which is injected with air and then produces a jump of electrons in the electrolyte solution so that gas bubbles are formed. In this condition oxidation reaction occurs at the anode and reduction at the cathode according to equations (1) and (2). Water molecules are broken down into reactive hydroxyl species (•OH) and hydrogen (•H) (Jiang et al., 2014). These reactive species •OH have a vital role in fertilizer synthesis or waste degradation. Hydroxyl radicals are oxidizing agents (with an oxidation potential of 2.8 mV) so they can play a role in oxidizing other compounds into more productive forms. The electrolyte solution will decompose into K<sup>+</sup>, SO<sub>4</sub><sup>2-</sup>, H<sup>+</sup>, O<sub>2</sub>, OH<sup>-</sup>, due to attack from H<sub>2</sub>O<sup>+</sup>(gas) from air injection and strong current flow from tungsten anode. The reactive species •OH, and •H diffuse across the electrolyte surface layer and react with each other or react with active substrates in solution (Liu et al., 2012). The electrochemical process of DC current results in the excitation of electrons to form a gas envelope which then creates a plasma in an electrolyte solution (Saito et al., 2015). Plasma is stable after reaching a critical voltage and under these conditions many reactive species are formed.

The concentration of K<sub>2</sub>SO<sub>4</sub> electrolyte solution has an important influence on plasma formation because the higher the concentration, the higher the conductivity. High electrical conductivity causes more stable plasma formation and increases the formation of reactive species, especially hydroxyl. Based on research on the Effect of electrolyte concentration on conductivity conducted by Gupta (2017), the more excellent the electrolyte concentration value, the higher the resulting conductivity. In this study, the electrolyte used was K<sub>2</sub>SO<sub>4</sub> because it has excellent conductivity for electrolysis processes and can produce highly reactive species. There are three zones formed in plasma electrolysis using K<sub>2</sub>SO<sub>4</sub> electrolyte, zoha ohmic, transition zone and glow discharge zone. In the ohmic zone (0<V<V<sub>B</sub>) occurs between the cathode and anode. Gas bubbles are formed which are then released in the electrolyte solution. At concentrations of 0.01 M, 0.02 M and 0.03 M K<sub>2</sub>SO<sub>4</sub> the voltage was significantly more than 200 volts. Current increases linearly with increasing voltage according to Ohm's law. The high current increase causes the rate of gas formation to be greater than the rate of release of gas bubbles from the electrode, and gas bubbles begin to form so that they cover part of the electrode surface (Gupta, 2015). In this study, because the cathode and anode are inert, the oxidation-reduction reaction that occurs is in accordance with equations (1) and (2).

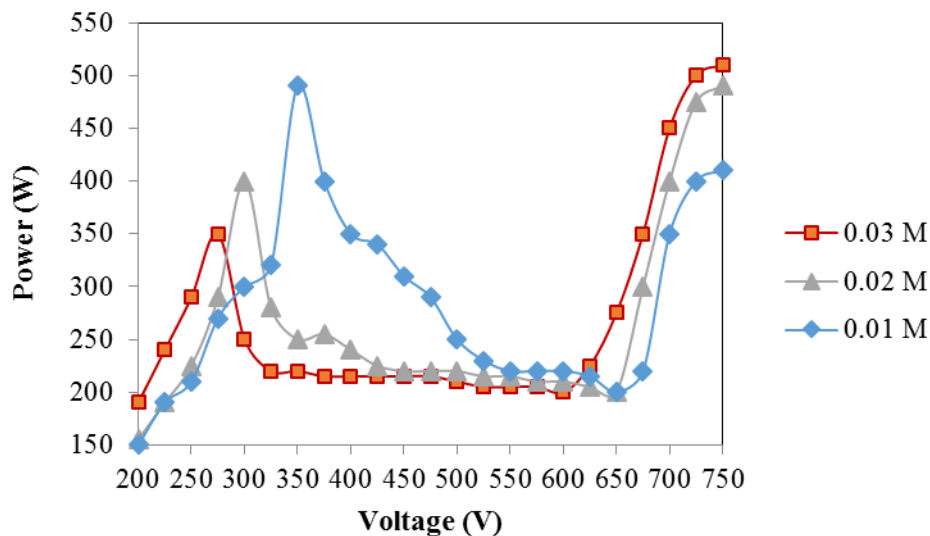


There is a reduction process in water (H<sub>2</sub>O) at the cathode. In this case, H<sub>2</sub>O has a more significant reduction potential than cations in the alkaline group (K<sup>+</sup>). Similarly, the process occurs at the anode where the water will be oxidized because the oxidation potential of the water is greater than the ions containing oxygen (SO<sub>4</sub><sup>2-</sup>) (Jin et al., 2010).

**Table 1. The Effect of electrolyte concentration K<sub>2</sub>SO<sub>4</sub> on the value of voltage and power**

Concentration (M)	Breakdown Voltage, V <sub>B</sub> (volt)	Breakdown Current, I <sub>B</sub> (ampere)	Energy, E <sub>B</sub> (watt)	Critical Voltage, V <sub>D</sub> (volt)	Critical Current, I <sub>D</sub> (ampere)	Critical Energy, E <sub>D</sub> (watt)
0.01	350	1.27	350	650	0.3	200
0.02	300	1.33	400	650	0.31	201.5
0.03	275	1.4	490	600	0.31	201.5

Table 1 shows that the electrolyte concentration of 0.03 M  $K_2SO_4$  reaches breakdown first, followed by 0.02 M and 0.01 M  $K_2SO_4$  electrolyte. The increase in voltage until it reaches breakdown ( $V_B$ ) varies in concentration at 490 volts, 400 volts and 350 volts, respectively. Volts with breakdown energy ( $E_B$ ) of 350 watts, 400 watts and 490 watts. In this study, an electrolyte solution with a concentration of 0.03 M  $K_2SO_4$  produces a breakdown voltage and the breakdown energy required to produce a gas envelope is lower than at concentrations of 0.01 M and 0.02 M  $K_2SO_4$ . This is because at high concentrations, the conduction current increases so that the ohmic heating increases resulting in a decreased voltage (Gupta ., 2015). In the electrolyte with a concentration of 0.01 M  $K_2SO_4$ , the resistance of the solution becomes higher, resulting in decreased conduction current and reduced ohmic heating so that the required voltage is higher (Ahmed et al., 2016).



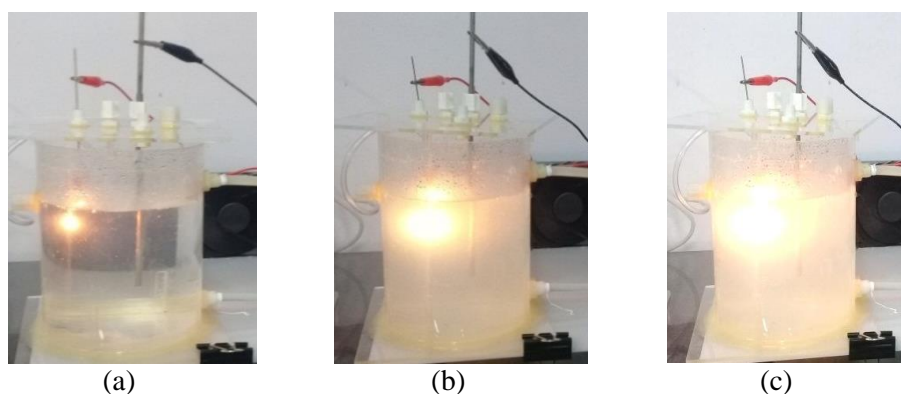
**Figure 3. Voltage-Power Characterization at Different Electrolyte Concentrations of  $K_2SO_4$**

Electrons move from the cathode to the anode, and the more conductive a solution, the mobility of electrons to the anode causes the electron population to increase. The small size of the anode contact area and the formation of gas bubbles cause the electrons to jump at low voltages. In Figure 3, the electrolyte solution concentration of 0.03 M  $K_2SO_4$  reaches its breakdown voltage first compared to the concentrations of 0.01 M and 0.02 M  $K_2SO_4$ . When the current reaches the breakdown voltage, the current decreases as the voltage continues to increase. This is because the gas formation around the anode causes current oscillations (Chen et al., 2012). In this phase, the process of forming and breaking the vapour envelope occurs, causing instability in the current. The formation of a vapour layer on the anode causes the anode and the solution to have no more extended contact so that the current cannot increase anymore and decreases while the voltage increases continuously (Seminar and Saksono., 2018).

Occasional splashes of plasma appear on some of the anode surfaces. The curve shows that there is a decrease in current to the critical voltage ( $V_D$ ) and this is called the transition zone, but then after passing through the critical voltage, the current increases again according to Ohm's law and plasma is formed so it is called the glow discharge zone. In the transition zone, the current is inversely proportional to the voltage due to the formation of a gas envelope around the anode which blocks the excitation of electrons. In the glow discharge zone, electrons are excited, resulting in ionization and a stable plasma begins to form. (Bruggeman et al., 2016). The lowest current is obtained at a concentration of 0.01 M, with a critical voltage ( $V_D$ ) of 600 volts and a critical power value of 200 watts. In this zone, the production of reactive species has not been maximized because the plasma formed has yet to be stable. The concentration of the electrolyte solution affects the formation of plasma in the glow discharge zone. At 0.03 M  $K_2SO_4$  plasma is formed at a lower voltage than 0.01 M and 0.02 M  $K_2SO_4$ . However, the critical voltage has decreased so that the

critical energy has increased. This is due to the high dielectric strength in the electrolyte solution resulting in the strength of the electrons in the formation of plasma (Ahmed et al., 2016).

The critical voltage point ( $V_D$ ) is reached more quickly at low conductivity and voltage. The low voltage is enough to shift the electrons to the anode, but the electrons will be quickly excited if given a high voltage. At a high concentration of  $K_2SO_4$ , the high conductivity affects the excitation of electrons. The electrons will be more easily excited in the electrolyte solution and the current oscillation will decrease. This is what causes plasma formation to occur more quickly (Salsabila et al., 2020). In this zone, the plasma is more dominant because the electron population is inhibited at the anode in large numbers, so more of it is exciting. As a result, the current increases and the plasma expands. The current in the glow discharge plasma zone ( $V > V_D$ ) begins to increase with increasing voltage which is indicated by a bright, bright colour intact at the end of the contact of the tungsten anode with the solution. The increase in critical voltage ( $V_D$ ) is directly proportional to the increase in critical energy ( $E_D$ ). As the voltage increases, the plasma begins to form in the solution. The zone in this study starts after the critical voltage ( $V_D$ ). In this zone, reactive species formed and can be used in nitrogen fixation or the synthesis of other compounds (Yang et al., 2017).



**Figure 4. Plasma at various concentrations (a) 0.01 M  $K_2SO_4$ , (b) 0.02 M  $K_2SO_4$  and (c) 0.03 M  $K_2SO_4$**

However, even though the critical voltage decreases, plasma formation's critical energy ( $E_D$ ) will increase with increasing solution concentration. This is due to the presence of resistance at the anode. In Figure 4 it is shown that the higher the electrolyte concentration  $K_2SO_4$  plasma stability is also achieved. The energy for plasma discharge will also be greater. This can be seen from the plasma flame that is getting brighter. The concentration of the electrolyte solution used in this study was 0.01 M, 0.02 M, and 0.03 M  $K_2SO_4$  had a conductivity of 4.13 mS, 3.98 mS, and 3.79 mS, respectively. High conductivity affects the energy used to achieve plasma stability. High conductivity will increase the number of electrons that move to the anode area where the plasma is formed. The large number of electrons excited in the plasma zone is indicated by the brighter the plasma formed in the solution (Sakakura et al., 2020).

#### **4. CONCLUSION**

The concentration of the electrolyte influences the formation of glow discharge in electrolysis. A high concentration of  $K_2SO_4$  has implications for high conductivity so that in this condition, the electrons will be more easily excited at the anode in solution and make a stable plasma formed faster. Stable plasma glow discharge is reached after the critical point is exceeded at a concentration of 0.02 M  $K_2SO_4$  and a voltage of 650 Volts with a conductivity of 3.8 mS. The stability of the plasma produces reactive species that can be used for nitrogen fixation or other plasma electrolysis processes.

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