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The Effect Of Clay Coating On Electrodes In Seawater Electrolysis Process To Produce Environmentally Friendly Hydrogen Energy

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Abstract

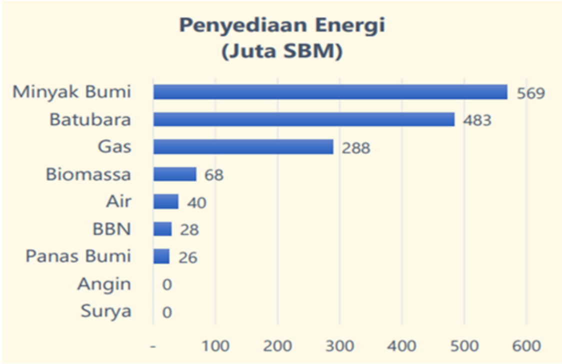
Hydrogen gas from seawater can be obtained through electrolysis process. However, until now, seawater electrolysis process has not been able to last long, because it contains chlorine that causes anodes to corrode. This study aims to analyze the effect of clay coating on electrodes to resist corrosion. The water displacement method is used to determine the volume produced during the electrolysis process, starting from 0 and progressed within 20 minutes of interval for each measurement until the hydrogen production reaches the saturation point. In addition to the volume, hydrogen rate and yield production tend to decrease after the electrolysis process lasts for a certain time. The results also show that the use of electrodes (copper) coated with clay has a longer resistance to corrosion due to chlorine contained in seawater, compared to electrodes (copper) not coated with clay. Electrodes (copper) that are not coated with clay have a shelf life of up to 9 hours and reach a maximum point of producing hydrogen at 280 minutes of 15 ml; While the electrode coated with clay turned out to have a durability of up to 12 hours and reached the maximum point in producing hydrogen at 560 minutes of 15.4 ml.

Keywords: Hydrogen, Electrolysis, Water displacement, Electrode, Clay

Introduction

Indonesia is a country that has large fossil energy reserves. The process to produce fossils energy could take millions of years. However, to extract this energy source, it only takes a short time. If the use of this energy is not limited, over time the availability of fossil energy sources will run out. In addition, the use of fossil energy also has a negative impact on the environment. Greenhouse gas pollution due to burning fossil fuels can cause a decline in people’s health. The figure below shows data from energy providers in Indonesia in 2018.

Figure 1. Energy supply data for 2018. Source BPP Tout look 2020 [1]



From the data above it can be concluded that the use of renewable energy must start now. Indonesia should focus more on the use of renewable energy, because it is very environmentally friendly and the cost is expected to be relatively cheaper than the energy derived from fossils. In fact, the use of renewable energy in Indonesia is still facing obstacles. Although the use of renewable energy can reduce the geographical gap between the location of energy sources and the location of energy needs, it still faces obstacles, one of which is the high cost of investment in new renewable energy-based energy technology . This obstacle is certainly a challenge for the government in formulating policies or regulations that can spur the use of renewable energy based technology, that in reality, Indonesia has got abundant source of energy, one of which is sea water. In fact, 97% of the total amount of water on planet earth is sea water; Meanwhile, Indonesia has an area of which 2/3 is the ocean. Therefore, sea water is very suitable as a substitute energy source from fossil energy which is also widely used today [2].

Seawater also qualifies as an electrolyte solution, because it can conduct electricity and also, it is observed that there are bubbles around the electrodes, which indicate the occurrence of hydrogen and oxygen gases. The ability of seawater to conduct electricity is due to the presence of soluble substances that break down into ions that can move freely [3]. Judging from its potential, seawater is certainly very possible to be used as a renewable energy source, for example by using it as a source for hydrogen production. One way to get hydrogen energy from seawater is through electrolysis , which is the process of breaking down the seawater molecules (H_2O) into hydrogen gas (H_2) and oxygen (O_2) using the help of electric current through the seawater. The results of El-bassuoni's research entitled "Hydrogen and Fresh Water Production From Sea Water" showed that hydrogen can be produced after desalination or directly by electrolysis using a special type of electrode. Moreover, it is encouraging that the relatively low initial cost estimate for this process will prompt further investigations into the utilization of different electrodes [4].

Meanwhile, Yun Kuang in his research entitled "Solar Driven Highly Suistained Splitting of Sea Water Into Hydrogen and Oxygen Fuels" said that developing electrodes that can maintain seawater separation without chloride corrosion, can overcome the problem of water scarcity in addition to producing hydrogen. His research used a multilayer anode consisting of a nickel-iron hydroxide (NiFe) electro-catalyst layer uniformly coated on the surface of a nickel sulfide (NiS_x) layer formed in the pores. Ni ($NiFe/NiS_x$-Ni) foam provides superior catalytic activity and corrosion resistance. Solar-driven alkaline seawater electrolysis operating at industrially required current densities (0.4 to 1 A/cm^2) can achieve over 1,000 hours duration. However, the results of the study reported by Yun Kuang said that there was a shortage in producing hydrogen by the seawater electrolysis method, namely chloride. Negatively charged chloride in salt seawater can damage the positive end of the electrode (anode) and cause a decrease in the anode lifetime due to corrosion. However, they had a solution that coating the anode with a negatively charged layer

,would repel chlorides and slow down metal corrosion. They carried out a nickel-iron hydroxide plating on top of the nickel sulfide, which covered the nickel foam core. Without the negatively charged layer, the anode only works for about 12 hours, but with this layer and the relatively small DC electric current from the solar panel, the electrode can last more than a thousand hours. However, the price of nickel iron hydroxide material to coat the electrodes is relatively expensive, thus allowing the high cost of producing hydrogen gas as a renewable energy source [5].

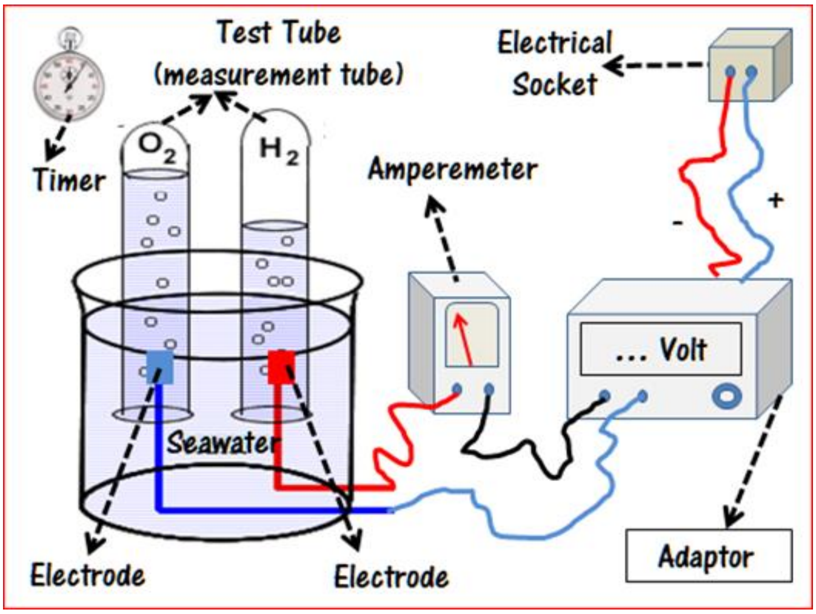
Referring to the results of these studies, this research is designed to produce hydrogen through seawater electrolysis. Meanwhile, to prevent corrosion of the electrodes caused by chlorine as explained by Yun Kuang , this research will utilize materials that are widely available, relatively inexpensive and easy to obtain, which is clay. This is supported by the results of Alshawabkeh research entitled "Basics and Application of Electrokinetic Remediation" which stated that clay generally consist of 3 different zones: clay particles with a negatively charged surface, flow pores with excess positive charge and free flow pores with zero charge network. The negative network charge on the clay particle surface requires an excess positive charge (cation exchangeable) which is distributed into the liquid zone adjacent to the clay soil surface to form a double layer diffusion [6].

Meanwhile, Utami with his research entitled "Study of Types of Clay Mineralogy and its Implications with Soil Movement" said that the surface of clay minerals usually contains electronegative charges that allow cation exchange reactions to occur, this is the result of one or more different reactions that occur. The negative charge on the surface of the clay particles along with a collection of counter ions that have a positive charge is called an electric double layer or diffuse double layer. Therefore, clay soils are worth trying in overcoming corrosion that occurs at the electrodes due to chlorine from sea salt. The purpose of this study is to analyze the effect of clay coating on the electrode lifetime from the seawater electrolysis process for hydrogen gas production. Hopefully, the results of this study can provide a solution to overcome the problem for corrosion on electrodes due to chlorine in the process of seawater electrolysis, in order to improve hydrogen production for the implementation of renewable energy that is environmentally friendly and inexpensive [7].

Materials and Methods

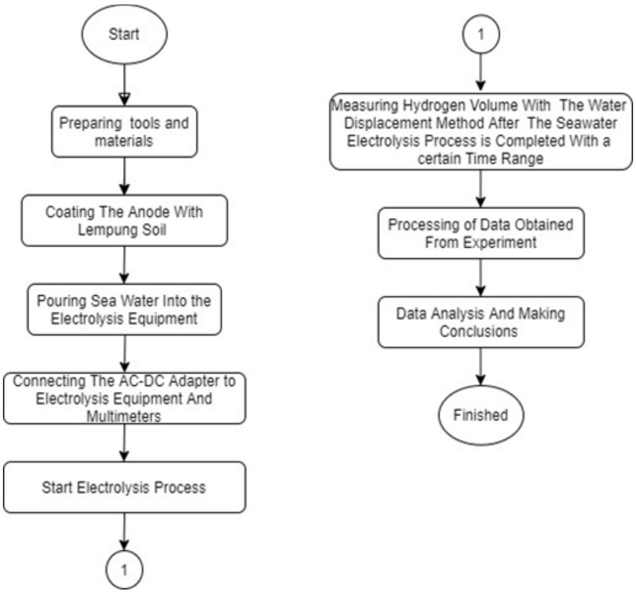
The research method used in this study is an experimental method with descriptive statistical analysis. In producing hydrogen from seawater, in this study using an electrolysis process. Seawater as an electrolyte solution is inserted into an electrolysis device which is composed of various tools, including: plastic box, AC-DC adapter, crocodile cable, 10 ml measuring cup, copper electrodes coated and not coated with clay and arranged as in Figure 3 [8].

Figure 2. Electrolysis Equipment Arrangement Schematic[8]



The research was carried out with the steps shown in the flow chart as follows.

Figure 3. Flow Chart



The water displacement method is used to determine the volume of hydrogen produced by measuring the sea level in the measuring cup before and after the electrolysis process for every 20 minutes. The production rate of hydrogen gas is calculated by dividing the volume of hydrogen produced by the measurement time required for the electrolysis process, as follows[9]:

$$\text{Hydrogen gas production rate} = \frac{\text{Volume of hydrogen gas produced}}{\text{Measurement time}} \quad (1)$$

Meanwhile, hydrogen yield is calculated by dividing the difference in the volume of hydrogen gas produced at the beginning and at the end of the electrolysis process by the total volume of hydrogen gas produced multiplied by 100%, as follows:

$$\frac{\text{Rated gas volume} - \text{Previous gas volume}}{\text{Total gas volume}} \times 100\% \qquad (2)$$

The volume, production rate and yield of hydrogen produced from the two electrolysis processes using coated and uncoated clay electrodes versus the measurement time of the electrolysis process are presented in Figures 4, 5 and 6. until the electrolysis process is turned off.

Result and Discussion

Figure 4 shows the affinity between the volume of hydrogen and each time of electrolysis process' measurement using both the clay-modified electrode and the unmodified electrode with the consecutive value of R2 are 0.83 and 0.88. R2 shows the coefficient of determination value used as information regarding the model-relation between variables [10]. The coefficient of determination value is between 0 < R2 < 1; therefore, if the value of R2 is close to 1, it indicates that the regression predictions almost perfectly fit the data, thus, shows that the free and bound variables in the data have strong regression. This graph also indicates that the volume of hydrogen gained from the electrolysis process using the unmodified electrode reached the maximum score at the minute of 280 with a total amount of 15 mL, yet the volume of hydrogen tended to keep dropping until the electrolysis process needed to be stopped at the minute of 520, though the hydrogen was still being produced in the process. However, the clay-modified electrode yielded the highest hydrogens volume (15.4 mL) at the minute of 460. The volume then gradually dropped down to the minute of 700 when the electrolysis process was stopped shortly after though the hydrogen was still being produced. It indicates that the clay-modified electrode makes the electrode much more durable toward corrosion in the seawater contained with chlorine. In other words, the use of clay-modified electrodes in the electrolytic process of seawater can extend the electrode's usage time.

Figure 4. The volume of hydrogen production for each measurement time using the clay-modified electrode and the unmodified electrode

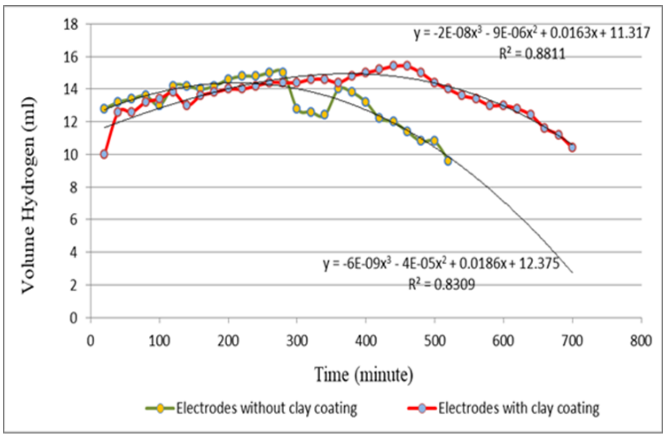
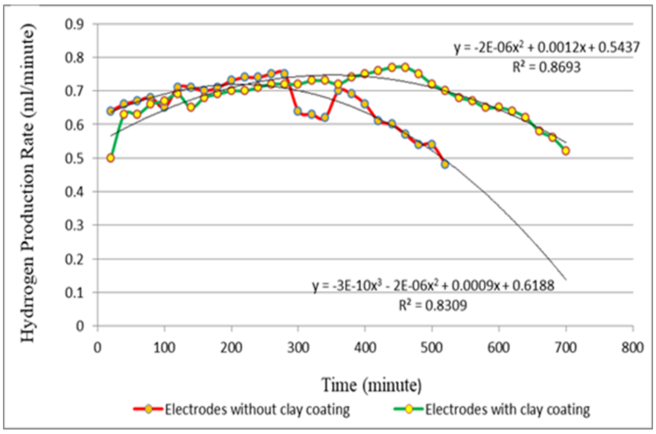


Figure 5. The graphic of hydrogen production rate per unit time using the clay-modified electrode and the unmodified electrode

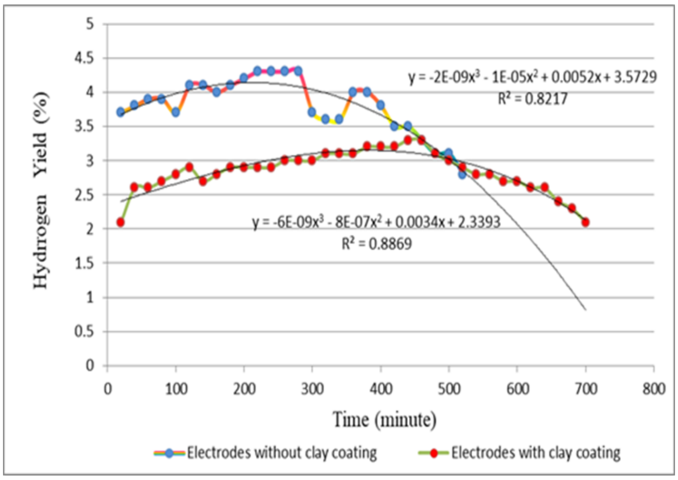


The affinity between hydrogen production rate and the measurement time of sea water's electrolytic process illustrated on the graphic gained the coefficient of determination (R2) with the value of 0.87 for the clay-modified electrode; while the unmodified electrode gained the coefficient of determination with the value of 0.83. R2 shows the affinity between hydrogen production rate and its measurement time. Therefore, the time variation can impact clay-modified electrode for 87%; and 83% for the unmodified electrode [10]. When clay-modified electrode gained its highest hydrogen volume in 15.4 mL at the minute of 460, its production rate can be determined for 0.77 mL/minute; and as for the unmodified electrode which gained its highest hydrogens volume in 15 mL and at the minute of 280, its production rate is determined for 0.75 mL/minute. If the hydrogen production rate keeps dropping, then it will result in a decrease of volume as well, as shown in figure 5.

On the other hand, figure 6 shows that the hydrogen yield gained in the electrolytic process using a clay-modified electrode and the unmodified electrode fluctuate and consecutively appears to have a polynomial dynamic system to the coefficient of determination with the value of 0.89 and 0.82. According to figure 6, the highest hydrogen yield at the rate of 3.3% was induced by the clay-modified electrode at the minute of 460. Meanwhile, the unmodified electrode reached their highest hydrogen yield, hitting the rate of 4.3% at the minute of 280. From this research, it can be inferred that using unmodified electrodes during the electrolytic process in seawater appears to have a higher hydrogen yield level than using the clay-modified electrode. However, it turns out that the unmodified electrode reached its maximum rate and produced more hydrogen faster compared to the clay-modified electrode before gradually dropped. The corrosion caused by chlorine contained in seawater (chlorine) might cause this, which makes the unmodified electrode has a shorter period of time when it comes to the durability of use.

Figure 6 also shows that the more time needed during the process, the more hydrogen yield increases. This matches Hakim L and Marsalin L's research in 2017, which stated that the hydrogen yield will eventually increase when more time is added. However, though the unit time is extended in this research, the hydrogen yield seems to have subsided at some point that might have been caused by the corrosion on the electrode, as stated before, thus reduced the electrode's productivity to produce hydrogen [11].

Figure 6. The graphic of hydrogen yield's measurement result by hydrogen Production



From the explanation and the result above, it can be concluded that the research hypothesis has been proved; there is indeed a significant impact of modified electrodes toward electrode's durability in seawater electrolytic processes to produce hydrogen. As explained above, the unmodified electrode reached its highest level in producing hydrogen before it quickly subsided than the clay-modified electrode that has electrons on its surface did [12] which also could prevent corrosion of the chlorine ions. This result extends equally to the research of scientists at Stanford University that discovers how anodic coatings with rich electrons will resist chlorine and suppress the corrosion rate caused by chlorine contents within the metal layer [13]. Research conducted by Yun Kuang using layered anodes consist of an electrocatalyst layer of iron-nickel alloy (NiFe) that coated on the layer of nickel sulfide (NiSx) and formed on porous nickel (Ni) foam (NiFe/NiSx-Ni) has potential to suppress the corrosion as well. Negatively charged polymers, which is the result of the anodizing of nickel sulfide-layers (NiSx) below the layers and the carbonate ions in an alkaline solution with a negative charge will suppress the corrosion on anodes caused by chlorine [5]. Meanwhile, Kovendhan M stated that electrodes on stainless steel that have been taken away with the condition of hydrogen and argon have good protecting layers and can withstand corrosion for 12 hours long. These two research have evolved electrodes that can withstand and prevent corrosion caused by chlorine, yet the process is quite complicated and relatively costs much for the equipment[14]. That being said, this research aims to be an alternative to prevent corrosion with affordable cost and easy application by coating and modifying the electrons with negatively charged clay on its surface [7].

Furthermore, this research shows a better hydrogen production compared to Slama (which tests various electrode materials, one of which is copper, and brings the result that the electrode in copper could only last for 6 hours with a total amount of 24.6 mL of hydrogens volume gained from an electrolytic process in seawater with the potential difference of 0.5 volts from the solar cell [15]. Meanwhile, research conducted by Nursina shows that using copper electrodes toward an electrolytic process could only last for 5 hours and 20 minutes to obtain a total amount of 82 mL of hydrogen volume with the potential difference of 12 volts. Those two research fundamentally support this research and show how using a clay-modified electrode, specifically at the anodes, can prevent corrosion caused by chlorine from happening at the copper electrode, extend its durability, and increase the volume of hydrogen to 475.6 mL and 342.2 mL consecutively for the electrolytic process using a clay-modified electrode and the unmodified ones with potential differences of 12 volts[16]. It extends equally to research conducted by Yufaraj and Santhanaraj, which studied the impact of various voltages on hydrogen production, that the use of 12 volts in potential difference is the optimal voltage to create hydrogen production rate for 81 cc/minutes in an electrolytic process[17].

Conclusion

The use of electrodes (copper) coated with clay in the seawater electrolysis process has more resistance to corrosion due to chlorine contained in seawater, compared to electrodes (copper) that are not coated with clay. Electrodes (copper) that are not coated with clay have a service life of up to 9 hours before the electrolysis process is stopped and reaches a maximum point in hydrogen production of 15 ml at 280 minutes; Meanwhile, the electrode coated with clay has a durability of up to 12 hours before the electrolysis process is stopped and produces a maximum hydrogen volume of 15.4 ml at 460 minutes before having a downward trend.

However, because in this reasearch the electrode coating process with clay used the traditional method, this reasearch has a weakness, namely when the electrolysis process takes place on the outermost layer of clay sometimes peels off and becomes less resistant to corrosion. Therefore, these shortcomings can be a reference for future research so that this research is better and more efficient in resisting corrosion.

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