

Research Article

Green Hydrogen Production Directly from Seawater with No Corrosion Using a Nonmetallic Electrode: A Novel Solution and a Proof of Concept

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Why Hydrogen. Nowadays, the energy industry and research laboratories are heavily working on developing ideas and methods to reduce and/or eliminate the carbon dioxide emission to control the problem of global warming. The solution relies on finding alternative green energy resources to reduce the world's dependence on conventional fossil hydrocarbon energy. Green hydrogen gas from water stands on the top of the alternative resources since it does not produce carbon dioxide when burned and in return does not add to global warming. Since seawater is the largest resource on earth, this makes the hydrogen production from seawater the most economically attractive solution. It is very important to avoid using fresh water as a source of hydrogen energy due to the dependence of all living creatures, humans, animals, plants, etc., on such very limited resources. In this paper, the applications of the proposed novel solution of green hydrogen production directly from seawater relies on solving one of the major problems, electrode corrosion. *Generating Hydrogen.* The direct method to produce green hydrogen from seawater is the electrolysis technique. This technique requires a direct current power supply for the positive and the negative electrodes. The outcome of the electrolysis is decomposing the saltwater to its positively charged hydrogen and sodium ions at the negative electrode and its negatively charged oxygen and chlorine ions at the positive electrode. *The Real Challenge.* Traditionally in the electrolysis analysis of water, both electrodes are made of metals. At the positive electrode, both the oxygen and the chlorine cause a high rate of corrosion to that electrode. This results in the interruption of the electrolysis process, bad water condition due to the corrosion deposits, and cost burden due to the need to periodically replace the corroded electrodes and/or use high-cost corrosion-resistant alloys. *The Novel Solution.* A low-cost but powerful solution to the corrosion problem is introduced, tested, and experimentally proved. The novelty of the solution relies on replacing the classic special high-cost metallic positive electrode with a nonmetallic, no-cost, one. The nonmetallic electrode is made of surface rock portions that have high porosity and pore volume and high permeability and pore connectivity and is saturated with saline water. Surface rocks with the above properties exhibit very low resistivity and hence conduct electricity like metallic electrodes. The voltage and the current conducted by such electrode are controlled by the electrode geometry, connectivity, and physical properties. *Results and Discussions.* Multiple experiments using the proposed nonmetallic high-porosity and high-permeability positive electrode are conducted and presented in this paper. The experimental work is based on testing multiple rock electrodes with different rock properties, sizes, and connectivity in comparison to the metallic ones. The comparison showed that the novel solution solved the corrosion challenges of the metallic electrodes with excellent efficiency.

1. Introduction

To meet the increasing demand for energy which the world is currently facing and at the same time reduce the amount of car-

bon dioxide that creates the global warming, scientists are heavily working in resolving the challenges facing the green hydrogen production from water. Multiple researchers addressed these issues from the economic side as well as the technical side.

The choice of hydrogen as the future resource of energy is based on multiple properties that make hydrogen not only a possible solution but the most desirable one. Some of the advantages of the green hydrogen are the following:

- (1) Hydrogen produces four times higher energy per weight when compared to conventional fossil gasoline
- (2) Hydrogen is one of the components of seawater, which is a vast resource on earth
- (3) When hydrogen is burned, it does not produce carbon dioxide and hence does not harm the environment or add to the global warming

1.1. The Economical Side Challenges. The need for economical and robust hydrogen production requires efficient technology which is discussed by multiple authors. Zou and Zhang [1] discussed the urgent need to develop a low-cost, high-efficiency, and robust electrocatalysts for the oxygen evolution reaction (OER). Yan et al. [2] showed the urgent need for hydrogen production using water splitting through the development of bifunctional catalysts for both the hydrogen evolution reaction (HER) and the oxygen evolution reaction (OER). Suen et al. [3] showed the need for the oxygen evolution reaction as a key to improve the efficiency of hydrogen gas evolution. They also discussed the cost due to the need to enhance the efficiency of the hydrogen splitting operation. Yu et al. [4] discussed the challenges from another direction where they showed that the water splitting to produce the hydrogen energy requires a large excess potential to expedite the reactions, 200-400 mA cm⁻² at cell voltages of 1.8 V-2.4 V in base, which results in less efficiency process. Fabbri and Schmidt [5] discussed the energy storage systems showing the immediate need for such technology. They also showed that to speed up the acceptance and the market for hydrogen as a potential energy resource, it requires the development of a stable, inexpensive, and highly active electrolysis technology. Hu et al. [6] showed that the alkaline-water splitting represents an attractive technique for sustainable production of hydrogen energy stressing on the urgent need to construct efficient electrocatalysts based on the structure-activity relationship. Wu et al. [7] also discussed the need for a low-cost but also high-efficiency electrocatalysis technology as an urgent requirement to address the energy crisis.

1.2. The Technological Challenges in Hydrogen Production and Storage. Khan et al. [8] studied the hydrogen evolution reaction and the oxygen evolution reaction electrocatalysts for water electrolysis through the noble metal-based materials. They showed that the high cost associated with this approach represents a serious limitation. They focused their approach on developing a non-noble metal-based electrocatalysts for alkaline, polymer exchange membrane (PEM), and solid oxide electrolysis. Li et al. [9] discussed the fundamentals and design of the electrolysis process of water using the iron, cobalt, nickel, etc., for the OER and the HER in the acidic-alkaline and neutral conditions. They also discussed

the catalysts in the photoelectrocatalysis, the photocatalysis systems, and the potential directions of integrating the photovoltaic with the electrolyzing, so called PV-E. Zhu et al. [10] provided an excellent review on the hydrogen production as a clean renewable energy to reduce the effect of the fossil energy on the environment. The review included an overview of the HER as an important step in the hydrogen production and the catalyst effectiveness and challenges. Suen et al. [3] discussed an important aspect in hydrogen production as a future energy resource which is the energy conversion and storage systems such as fuel cells to convert the produced hydrogen to electricity storage through batteries such as lithium-ion or metal air batteries. Wang et al. [11] discussed the role of the catalyst in the water electrolysis for efficient hydrogen production. They discussed the critical properties of the catalyst being low cost and stable and its activity in enhancing the efficiency of the electrolysis process. Zhong et al. [12] developed a highly active and stable oxygen evolution reaction design using an enhanced cobalt-induced strategy with electronic structure modulation reaching a current density of 10 mA cm⁻² at an overpotential of 182 mV. Wang et al. [13] discussed the efficiency of the electrolysis process for hydrogen production to meet the high commercial-scale demand. They discussed the advances in the noble metal- and non-noble metal-based electrocatalysts through exploring the structure, morphology, composition, and active sites of the nanostructured.

1.3. The Electrolysis Process. Godula-Jopek and Stolten [14] discussed the basics of hydrogen production from water through the electrolysis process. Electrolysis is simply a flow of current through a conductive liquid medium resulting in the chemical decomposition of the medium into its ionic components. If the conductive medium is water, then one of these ionic components generated by electrolysis is the hydrogen gas. Since ninety-seven percent of the water on earth is saltwater, then utilizing these vast water supplies for electrolysis rather than fresh water would be advantageous. Multiple research and experimental work are performed to fully understand the electrolysis process, requirements, challenges, and limitations. Normally, the electrodes in the electrolysis process are made of metals. All metals face corrosion problems due to the existence of the negatively charged ions generated in the process. Different metals react differently with the corrosion process which was discussed by Tafel in 1902 [15] in his trial to study the hydrogen evolution reaction (HER) to predict the corrosion current or corrosion potential. In his experiments, Tafel found an exponential relationship between the applied current and the potential, called Tafel equation.

$$\eta = a + b \log(i). \quad (1)$$

It was convenient to present the relationship via plotting the potential versus the logarithm of the current (Figure 1), where η is the voltage, i is the current density defined as the current per unit area of the electrode, and a and b are the constants. This behavior will be examined in this paper

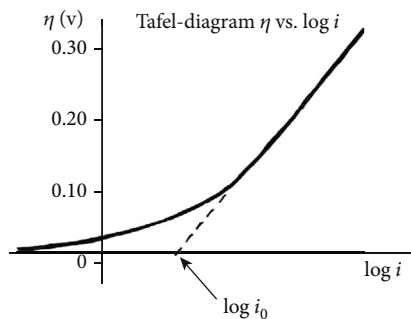


FIGURE 1: Tafel equation.

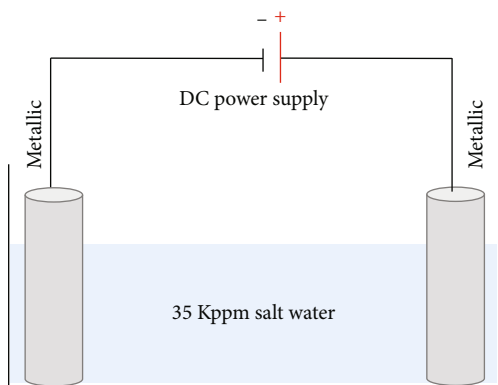


FIGURE 2: A schematic of electrolysis setup.

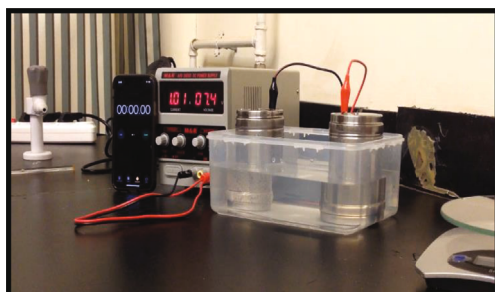


FIGURE 3: The experimental setup.



FIGURE 4: The experiment after 7.5 minutes.



FIGURE 5: The corrosion deposits after only 7.5 minutes.



FIGURE 6: The corrosion effect on the positive electrode after only 7.5 minutes.

to see if the rock electrode will act like the metallic electrodes as observed by Tafel.

Tafel's approach represents the ideal case, but the real reactions usually deviate from Tafel's observation because of the passivation and the diffusion limitation. Diffusion limitations lead to an independent potential current in the oxygen reduction reaction (ORR). The reaction and the current can only occur when new oxygen diffuses to the direction of the electrode. In this case, the current is independent of the potential but rather dependent on the movement of oxygen.

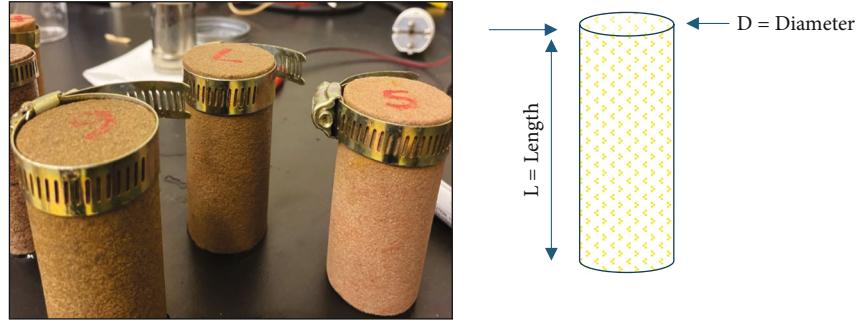


FIGURE 7: Nonmetallic rock sample electrode from surface rocks.

TABLE 1: Dimensions, porosity, and permeability for the nonmetallic rock sample electrodes.

Sample no.	Sample diameter (mm)	Sample length (mm)	Porosity (%)	Permeability (md)
1	25.18	74.04	28.99%	804.75
2	25.09	76.56	25.07%	43.57
3	25.08	75.02	21.48%	61.85
4	25.04	74.56	27.07%	529.93
5	37.74	71.83	24.14%	428.42
6	37.73	73.22	23.63%	182.42
7	37.74	74.46	20.65%	216.84

Rochambeau [16] showed that corrosion during the electrolysis process takes place when dissimilar metals are unphysically in contact in the presence of a conductive electrolyte, such as seawater. He also showed that there are two types of corrosion: galvanic corrosion, which is caused by an electric current due to the difference in electrical potential between the two metal electrodes, while the second is electrolytic corrosion. He also showed that electrolytic corrosion is an exponentially accelerated corrosion compared to galvanic reaction resulting from the use of current from an external source which speeds up the oxidation rate. Bennett [17] determined the relative chlorine and oxygen efficiency in seawater at different temperatures and salinities for different electrode materials. He showed that oxygen evolves exclusively below the theoretical voltage for chlorine evolution at too low current density ($<1 \text{ mA/cm}^2$). He also showed that the current density for chlorine evolution in seawater is variable and depends on the water salinity, temperature, cell design, and flow considerations ranging from 100 to 1000 mA/cm^2 . An important conclusion from this work is that the use of conventional electrode materials will result in significant evolution of chlorine in the form of sodium hypochlorite. Bouazizi et al. [18] did an excellent work on discussing the factors that affect the corrosion of the electrodes in the electrolysis process. They summarized them in six main factors: the pH, temperature, corrosion product precipitation, increase in electrolyte mass concentration, time, and applied potential. They showed that the effects are as follows: the first is the pH value of the electrolyte which represents one of the main factors because the corrosion occurs quickly when the pH deviates from neutrality ($4 < \text{pH} < 9$) values. The second factor is the temperature because the corrosion greatly increases in rate when

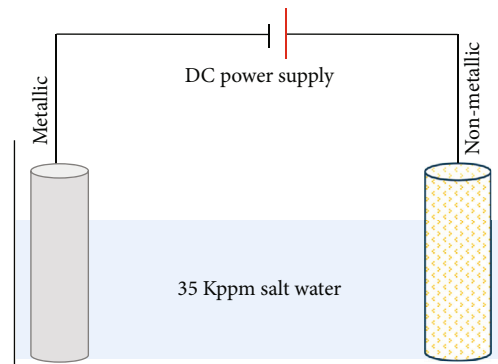


FIGURE 8: A schematic of the modified electrolysis setup.

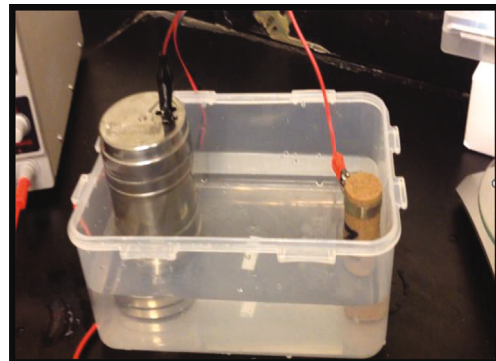


FIGURE 9: The modified experimental setup.

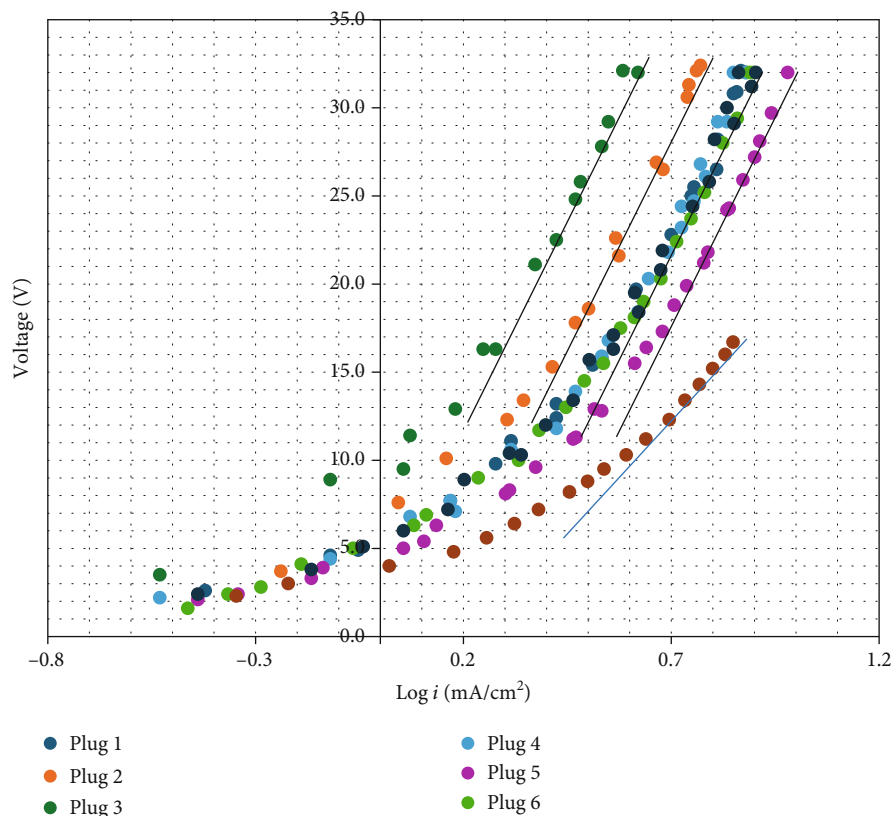


FIGURE 10: The Tafel plot for the nonmetallic electrodes.

temperature increases due to the thermal activation of the electrodes. The third is the effect of the corrosion product precipitation on the surface of the electrodes, deposit effect, causing pitting on the surface of the electrode. The fourth is the increase of the mass concentration of the electrolyte because the resistance of electrodes is a function of the solution's concentration, called electrolyte concentration effect. The fifth is the duration time of the electrolysis operation because when time duration of water electrolysis increases, the corrosion effect increases which eventually minimizes the flow of hydrogen production. The sixth is the applied potential which is affected by the electrode's composition, surface condition, shape, and their contact with the electrolyte. Abdel-Aal et al. [19] studied the effect of water salinity on the required electric power for the electrolysis operation. They tested the electrolysis using different water salinities ranging from 4,000 to 60,000 ppm and a power source ranging between 6 and 20 V, and up to 1,000 coulombs of energy was used. The hydrogen production rate in Abdel-Aal et al.'s work shows to be heavily dependent on the applied current density in the solutions. They found that the production of hydrogen has a direct relationship with the TDS, total dissolved solids. Since the higher the salinity, the higher the reduced resistance, a rise in salt level results in a proportionate increase in hydrogen production. The rate of the hydrogen production increase is not significant at low voltages since it is also significantly reliant on the current density. However, at higher voltages, the higher dependency on current density diminishes. They also made an important rec-

ommendation showing that if water is considered as the raw material for hydrogen production, it would be wise to utilize these abundant saline water resources for electrolysis rather than using fresh water. Izumiya et al. [20] investigated the effect of using different, selective oxygen evolution reaction (OER) electrodes on the electrolysis process. They started with testing the different electrodes at a low pH of 0.5 M NaCl electrolyte. They also examined the same electrolyte at a high pH of 8. They modified the electrode materials with adjusted manganese-based electrode materials which resulted in remarkable oxygen efficiencies. In the Energy Information Administration (EIA) [21] review on hydrogen, challenges showed that there are several methods of handling the corrosive chlorine problem in seawater electrolysis. The first, electrocatalyst such as manganese dioxide can be used to inhibit the evolution of chlorine. The second is that the chlorine evolution can be used for water desalination as a hybrid system to produce hydrogen gas and fresh water.

2. The Classical Electrolysis and Its Challenges

The classical method of water electrolysis is to use two metallic electrodes: one is connected to the negative terminal of a direct current (DC) power supply, while the second is connected to the positive terminal. It is of optimum value if the direct current power supply is generated using solar energy. In all experiments conducted in this paper, the power supply is not generated using solar panel but from a

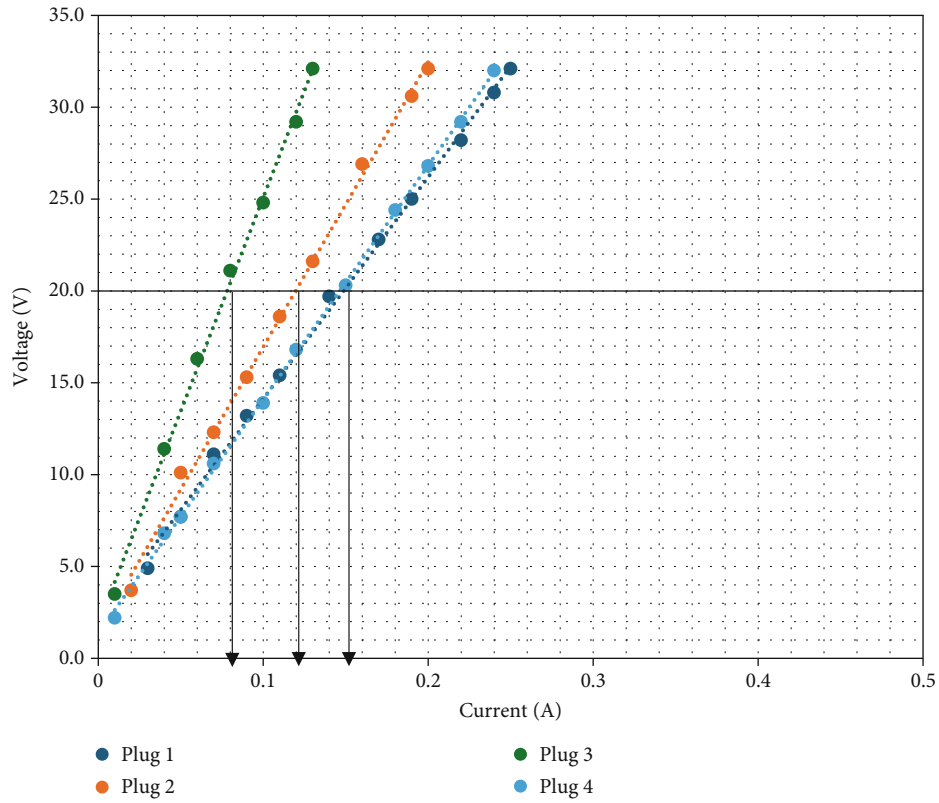


FIGURE 11: Voltage versus current—small diameter plugs.

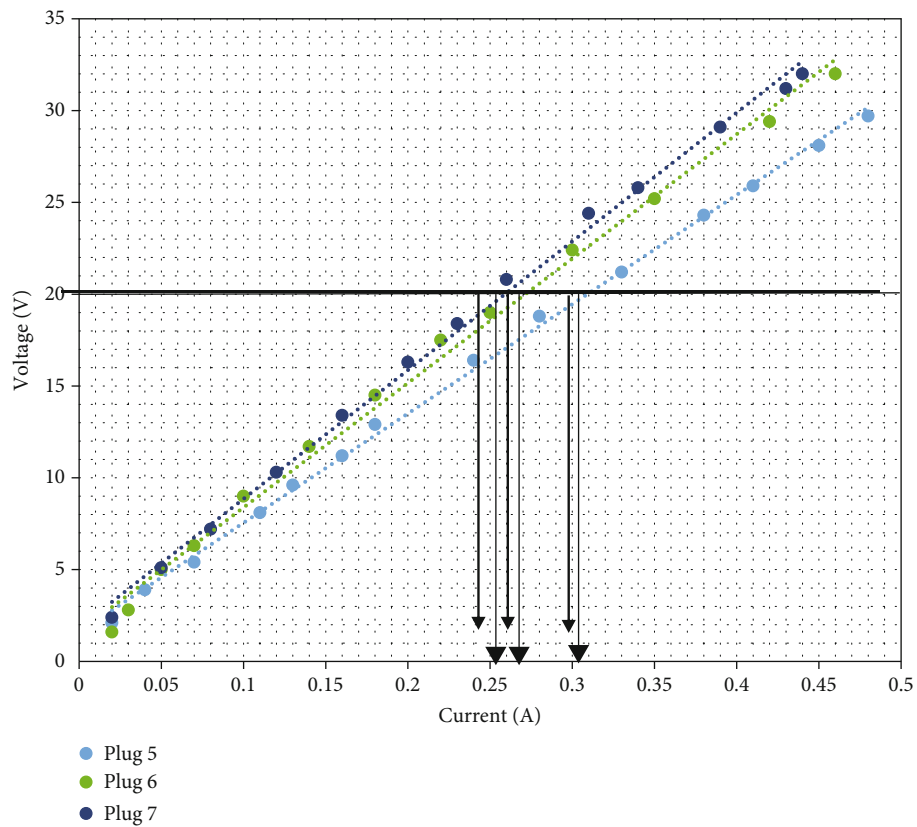


FIGURE 12: Voltage versus current—large diameter plugs.

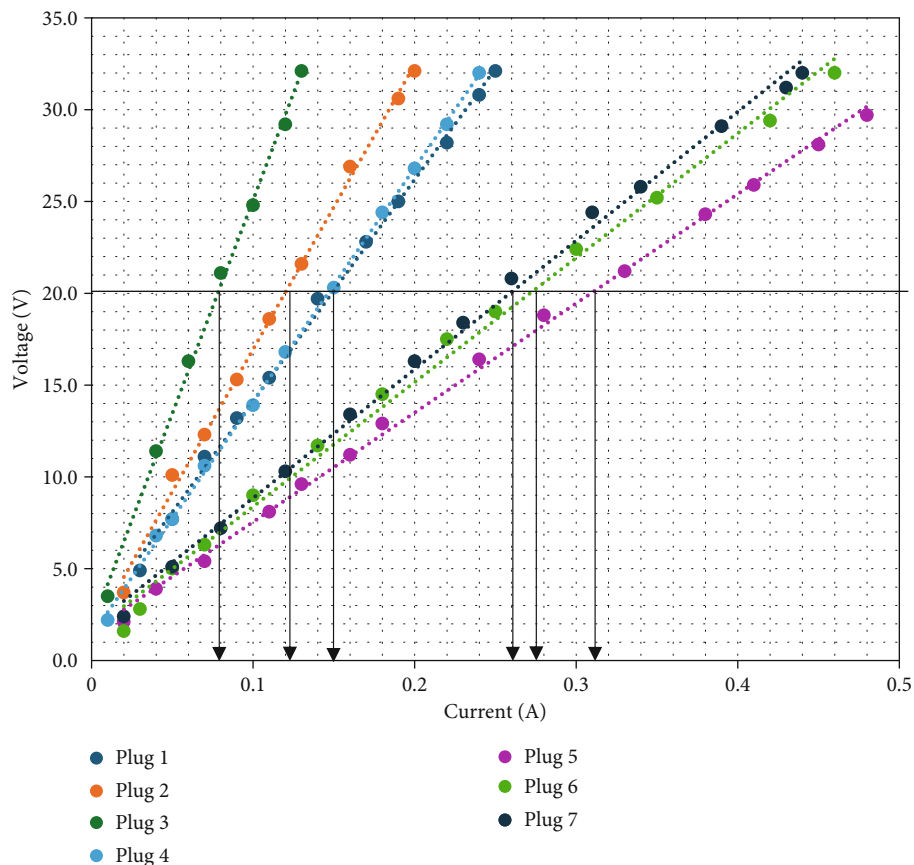


FIGURE 13: Voltage versus current—all plugs.

TABLE 2: Calculated pore volume for the nonmetallic rock sample electrodes.

Sample no.	Sample diameter (mm)	Sample length (mm)	Porosity (%)	Pore volume cubic centimeter
3	25.08	75.02	21.48%	7.96
2	25.09	76.56	25.07%	9.49
4	25.04	74.56	27.07%	9.94
1	25.18	74.04	28.99%	10.69
7	37.74	74.46	20.65%	17.20
6	37.73	73.22	23.63%	19.34
5	37.74	71.83	24.14%	19.40

conventional AC to DC power supply to provide more variability of current and voltage for the different experiments. A schematic diagram of the setup is shown in Figure 2. This simple setup greatly illustrates all the challenges to the generation of hydrogen gas and the corrosion process. To illustrate the seriousness of these issues, the setup (Figures 2 and 3), using a 35 kppm NaCl saltwater representing the average sea-water salinity is used. The power supply is a variable DC power supply that generates a variable DC voltage, up to 32 volts, variable DC current up to 5 amperes, and variable power up to 160 watts. In this experiment, the voltage is set to 7.4 volts and a DC current of 1.0 ampere which deposits a power of 7.4 watts. The experiment was run for only 7.5 minutes where the outcome can be summarized as follows:

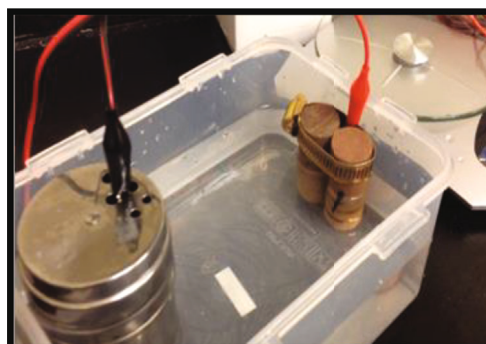


FIGURE 14: Parallel connectivity of nonmetallic electrodes.

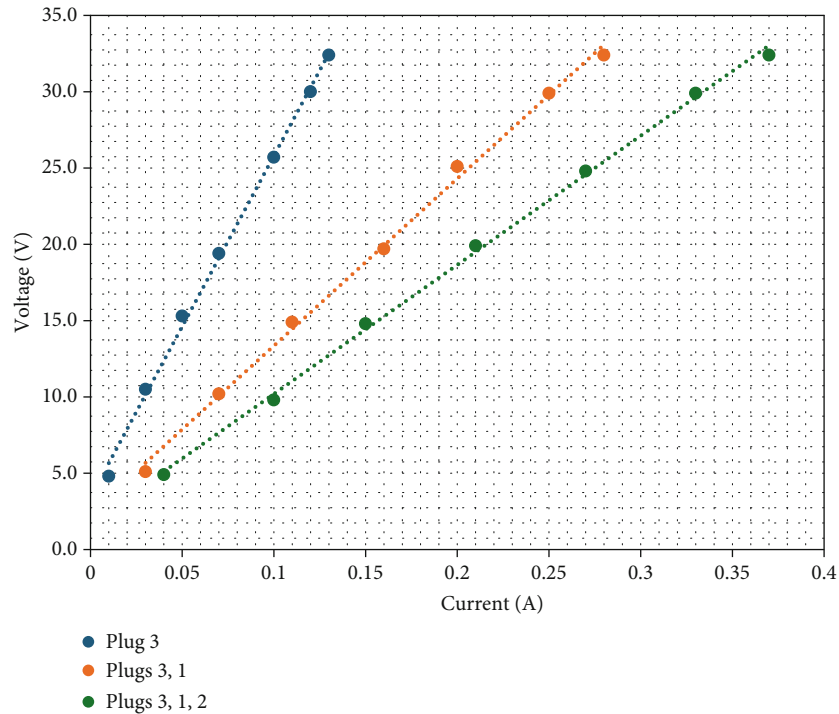


FIGURE 15: Dragged current using parallel nonmetallic electrodes.

- (1) Clear corrosion deposits in the water (Figure 4. A sample of the water is left to settle (Figure 5), where corrosion deposits are clearly observed at the bottom of the beaker
- (2) The effect of the corrosion on the positive electrode is shown in Figure 6

3. The Novel Solution

The proposed novel solution to overcome the corrosion problem of the saltwater electrolysis and to eliminate the interruption of the electrolysis operation is investigated. The solution is based on replacing the metallic positive electrode, where the corrosion takes place, with a nonmetallic conductive electrode. The nonmetallic electrode is made of formation rocks that have high pore space, voids between grains called rock porosity, and high connectivity between the pores called rock permeability. Most of the surface rocks have such high porosity and high permeability due to the low compaction exerted on the rocks at the surface. Multiple samples are taken from different rocks, where the porosity and the permeability are measured on all samples. The measurements of porosity and permeability on rock samples are a routine process which is well known and widely used in the petroleum industry called “core plugs.” An example of the rock sample electrodes is shown in Figure 7.

Table 1 contains the dimensions, porosity, and permeability for the different rock samples used in the experiments. The measurements are performed at the Petroleum Engineering Core Laboratory at the American University in Cairo.

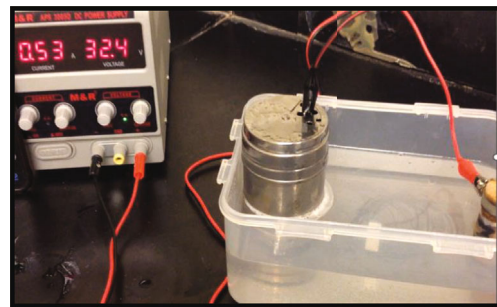


FIGURE 16: Hydrogen production using nonmetallic electrode.

From Table 1, the porosity variation ranges from 20% to 29% while the permeability ranges from 43 millidarcies to 805 millidarcies providing good variations of porosity and permeability values. Also, the samples contain two different sets of sizes to examine the effect of the surface area on the dragged electric current.

4. Generating the Tafel Plot

The rock samples (Table 1) are used to examine the behavior of the rock electrodes compared to the metallic ones as per Tafel experiments. The nonmetallic electrodes are soaked in 35 kppm saline water, representing the average seawater salinity, for two days to ensure full saturation of the samples pore spaces with the saline water. The variation of permeability between the different nonmetallic electrodes determines the time required for the full saturation of the pore volume. The experimental setup is shown in Figures 8 and 9.

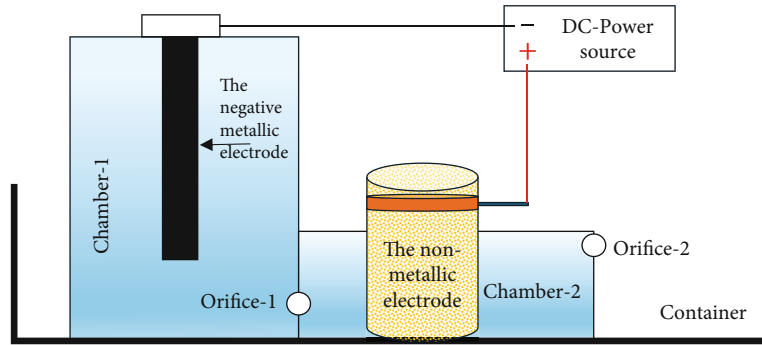


FIGURE 17: Hydrogen collection using nonmetallic electrode.

To compare the behavior of the nonmetallic rock sample electrodes to the metallic ones, Tafel plot, the voltage is plotted versus the logarithmic of the dragged current per unit area, current density (Figure 10). All the seven samples with their different sizes, pore volumes, and permeability values showed the same behavior of the metallic electrodes. They also showed the same slope (b) since they all are taken from the same sandstone rock because the slope depends on the rock type (or the metal type in case of metallic electrodes as per Tafel). This finding also explains the difference in slope between the rock electrodes when compared to that of the metallic electrode.

5. The Dragged Current

Another set of experiments is conducted to study the effect of the rock properties on the dragged current. The voltage is plotted against the dragged current for all seven samples (Figures 11–13). Figure 11 shows that the least current is dragged by plug 3 since it has the lowest pore volume and hence has the highest resistivity. A higher current is dragged by plug 2 since it has higher porosity and pore volume compared to plug 3. The highest current is dragged by plug 1 and plug 4 since they both have the highest porosity amongst all samples. Figure 12 shows the dragged current for the larger diameter plugs. The least current is dragged by plug 7 since it has the lowest porosity and hence the highest resistivity. The second highest current is dragged by plug 6 which has higher porosity compared to plug 7. The highest current is dragged by plug 5 since it has the highest porosity. Figure 13 combines all plugs to compare the dragged current by all different plugs. In conclusion, the dragged current is a function of two factors:

- (1) The porosity of the nonmetallic electrode
- (2) The size of the nonmetallic electrode

The effect of the size of the electrode relies on increasing the pore volume. The pore volume is defined as

$$\text{Pore volume} = \text{porosity} * \text{plug volume}. \quad (2)$$

Using equation (2), the pore volume is calculated and shown in Table 2. The plugs are arranged in the table based on their pore volume in an ascending order. The order of the

plugs in the table agrees with the order of the plugs presented in Figure 13.

6. Methods to Increase the Dragged Current

The dragged current can be increased using the nonmetallic electrodes by simply reducing the plug resistivity. This can be achieved by using multiple nonmetallic electrodes connected in parallel since the parallel connection of resistivities results in a lower total resistivity.

$$\frac{1}{R_t} = \frac{1}{R_1} + \frac{1}{R_2} + \dots \quad (3)$$

Figure 14 shows the setup of the parallel nonmetallic electrode's connection while Figure 15 shows the plot of the voltage versus the dragged current. When three plugs are connected in parallel, more current is dragged compared to only two parallel electrodes which in turn drag more current compared to only one electrode. Therefore, if high dragged current is required, then multiple electrodes connected in parallel are recommended.

The nonmetallic electrode is tested (Figure 16) using a similar setup used in the metallic one (Figure 3) to show its ability to produce hydrogen and at the same time overcome corrosion problems. The setup shows the produced hydrogen with no signs of corrosion and no corrosion deposits. More details on the production rates and the efficiency of the process will be discussed in another paper.

7. The Effect of DC Current and Voltage on Rock Plugs

The effect of applying direct current and voltage on the property of the formation rock has been intensively studied by Ghosh et al. in 2012 [22]. They used the X-ray diffraction (XRD) and inductively coupled plasma-mass spectroscopy (ICP-MS). They found that applying a DC current enhanced the rock properties, especially the rock permeability up to 180%. The increase of the rock permeability increases the pore connectivity and hence increases the dragged current as a function of time.

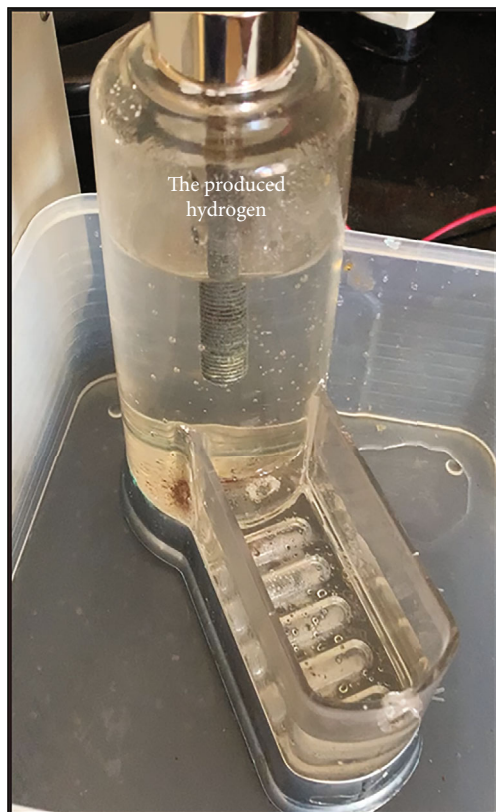


FIGURE 18: The setup showing the produced hydrogen volume.

8. The Hydrogen Production

The nonmetallic electrode is tested (Figure 16) using a similar setup used in the metallic one (Figure 3) to show its ability to produce hydrogen and at the same time overcome corrosion problems. The setup shows the produced hydrogen with no signs of corrosion and no corrosion deposits. More details on the production rates and the efficiency of the process will be discussed in another paper.

9. Hydrogen Collection Experiments

Another set of experiments is performed to collect the produced hydrogen and to examine the productivity of the non-metallic positive electrode. The setup is shown in Figure 17.

The setup is composed of two chambers, chamber 1 containing the metallic cathode connected to the negative DC voltage while chamber 2 contains the nonmetallic formation rock anode electrode connected to the positive DC voltage. The two chambers are connected through orifice 1. The generated hydrogen in chamber 1 pressures the water through orifice 1 to chamber 2 which in turn allows the displaced water to flow through orifice 2 to the container. The collected water volume in the container reflects the volume of the produced hydrogen in chamber 1. Figure 17 shows the actual setup for one of the set of experiments. The setup parameters and the displaced water are as follows:

Voltage = 1.8 volt

Dragged current = 0.023 ampere



FIGURE 19: The input voltage and current.

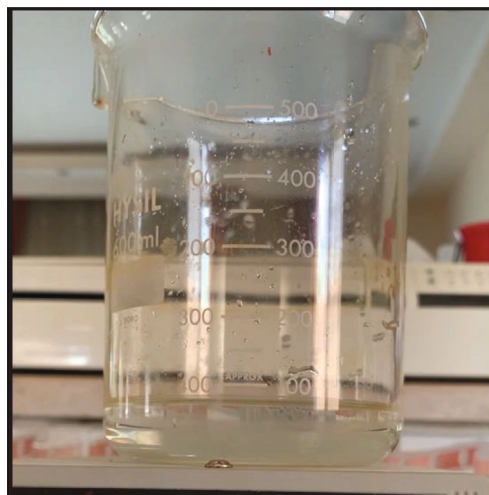


FIGURE 20: The displaced water volume.

Operating time = 10 hours

Hydrogen gas volume generated = 85 cc

Figure 18 shows a photo of the actual setup after 10 hours of operation where approximately 85 cc of hydrogen is generated. Figure 19 shows the displaced water volume while Figure 20 shows the DC power supply used in the experiment.

10. Results, Conclusions, and Current Research

The most challenging problem in hydrogen production from seawater is the corrosion of the electrodes which results in interruption of the operation and in increasing the cost of the hydrogen production. The use of metallic electrodes, especially the positive electrode, is the reason behind these challenges. In this study, a novel solution is investigated that eliminated the corrosion process and hence resulted in corrosion free and uninterrupted hydrogen gas production

from saline water. The novel idea is to replace the positive metallic electrode with a high-porosity and high-permeability surface rock portion that is saturated with saline water. The results are clearly overwhelming and resolved all issues of the corrosion in the electrolysis operation. The dragged current using the nonmetallic electrode showed to be dependent on the pore volume of the electrode where higher pore volume results in higher dragged current. Also, the nonmetallic electrode showed the same behavior as the metallic ones following the Tafel approach. An experiment showing the hydrogen production, the input parameters, and the hydrogen production showed the validity of the nonmetallic rock anode. A full range of the hydrogen rates and the hydrogen production efficiency are currently being investigated and will be published in an upcoming publication.

Data Availability

Data will be made available upon request. Also, all data will be in the paper.

Ethical Approval

The authors hereby confirm abiding with all ethics including copy rights, trademarks, and commercial statements.

Conflicts of Interest

The authors hereby confirm no conflict of interest in this publication regarding any financial or personal relationship with a third party whose interests could be positively or negatively influenced by the article's content.

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