Preliminary Study on The Effect of Time on Hydrogen Production from Electrolysis of The Seawater

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Abstract. To know the effect of electrode type on the production of hydrogen gas through the electrolysis of sea water, this research was conducted. At a constant potential difference of 12 Volt, the electrolysis process is carried out by alternately using graphite and copper as electrodes. The electrolysis process time was varied from 10 to 55 minutes with increments every 5 minutes for each electrode. The results showed that the use of copper in the electrolysis of sea water produced a maximum of 82 ml of hydrogen gas better than 76 ml of graphite with a total processing time of 5 hours and 25 minutes. The results also show that the production of hydrogen gas in graphite has the largest hydrogen production rate in the first 10 minutes, but continues to decline, while the copper electrode has the largest hydrogen production rate at 220 minutes and decreases when the electrolysis process reaches 270 minutes when the electric current experiences drop. This can be understood due to the corrosion of the electrode by chlorine, which causes the electrode life to be limited. Meanwhile, the water displacement measurement method is used to determine the volume of hydrogen gas produced from the electrolysis of seawater in this study.

1. Introduction

Seawater as one of the renewable energy sources is abundantly available on our planet, approximately 97% of the total water on our planet. Therefore, seawater is very suitable as a substitute for the fossil energy used at this time [5]. One of the energies that can be produced from seawater is hydrogen gas. This gas can not only be used directly as clean fuel, but also hydrogen energy can be stored because it can be transported over long distances, does not cause pollution, is light, and is sustainable because it can be produced from widely available seawater. Several ways to extract energy from seawater are through the process of a thermal gradient, wind and wave generators, electrolysis, and photolysis. Electrolysis of seawater for the production of hydrogen gas is a promising technology and the simplest.

Departing from the potential of seawater as a renewable energy source that can be extracted to produce hydrogen gas through the electrolysis process, this preliminary research was designed to analyze the effect of the electrolysis process time and the type of electrode used on the production rate and volume of hydrogen gas produced through the electrolysis of seawater. It hopes that through this research it can be seen which types of electrodes are more effective and efficient to produce hydrogen gas at a certain time of the electrolysis of seawater. In other words, this research was designed to determine the best type of electrode and processing time to produce hydrogen gas through the electrolysis of seawater. Finally, this applied research can provide basic information about what, why, and how to produce environmentally friendly alternative energy to replace the use of fossil energy in answering the energy crisis problems that may be faced at the future.
1.1 Seawater

Water is the largest part of the earth and seawater alone accounts for 97% of all the water on earth, therefore the use of water is very important for mankind. Water itself is a very useful solvent for dissolving larger amounts of other substances, for example, seawater which can dissolve nearly 48,000 trillion tons of salt consisting of 38,000 trillion tons of sodium chloride, 3000 trillion tons of sulfates, 1600 trillion tons of magnesium, 480 trillion tons of potassium and 83 trillion tons of bromide. Sodium Chloride (NaCl) is a substance that is mostly contained in seawater. NaCl or table salt contains a large percentage of Chloride \[4\]. Because of the salt content (salinity), seawater has a salty taste. Salinity is the number that shows how many grams of salts dissolved in per kilogram (gr/kg) of seawater is namely.

Other physical property of seawater are temperature, seawater temperature is often referred to as SST (Sea Surface Temperature) or SPL (Sea Surface Temperature) with SI units of Celsius (0°C). When measuring temperature differences (deltas), it must be measured in Kelvin (K) units \[1\]. The factors that influence sea surface temperature are the location of the altitude from sea level (Altitude), the intensity of sunlight that is received, the season, weather, water depth, air circulation, and cloud cover. Then the physical characteristic of seawater which is no less important is the density. Density is one of the most important parameters in studying ocean dynamics. Density \((\rho)\) is defined as mass per unit volume \((g\ cm^{-3})\). The density of seawater depends on the temperature \((t)\) and salinity \((s)\) of the sample and also the seawater pressure \((p)\) as a result of the compressibility of the water \[1\].

Seawater has six elements and compounds that make up 99% of seawater, namely 55% chlorine \((Cl^-)\), 31% sodium \((Na^+)\), 8% sulfur \((SO_4^{2-})\), 4% magnesium \((Mg^{2+})\), 1% calcium \((Ca^{2+})\), and 1% potassium \((K^+)\). There are also atmospheric gases that can be found in seawater, namely: nitrogen, oxygen, carbon dioxide, argon, helium, and neon. Weathering of rocks on land, volcanic gases, and hydrothermal circulation on the seabed are the main sources of these seawater minerals. The chlorine is aggressive in forming compounds that can cause damage or corrosion to the metal (electrode) in the electrolytic process and further it will impact on the length of time of the electrode used \[2\].

1.2 Electrolysis

Electrolysis is a chemical change or decomposition reaction in an electrolyte by an electric current. Electrolytes dissolve in polar solvents (such as water) by dissociating into positive ions (cations) and negative ions (anions). Negative ions are called anions because during the electrolysis the solution is attracted to the positive charge on the anode; while positive ions are called the cathode because through the solution they move towards the negative charge (cathode). Water as a solvent is a polar. Polar molecules have a charge at the end of the molecule, which is a positive and negative charge. This charge can interact with charges on other polar molecules to dissolve them. Between these molecules, there is a transfer of hydrogen atoms to form hydronium ions.

The addition of electrolytes, such as acids, bases, or salts can increase the conductivity of the water so that the water electrolysis process is faster. In the electrolysis cell, there will be a change in electrical energy into chemical energy. The quantitative relationship between the amount of electric charge used and the amount of substance involved in the reaction was formulated by Faraday. This can occur because it involves a reduction-oxidation reaction which relies on the role of charged particles as conductors of electric charge. Water is a very weak electrolyte, which can ionize to form ions and OH. Therefore, it is possible to electrolyte them into gases and. Gas can be obtained at the cathode due to the ion reduction reaction; meanwhile, gas is obtained at the anode due to the OH\(^-\) oxidation reaction. (Isana, 2010). The electrochemical equation of electrolysis can be described as follows

\[
\begin{align*}
\text{At the cathode:} & \quad 4\text{H}^+(aq) + 4e^- & \rightarrow & \quad 2\text{H}_2(g) \\
\text{At the anode:} & \quad 2\text{H}_2\text{O}(l) & \rightarrow & \quad \text{O}_2(g) + 4\text{H}^+(aq) + 4e^- \\
\text{Complete reaction:} & \quad 2\text{H}_2\text{O}(l) & \rightarrow & \quad 2\text{H}_2(g) + \text{O}_2(g)
\end{align*}
\]

However, the electrolysis of most abundant sea water rather than the purified or fresh water is a more promising way to generate clean hydrogen energy. Hydrogen can be used as an alternative fuel because it can replace fossil energy and has a very minimal negative effect on the environment. One of the factors
that influence the electrolysis process of seawater is the type of electrode that has good corrosion resistance due to chlorine, which greatly affects the lifetime of the electrode in the electrolysis process of seawater. Corrosion is defined not only as the destructive oxidation of metal materials, but also the degradation of non-metallic materials and these materials lose their function due to chemical or electrochemical interactions with the environment (Song & Xie, 2018).

Corrosion itself is defined as a process of material degradation due to interaction with the surrounding environment. This interaction causes a corrosion reaction which is generally an electrochemical reaction. Four factors influence and play a role in electrochemical reactions that can lead to corrosion, including Anode, Cathode, Electrolyte solution, and conductors, in the electrolytic process, corrosion will cause the electrode to decrease in effectiveness so that the production rate and volume of hydrogen gas produced will be smaller [3].

1.3 Electrode

An electrode is a conductor through which an electric current passes from one medium to another, usually from a power source to a device or material. The electrodes themselves can take several different forms, including wire, plate, or stick, and are most often made of a metal, such as copper, silver, lead, or zinc, but can also be made of non-metallic electrical conducting materials, such as graphite. Electrodes are used in welding, electricity, batteries, medicine, and industry for processes involving electrolysis.

The process that occurs at the electrode is the occurrence of an oxidation-reduction balance that is formed between the metal and what is in the solution. An electrode consists of an anode and a cathode, The anode receives current or electrons from the electrolyte mixture, so it becomes oxidized, and then when the atom or molecule is close enough to the electrode surface, the mixture in which the electrode is placed donates electrons. This causes the atom to become a positive ion. And, the opposite occurs at the cathode where electrons will be removed from the electrode and the solution around it decreases.

There are various forms of electrodes, namely in the form of wire and plate that usually are made of metal and non-metal with an electrical conducting material such as copper and graphite, respectively. Copper and Graphite were chosen as electrodes in this research. Graphite is formed from carbon, whereas graphite is one of the softest materials and is usually used in pencils. Graphite is a native element mineral with a C (carbon) composition. This mineral has many unique characteristics. Graphite has a hexagonal crystal system appeared as a foliated mass or loose thin sheets, has an opaque structure, and is generally black in color. Graphite is a dimorphism of a diamond but has a very low hardness level (1-2). Graphite has a specific gravity of 2.23, good/clear cleavage, and when you feel it feels oily. This mineral is very resistant to heat and does not dissolve easily in water. Graphite is also the only non-metallic mineral capable of conducting electricity. Graphite is a good conductor of electricity which makes it useful in batteries and solar panels, graphite has mechanical properties such as metal, is light and cheap which makes it suitable as an electrode in the electrolysis process [11]

Whereas, copper is a metal element in the form of crystals with a reddish color. The chemical name Cupprum is denoted by Cu. Copper is a transition metal for group IB which has an atomic number of 29 and an atomic weight of 63.55 g / mol. Copper in nature is found mostly in compound form or as a solid compound in mineral form (Palar, 2004). Copper has physical properties such as: a reddish-yellow color; malleable so that it is easily formed into pipes, thin sheets, wire; a good conductor of heat and electricity for the flow of electrons; hard when it is not pure; and it has a melting point of 1,084.62 ° C, while a boiling point of 2,562 ° C. While, it chemical properties include: a relatively unreactive element so it is resistant to corrosion; in humid air, the surface of the copper is covered by a layer that is green in color which attracts the basic copper carbonate, Cu (OH) 2CO3; at about 300 ° C, copper can react with oxygen to form black CuO. Whereas at higher temperatures, around 1,000 ° C, red copper (I) oxide (Cu2O) will be formed; it is not attacked by water or water vapor and aqueous, non acids such as dilute HCl and dilute H2SO4 but concentrated and boiling HCl attacks the copper metal and liberates hydrogen gas; peer does not react with alkalis but dissolves in ammonia in the presence of air to form a blue solution of the Cu (NH3) 4+ complex; and a hot copper can react with sulfur and halogen vapors. Reacting with sulfur to form copper (I) sulfide and copper (II) sulfide and for reaction with halogens to form copper (I) chloride.
Copper is known as a good raw material for electrodes according to [10] this is because copper material has good heat resistance, very high electrical conductivity, and high tensile strength even though at high temperatures besides copper also has a relatively cheap price so that making them suitable as electrodes in the electrolysis process.

1.4 Hydrogen Gas
Hydrogen gas is an element that is so abundant that hydrogen alone makes up about three-quarters of the mass of the universe. Hydrogen is present in the water, which covers 70% of the earth's surface and in all organic matter. Hydrogen itself is very simple, consisting of only one proton and an electron. Hydrogen is very environmentally friendly because when "released" hydrogen gas will immediately diffuse into the air, and does not pollute soil or groundwater because hydrogen is colorless, smelly, and non-toxic and does not cause acid rain, hollow out ozone or produce harmful emissions while the weight of hydrogen itself is 14 times lighter than air.

Hydrogen is a good and efficient choice for fuel because it has the highest combustion energy per kilogram compared to other fuels, meaning it is more efficient for the same weight than the fuels used today. Hydrogen generally offers 2-3 times more energy than most common fuels. It combines easily with oxygen, releasing a large amount of energy in the form of heat. Currently, hydrogen can be produced by electrolysis using an electric current to reduce water to hydrogen and oxygen.

Hydrogen can be used as an alternative fuel because the hydrogen molecules that have been released from water can produce energy. This energy will be captured by the combustion engine or a device called the Fuel Cell. In Fuel Cell, hydrogen energy can be converted into electrical energy with a high level of efficiency. Fuel Cell is a promising technology to be used as a source of electricity for housing, and as a source of electricity to drive or run vehicles [12].

2. Method
The method used in this research is an experimental method with descriptive quantitative analysis. In this research, a study was conducted on the production of hydrogen gas through the electrolysis of seawater. After the electrolysis reactor has been designed and built, the seawater electrolysis process can further be carried out. The electrolysis process in seawater is carried out to analyze how the influence of time variations and types of electrodes in the production of hydrogen. The main tools and raw materials used are seawater which can also function as an electrolyte solution and a set of electrolysis equipment that has a test tube that acts as a storage of the produced hydrogen gas [13]

The volume of hydrogen produced by the electrolysis of seawater is measured by determining the amount of water present in the test tube before and after the electrolysis process occurs within a certain measurable time, namely the "water displacement" method which will also be used to calculate the rate of hydrogen gas production. An AC-DC adapter was connected using a crocodile cable to the positive pole (anode) and negative pole (cathode) and also connected to the ammeter to determine electric current that was used. A pair of electrodes made of copper and graphite was used interchange and inserted into the test tube placed up-side down in a large container box filled with 400 ml of seawater for hydrogen gas produced through the electrolysis process. The use of test tubes in the electrolysis process in this study is due to the small volume of hydrogen gas produced.

Data collection of the hydrogen volume that was done by measuring and recording the water level within the test tube before and after of the electrolysis process at a certain time. The measurement time of electrolysis process varied from 10 – 55 minutes with an increment of 5 minutes and a constant voltage of 12 volts. Therefore, the rate and volume of hydrogen gas produced by the electrolysis of seawater using a graphite and copper electrode will be compared to analyze which electrode is more effective and efficient in producing hydrogen gas within a certain measurement time of the seawater electrolysis process. The following diagram shows the setup of the electrolysis equipment (adapted from [16].
3. Results and Discussion.

The table and graph below shows the measurement results of the volume of hydrogen gas produced from the electrolysis of seawater.

Table 1. Total Time of Electrolysis Process against the Production of Hydrogen Gas using Graphite and Copper Electrodes

| No | Time of the Electrolysis Process (minute) | Graphite Electrode | Copper Electrode |
|----|------------------------------------------|--------------------|------------------|
|    | Current (A) | Volume | Rate of Production | Current (A) | Volume | Rate of Production |
| 1  | 10          | 0.41   | 6.0               | 0.60        | 0.25   | 1.5              |
| 2  | 15          | 0.35   | 6.5               | 0.43        | 0.35   | 2.5              |
| 3  | 20          | 0.33   | 7.0               | 0.35        | 0.38   | 3.0              |
| 4  | 25          | 0.31   | 7.5               | 0.30        | 0.40   | 4.5              |
| 5  | 30          | 0.29   | 7.5               | 0.25        | 0.42   | 6.0              |
| 6  | 35          | 0.29   | 8.5               | 0.24        | 0.48   | 8.0              |
| 7  | 40          | 0.23   | 8.5               | 0.21        | 0.48   | 11.0             |
| 8  | 45          | 0.20   | 9.0               | 0.20        | 0.50   | 14.5             |
| 9  | 50          | 0.17   | 9.0               | 0.18        | 0.49   | 17.0             |
| 10 | 55          | 0.17   | 9.5               | 0.17        | 0.44   | 16.5             |
|    | Total       | 325    | 79.0              | 84.5        |

The table above and following graphs and show the difference in the volume and rate of production of hydrogen gas produced through the electrolysis of seawater with a constant voltage of 12 volts, and with different times and types of electrodes as mentioned above. As shown in the table above that at first, of 35 minutes the volume of hydrogen produced by electrolysis process using graphite electrode was higher than using copper electrodes. When the time of the electrolysis process reached 40 minutes, the volume of hydrogen produced by electrolysis process of seawater with copper electrode starting to increase higher than graphite electrode. Accordingly, the production rate of hydrogen that was produced by electrolysis process using copper electrode was also increased during the time range of process. It was contrary different with the production rate of hydrogen using graphite that was decreased as shown in the table and graph.
Interestingly, at time process of 55 minutes (total of 325 minutes or 5 hours 25 minutes into using electrodes), the volume of hydrogen that was produced by using a copper electrode indicated decreasing; while for graphite electrode was increased. The longest time of the electrolysis process of seawater caused a trend in decreasing the electric current through the equipment. And further it will cause decreased in volume and rate production of hydrogen. The decreasing of electric current through the equipment of electrolysis process may be assumed because of corrosion process of electrodes, especially for copper electrode. It was different with graphite which showed that the current was decreased after the first 10 minutes. Accordingly, [9] indicated that the greater the electric current supplied, the faster the decomposition reaction so that there is also an increase in the production of hydrogen that occurs from the cathode poles. While, [7] described that decreasing in current occurs because the longer the electrode is used, it will experience oxidation due to corrosion of chlorine in seawater; so the effectiveness of electrodes will be decreased and this is what causes a decrease in current. It was supported by the results of research by [2] which explained that the result of the corrosion process on the voltaic cell electrodes will reduce the service life of the electrodes. This of course has an impact on the reduction of hydrogen gas produced in the electrolysis of seawater. However, after that total time process of 5 hours 25 minutes, the electrolysis process of using graphite and copper electrode produced 79 ml and 84.5 ml of hydrogen gas, respectively. It was in agreement with the research conducted by [17] where after a few hours of electrolysis there was a decrease in the production of hydrogen gas. The results obtained in this study indicate that copper electrodes are better than graphite electrode which was in accordance with the results of research conducted by [17] which concluded that copper electrodes are superior to graphite electrodes in terms of efficiency.

4. Conclusion
From the data analysis obtained in this study, it can be concluded that the total volume of hydrogen gas produced in the electrolysis process of seawater by using copper electrodes was much greater than the total volume of hydrogen gas produced by using graphite electrodes. However, the lifetime of copper electrodes was longer than graphite electrodes during the electrolysis process of seawater. The suggestions need to be considered and made for further research is to further wide the range time of process to clearly identify the service life of the electrodes. Another method such stoichiometry can be utilized to accurately determine the volume of hydrogen gas produced by the electrolysis of seawater.
sensor which is able to accurately measure the water displacement was also suggested to be used for next research of hydrogen production based on the electrolysis seawater.

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