

# A Comprehensive Analysis of the Hydrogen Generation Technology Through Electrochemical Water and Industrial Wastewater Electrolysis

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Most renewable energy sources are intermittent and seasonal, making energy storage and consumption problematic. Hydrogen gas can save and convey chemical energy, making it a promising sustainable energy source. Electrochemical water electrolysis technology's sustainable and efficient hydrogen gas production attracts global attention. Higher hydrogen production rates enhance hydrogen volumetric energy capacity by storing intermittent hydrogen gas in high-pressure tanks. Pressurized storage tanks are cost-effective and efficient. Hydrogen gas may be stored economically and efficiently in pressurized tanks, making electrochemical water electrolysis a sustainable energy source. This paper introduced hydrogen as an alternative to natural gas, detailed water electrolysis technologies for hydrogen production, and highlighted how they can manufacture hydrogen efficiently and cost-effectively. The theoretical volume of gaseous hydrogen and oxygen that could be produced by electrolyzing water under typical temperature and pressure (STP) circumstances, assuming a 100% efficiency rate of the process. Since there are always two moles of hydrogen produced by electrolysis and one mole of gas occupies the same volume, the volume of hydrogen developed from water is twice that of oxygen. The volume of liberated oxygen is 0.21 (L/min), and the volume of liberated hydrogen is 0.42 (L/min) with a current density of 30 A, for instance, the tracer's diffusion coefficient for all conceivable flow rates. A maximum value of 90 liters per hour was determined to be the threshold at which the diffusion coefficient increased with increasing flow rate. It would appear that the diffusion coefficient remains unchanged at flow rates greater than 90 liters per hour.

**Keywords:** Renewable Energy; Green hydrogen; Water electrolysis technologies; Electrochemical; Waste-water Treatment.

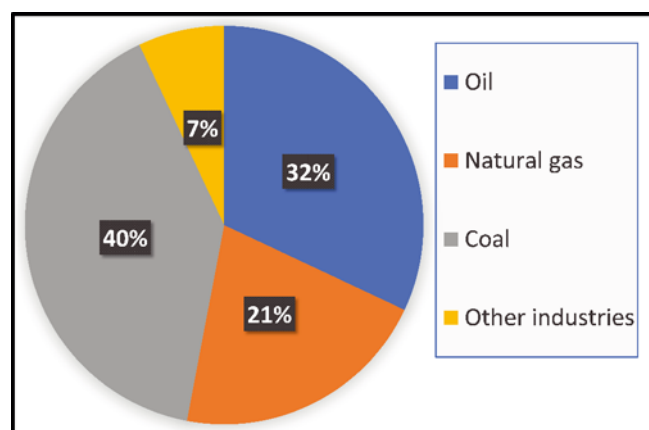
## INTRODUCTION

In light of the ongoing problems caused by global warming and the growing interest in creating clean energy on a worldwide scale, the globe is currently looking for potential alternative renewable fuel sources that would help lower the levels of emissions<sup>1, 2</sup>. Renewable energy sources, such as solar, wind, hydroelectric power, etc., are being explored as potential ways to produce energy with minimal environmental impact. Nowadays, numerous countries are investing in renewable energy initiatives and researching innovative technologies that could reduce the use of traditional fuel sources, as was the case in the United States of America, where the consumption of primary energy from renewable sources amounted to around 13.1% of the total in 2022. These renewable energy sources are not only more environmentally friendly but also provide the potential to reduce energy costs for businesses and households<sup>3–5</sup>. So far, renewable energy sources still have a long way to go before they can completely replace traditional forms of energy. Solar and wind power, for instance, are examples of intermittent forms of energy generation, meaning

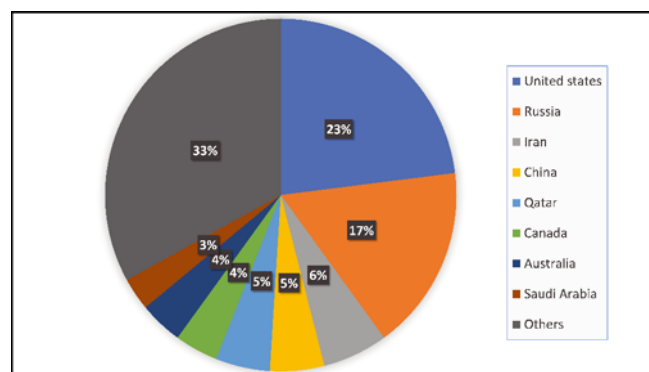
they only generate power when the sun is shining or the wind is blowing<sup>6–8</sup>. That means they cannot provide a constant power source, unlike coal or natural gas. As a result, there needs to be a storage system in place to store the energy produced during peak times and then release it when needed.

Additionally, renewables require more land than traditional forms of energy, making them difficult to implement in densely populated areas<sup>9, 10</sup>. Natural gas can be produced from gas fields and some oil fields whose combustion as fuel causes the emission of large quantities of carbon dioxide and greenhouse gas emissions<sup>11, 12</sup>. Carbon dioxide emission by fuel type amounted to about 34.81 billion tons in 2020, and its percentage of gaseous fuels represents approximately 21% of the total gas emitted from other kinds of fuels<sup>13, 14</sup>, as shown in Figure 1. The globe is currently looking for viable alternative renewable fuel sources that would lessen the emissions problem. The continuous threat of climate change and the rising global interest in developing renewable energy sources motivate these actions<sup>1, 2</sup>. Renewable energy sources, such as solar, wind, hydroelectric power, etc., are being explored as potential ways to produce energy with

minimal environmental impact. Nowadays, numerous countries are investing in renewable energy initiatives and researching innovative technologies that could reduce the use of traditional fuel sources, as in the United States, where renewable energy sources accounted for about 13.1% of the total primary energy consumption in 2022. These renewable energy sources are not only more environmentally friendly but also provide the potential to reduce energy costs for businesses and households<sup>3-5</sup>. So far, renewable energy sources still have a long way to go before they can completely replace traditional forms of energy. For example, solar and wind power are intermittent, meaning they only produce power when the sun shines or the wind blows<sup>6-8</sup>. They cannot provide a constant power source, unlike coal or natural gas. As a result, there needs to be a storage system in place to store the energy produced during peak times and then release it when needed. Additionally, renewable requires more land than traditional forms of energy, making them difficult to implement in densely populated areas<sup>9, 10</sup>. Natural gas can be produced from gas fields and some oil fields whose combustion as fuel causes the emission of large quantities of carbon dioxide and greenhouse gas emissions<sup>11, 12</sup>. Carbon dioxide emission by fuel type amounted to about 34.81 billion tons in 2020, and its percentage of gaseous fuels represents approximately 21% of the total gas emitted from other kinds of fuels<sup>13, 14</sup>, as shown in Figure 1.



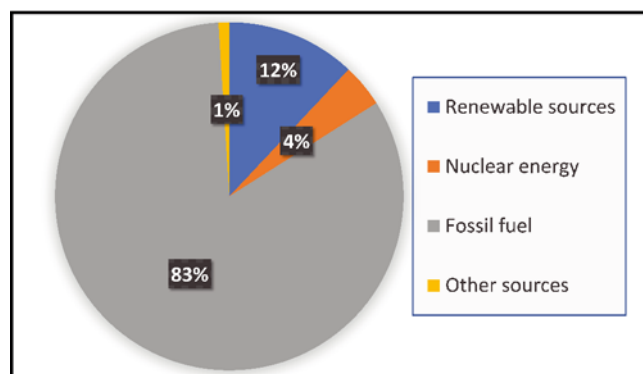
**Figure 1.** The percentage of carbon dioxide emission by fuel type in 2020<sup>12</sup>



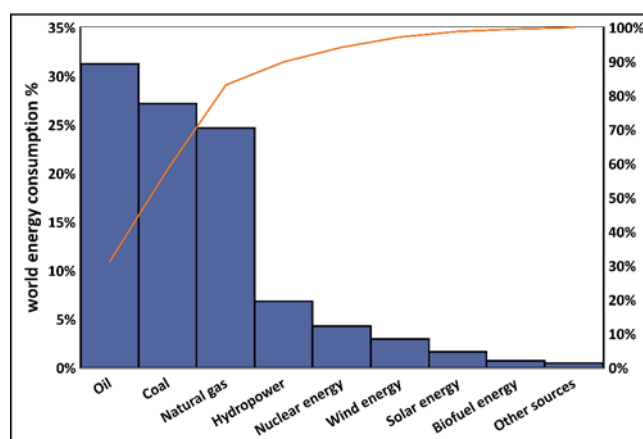
**Figure 2.** Natural gas production percentage in 2021<sup>13</sup>

Figure 2 shows countries that produce the most natural gas in the world, led by the United States, with an estimated production rate of 934.6 billion m<sup>3</sup> for the year 2021 out of a total of 4.04 trillion m<sup>3</sup>, equivalent to 23% of the global production volume.

According to statistical assessments for 2021<sup>15</sup>, the world's energy demands still primarily depend on fossil fuels at a rate of 83%; by contrast, just 12% of the energy comes from renewable sources, and only 4% from nuclear energy as shown in (Fig. 3a). The detailed percentages of global consumed energy sources are shown in (Fig. 3b).



(a) Fossil fuel, renewable, and nuclear energy

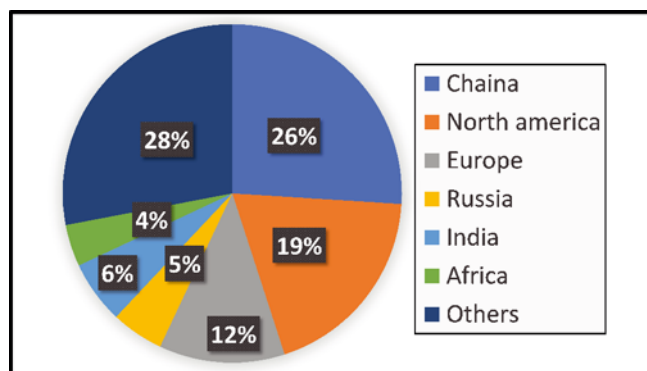


(b) Detailed consumed energy sources

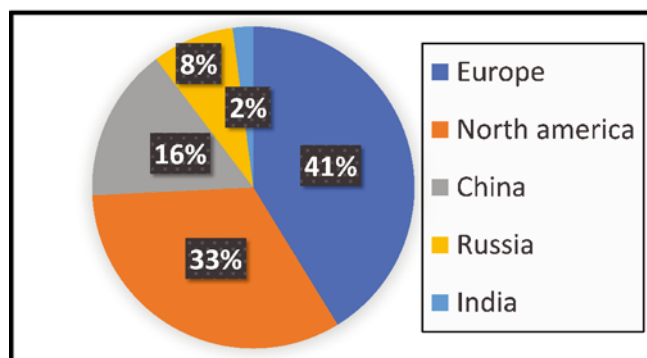
**Figure 3.** The world consumed fuel type percentage in 2021<sup>15</sup>

The consumption of different energy sources globally in 2021 is illustrated in Figure 4. China consumed the most fossil fuels globally, accounting for 26% of all usage (Fig. 4a). In contrast, Europe utilized 40% of the world's nuclear energy (Fig. 4b). Furthermore, the global distribution of renewable energy usage percentages is illustrated in (Fig. 4c).

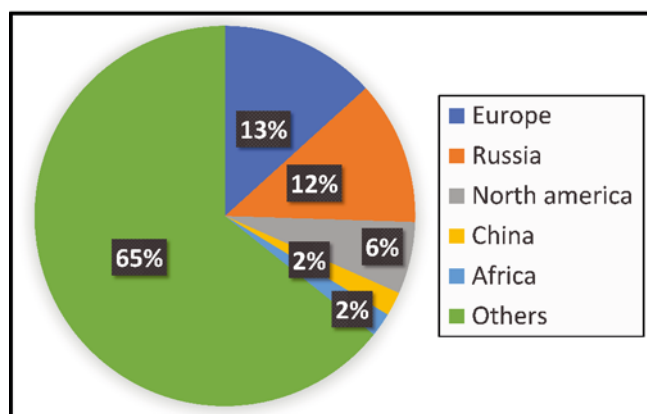
All these countries listed above are qualified and able to replace natural gas production with hydrogen gas production through electrolysis due to their water resources, whether seas or oceans, in addition to ready-made infrastructure and pipelines transmission network that does not require any modifications to change the strategy of natural gas production and gradually transform it into production hydrogen gas. Hydrogen is essential as a future source of clean energy<sup>16</sup> and is an excellent alternative to natural gas<sup>17, 18</sup>, whose primary source is methane<sup>19, 20</sup>. Most hydrogen processes fossil fuels (for example, hydrocracking), creates steel and metallurgy, manufactures chemicals, and processes food<sup>21</sup>. Additionally, it can be burned to generate heat or mixed with oxygen in fuel cells to generate electricity directly when burned, producing water<sup>22</sup>. Although hydrogen is used as a fuel in some countries, its use is limited. Hydro-



(a) Fossil fuels sources



(b) Nuclear energy sources



(c) Renewable energy sources

**Figure 4.** The utilization of different energy sources worldwide in 2021<sup>15</sup>

gen is already being used as fuel in cars that run on hydrogen fuel cells in Japan, Germany, and the United States. Hydrogen can be expanded to include the areas of power vehicles, generating electricity, power industry, and heating our homes and businesses<sup>23</sup>. Considering everything discussed above, this research article will introduce hydrogen gas as a natural gas alternative and provide a detailed analysis of the various water electrolysis methods for efficient and affordable green hydrogen generation.

This work aims to present hydrogen as an alternative to natural gas and detail water electrolysis technology for hydrogen production that can be used efficiently and cost-effectively. Our final suggestion is to conduct more research and development. Many methods can make hydrogen, including water electrolysis. Green hydrogen production technologies and materials are listed in this review. The water electrolysis process, an environmen-

tally friendly green hydrogen production method, must be more cost-effective for large-scale manufacturing.

## HYDROGEN PRODUCTION TECHNIQUES

Hydrogen is an energy source that can be used as an alternative to traditional fossil fuel in fuel cells<sup>24</sup> or combustion engines<sup>18</sup> without producing greenhouse gas emissions when combusted with oxygen<sup>24</sup>. Furthermore, Table 1 illustrates the characteristics of hydrogen's combustion that distinguish it from natural gas and make it a suitable alternative<sup>25, 26</sup>.

**Table 1.** Typical combustion properties of natural gas and hydrogen

Typical combustion property	Natural gas	Hydrogen gas
Flash Point,	-188 °C	-253 °C
Flammability Limits	LFL 4 -UFL 15	LFL 4 -UFL 75
Autoignition temperature	537 °C	537-585 °C
Minimum Ignition Energy	0.29 MJ	0.02 MJ
Burning Velocity	0.36 m/s	3.35 m/s
Flame Temperatures	1953 °C	2127 °C
Heating value	21500–24000 Btu/lb	51500–61084 Btu/lb
Expansion ratio	1:600	1:848

Although the chemical properties of hydrogen are distinguished from natural gas, especially the high heating value that reaches three times the heating value of natural gas<sup>27, 28</sup>, the properties of storage and use are more hazardous; a substance's flammability risk is increased when the following factors are present<sup>29, 30</sup>:

- Wide flammability limits (fuel-to-air concentrations): hydrogen has a more comprehensive flammable range (4–75%) compared to natural gas's flammable range (4–15%). Thus, hydrogen is considered a relatively highly hazardous fuel since it has a higher probability of ignition than natural gas. The gas is too lean or rich to burn below the Lower Explosive Limit (LEL) and above the Upper Explosive Limit (UEL).

- Low minimum autoignition temperature: Same temperature for both fuels.

- Low minimum ignition energy: The energy required to ignite hydrogen is about 14 times more than that needed to ignite natural gas.

- High burning velocity: The burning rate for hydrogen is almost ten times greater than for natural gas.

- Increasing the temperature of the fuel or the flame temperature: The flame temperature of a hydrogen flame is 174°C greater than that of a natural gas flame.

- Oxygen-enriched atmosphere.

Hydrogen does not exist independently on Earth, but it is found combined with other elements in compounds such as water. To produce it independently requires separating it from elements combined in water or fossil fuels. Outlines how this separation will achieve sustainable hydrogen energy. Hydrogen is produced commercially with 70 million metric tons annually from non-renewable and renewable resources<sup>31</sup>, such as natural gas steam reforming<sup>32</sup> or steam methane reforming process (SMR)<sup>33</sup>, oil reforming<sup>34</sup>, coal gasification<sup>35</sup>, biomass<sup>36</sup>, nuclear power reactors<sup>37</sup>, water electrolysis thermolysis

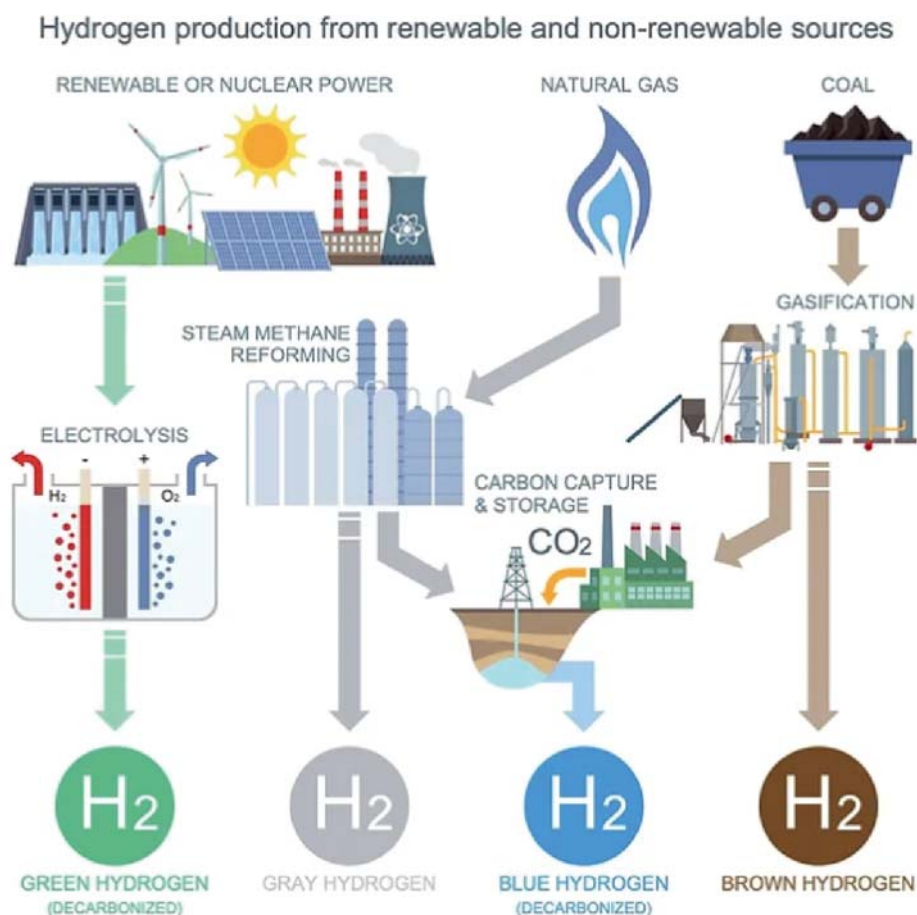


Figure 5. Hydrogen production from non-renewable and renewable sources<sup>40</sup>

and thermochemical cycles technologies<sup>38,39</sup> as illustrated in Figure 5.

The color of hydrogen indicates the source of hydrogen generation and the quantity of greenhouse gases released throughout the process. Carbon-rich resources, such as coal, are extracted and converted into hydrogen and carbon dioxide to produce brown hydrogen. Blue hydrogen is made from the steam reforming process; however, it varies from grey hydrogen in that the emitted carbon emissions are caught and stored. The steam reforming process, which is used to separate hydrogen from natural gas, produces grey hydrogen; this method does not require the release of carbon dioxide.

On the other hand, green hydrogen does not produce any emissions during its whole life cycle because it uses renewable energy sources for its creation<sup>41,42</sup>. One of the factors contributing to the increased interest in green hydrogen is the worldwide trend toward the exploitation of renewable energy sources, which has caused their prices to decrease dramatically. As a result, the rate of carbon emissions must drop significantly, and clean power for industry and transportation must be made available. Green hydrogen production methods are categorized based on the driving energy sources and applications. Figure 6 illustrates the several routes using diverse energy that may be utilized to produce green hydrogen.

Another factor in categorizing these systems is the quantity of energy sources used to produce green hydrogen. Various green hydrogen production techniques, such as electrolysis, thermolysis, thermic analysis, etc., use just one energy source. Other techniques, known as hybrid

techniques, use two energy sources simultaneously, such as photo-electrolysis, bio-photolysis, thermophilic digestion, etc. All these production methods are classified and listed in Table 2.

Via these various production techniques, each has benefits and drawbacks, as listed in previous reviews and studies<sup>45–48</sup>. The water electrolysis process is one of the progressive methods used to produce green hydrogen. It is driven by a continuous movement of electrons through an external circuit, using a direct electrical current to decompose water molecules into oxygen and hydrogen inside an electrolyzer<sup>49</sup>. Therefore, this review will focus on green hydrogen production through water electrolysis.

## WATER ELECTROLYSIS TECHNOLOGIES

In recent years, electrochemical techniques have reached an impressive level of effectiveness and efficiency compared to other hydrogen production technologies<sup>45,50,51</sup>, especially considering the multiple applications of these technologies. Numerous studies have studied the operational conditions, diversity, sophistication of designs<sup>52</sup>, and the advantages of scale-up electrochemical techniques<sup>53,54</sup>. Electrolysis is the electrochemical decomposition of water ( $H_2O$ ) into hydrogen ( $H_2$ ) and oxygen ( $O_2$ ) under the influence of electricity, as demonstrated in the following reactions (equations 1–3)<sup>55</sup>. Especially for water electrolysis processes operated in constant current mode at elevated temperatures to speed up homogeneous/heterogeneous reactions, these processes required only economically physical pretreatment for continuous production.

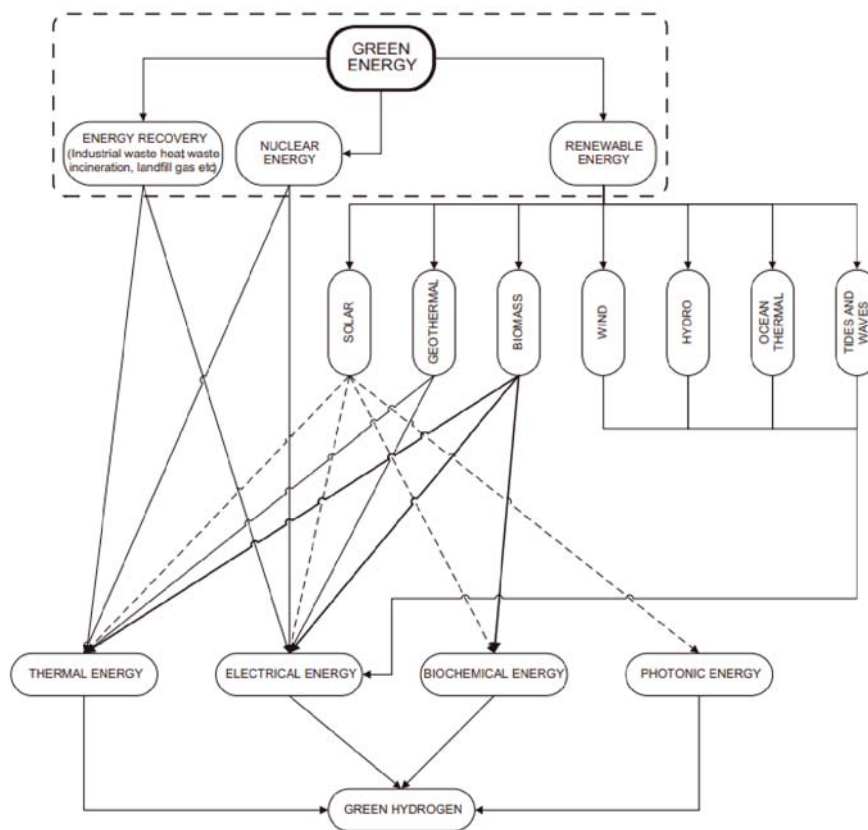
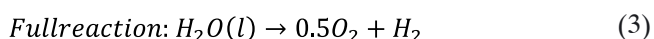
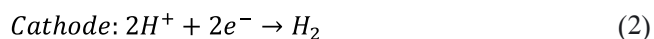
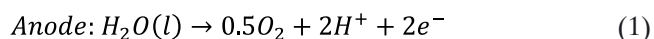


Figure 6. Green hydrogen production routes from renewable energy sources<sup>43, 44</sup>

Table 2. Green hydrogen production technologies are categorized according to several driving energy sources<sup>43, 44</sup>

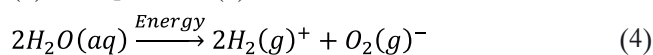
Hydrogen production method	Hydrogen extraction material sources	Driving energy
Production methods use one energy source		
Electrolysis	Water	Electrical
Thermolysis	Water	Thermal
Thermocatalysis	Hydrogen sulfide	
Thermochemical processes	Biomass water/water Biofuels Hydrogen sulfide	
PV-electrolysis	Water	Photonic
Photo-catalysis		
Photo-electro-chemical method		
Bio-photolysis		
Dark fermentation	Biomass	Biochemical
Enzymatic	Water	
Production methods use two energy sources (hybrid techniques)		
Photo-electrolysis	Water	Electrical + Photonic
Thermophilic digestion	Biomass	Biochemical + Thermal
Bio-photolysis	Biomass, water	Photonic+ Biochemical
Artificial photosynthesis		
Photo-fermentation		



In the simplest form, an electrolytic cell consists of two electrodes (anode and cathode). These two electrodes are submerged in an electrolyte, a liquid that conducts electricity. An electrical circuit links anode and cathode electrodes with a current source and a control device outside the solution; oxidation and reduction reactions inside the electrolysis cell occur at the electrode-electrolyte interface. At the cathode, reduction takes place, while at the anode, oxidation takes place. The cathode is the electrode associated with decrease. For an electrochemical cell, the current flow is maintained by the

electrons that are produced as a result of the driving force of the electrical source<sup>56</sup>.

According to the investigation’s findings into the thermodynamic behavior of fluids and energy involved in the chemical reaction that occurs during the process of electrolytic water separation, the reaction is not spontaneous (endergonic) at room temperature. It requires the injection of external energy for it to take place. The calculation details of the free energy (of water electrolysis chemical reaction (Equation (4)) includes the change in the thermodynamic quantities are listed from Equations (5) to Equations (7)<sup>55, 83</sup>:



$$\Delta H = \sum nH_{Products} - \sum nH_{Reactants} \quad (5)$$

$$\Delta S = \sum nS_{Products} - \sum nS_{Reactants} \quad (6)$$

**Table 3.** Calculations for the change in free energy

Quantity	2 H <sub>2</sub> O	2 H <sub>2</sub>	O <sub>2</sub>	Change
Enthalpy ( $\Delta H$ )	2 x (-285.83) kJ	0	0	$\Delta H = + 285.83$ kJ
Entropy ( $\Delta S$ )	2 x 69.91 J/K	2 x 130.68 J/K	205. 14 J/K	$T\Delta S = 48.7$ kJ
Free energy ( $\Delta G$ )	-237.1	0	0	$\Delta G = +237.1$ kJ

$$\Delta G = \Delta H - T\Delta S \quad (7)$$

Where  $\Delta G$  is the change in free energy,  $\Delta H$  is the enthalpy change, and  $T\Delta S$  is the thermal entropy change. Table 3 shows the calculated values for the difference in free energy, thermal entropy, and enthalpy for the water electrolysis reaction.

The thermodynamic decomposition of water requires a direct electric current (DC) or electric energy necessary to sustain the electrolysis. The water electrolysis process is accompanied by the liberation of gases (hydrogen and oxygen), a change in internal energy, and the system's enthalpy. Enthalpy is essential in determining the energy needed to continue the decomposition process. Since the reaction showed that the  $|\Delta H| \gg |T\Delta S|$  as shown in Table 3, the reaction is enthalpy-driven, which will contribute to changing the sign of the free energy of formation to negative in the process of water split. Also, internal energy will change during the decomposition process, increasing thermal entropy ( $T\Delta S$ ) and contributing energy to the reaction. This energy is 48.7 kJ; thus, the external electrical energy required for water decomposition is 237.1 kJ instead of 285.83 kJ. The temperature of the water electrolyzer helps in the electrolysis process. It increases the process efficiency, increases the demand for decomposition, and reduces the required electricity to split the water into hydrogen and oxygen, reducing the cost of the produced hydrogen. Temperature is one of the most essential parameters in electrolysis and should be considered in the process design. The free energy ( $\Delta G$ ) helps the flow of electrons through a conductive electrolyte, and the free energy in the standard electrochemical cell can be expressed by Equation (8)<sup>83, 84</sup>.

$$\Delta G_0 = -nFE_0 \quad (8)$$

$E_0$  represents the standard cell potential (V),  $n$  represents the number of electrons, and  $F$  represents the constant 96,485 (C) that Faraday uses. In Equation (8), the free energy ( $\Delta G_0$ ) depends on the input volts to the cell or the system, assuming perfect faradaic efficiency. At the optimal conditions for the reaction, the quantity of hydrogen created is twice as much as the quantity of oxygen produced, and both amounts are proportional to the total electrical charge that is carried by the solution. Industrial wastewater could be used instead of pure water in electrolysis. Alkaline industrial plant wastewater is recommended for use in the electrolysis process because it is easier to control corrosion and allows for using less expensive building materials than acidic water electrolysis technology<sup>87-89</sup>. Because the oxygen evolution reaction is so slow, the typical water electrolysis process has a large overpotential, which causes it to be overpotential. The hybrid water electrolysis (electrocatalysts) technique was used instead of the conventional electrolysis process mainly to overcome this problem by speeding up the reaction rate and improving current density<sup>57, 58</sup>. A homogeneous or heterogeneous catalyst

was utilized in the electro catalyst method to promote hydrogen synthesis with chemical species' assistance<sup>59-62</sup>. Homogeneous catalysts are more economical and have a greater turnover rate than the rare metals that are frequently utilized; they can be suspended or dissolved in the electrolyte as a favorable option. During electrolysis, platinum is typically put into the electrodes to carry out heterogeneous catalysis, which is done to conduct the procedure<sup>43, 63, 64</sup>.

### PRODUCE HYDROGEN ECONOMICALLY AND EFFICIENTLY

Producing hydrogen capably means that this technique gives the user the flexibility to design the cell and electrodes, minimize the power consumption, and control the potentials because it has lower temperature requirements than non-electrochemical processes. Overpotentials at the anode are the principal cause of energy loss during oxygen evolution in water electrolysis because the oxygen evolution reaction (OER) functions sluggishly.

Although the evolution of hydrogen is produced by the action of the cathode electrode, attention and appropriate selection of the positive electrode are very important<sup>65</sup>. In the electrochemical process, some electrodes can be used as active anodes, which use low voltage for oxygen evolution and are suitable electro catalysts for oxygen evolution reactions. It also exhibits a high oxidation state, where the used water is oxidized indirectly by absorbed hypochlorite ions ( $\text{ClO}_2$ ), facilitating complete combustion. An example of these electrodes, ruthenium oxide ( $\text{RuO}_2$ ), is a notable electrode in the industry because it is widely used to produce chlorine ( $\text{Cl}_2$ ) and oxygen ( $\text{O}_2$ ) gases with exceptional chemical stability<sup>66, 67</sup>. Also,  $\text{RuO}_2$  has suitable conductivity and barrier properties against oxygen diffusion, with adopted stability at elevated temperatures (up to 800°C) and high cell potentials<sup>68</sup>. Another example is iridium dioxide ( $\text{IrO}_2$ ), considered one of the most active materials for oxygen evolution reactions (OER) during water electrolysis<sup>69, 70</sup>. This anode exhibits an excellent trade-off between catalytic activity and alkaline/acidic media stability. However, it is highly costly since iridium is one of the least abundant elements on Earth<sup>71</sup>. Many noble metal oxides have been studied in recent years. They can be used in acidic and alkaline environments, such as platinum oxide ( $\text{PtO}_2$ ), rhodium dioxide ( $\text{RhO}_2$ ), cobalt (Co), nickel (Ni), and iron (Fe) based electrodes<sup>72, 73</sup>. The density functional theory (DFT) applied to investigate the electronic structure found the OER activity decreasing in the order of  $\text{RuO}_2 > \text{IrO}_2 > \text{PtO}_2 > \text{RhO}_2$ . Another testing parameter for the OER is the charge transfer resistance ( $R_{ct}$ ). The transfer resistance testing values for these catalysts drop as the overpotential increases, revealing that charge transfer occurs more efficiently at the surface of  $\text{RuO}_2$  metal oxide than at the surface of the other catalysts. demonstrates the resistance of charge transfer for catalysts made of  $\text{RuO}_2$  and  $\text{IrO}_2$ <sup>74</sup>. Figure 7 Explain the Charge transfer resistance for  $\text{RuO}_2$  and  $\text{IrO}_2$  catalysts.

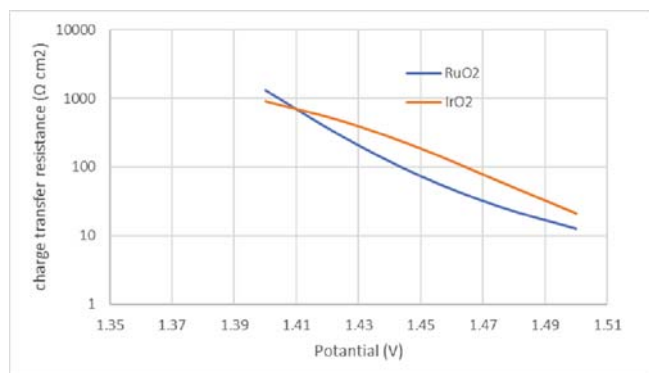


Figure 7. Charge transfer resistance for RuO<sub>2</sub> and IrO<sub>2</sub> catalysts<sup>74</sup>

Various types of electrochemical reactors can be used for hydrogen production. Such as the parallel plate reactor<sup>75</sup>, flow cell mesh anode<sup>76, 77</sup>, rotating disc reactor<sup>78</sup>, cylindrical reactor<sup>79</sup>, advanced three-dimensional electrodes [80], and the conventional stack cell, etc.<sup>81</sup>. The electrochemical reactors' efficiencies are affected by several conditions, such as current density, supporting electrolyte concentration, initial pH, circulation flow rate, electrode material, and electrolysis duration<sup>62, 82</sup>. Figure 8 shows the input and output parameters during the water electrolysis process.

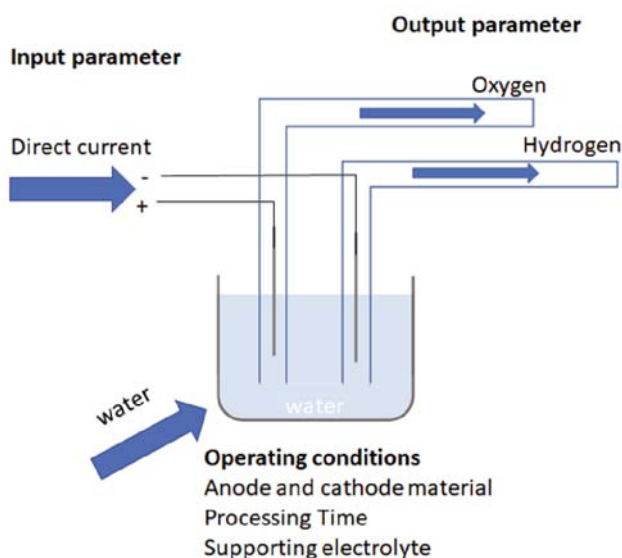


Figure 8. Input and output parameters in the electrochemical cell

According to Equation (3), the theoretical volume of hydrogen and oxygen gases that form during the electrolysis process can be calculated using the following equations<sup>55, 83, 84</sup>, which suppose an ideal water electrolysis efficiency.

$$V_{H_2} \left( \frac{L}{min} \right) = \frac{R(273 + T)}{P} \left( \frac{L}{mol} \right) \frac{t(60s)}{min} \frac{I(A)}{F \left( \frac{SA}{mol} \right)} \quad (9)$$

$$V_{O_2} \left( \frac{L}{min} \right) = \frac{R(273+T)}{P} \left( \frac{L}{mol} \right) \frac{t(60s)}{min} \frac{I(A)}{F \left( \frac{SA}{(0.5)mol} \right)} \quad (10)$$

Where  $V_{H_2}$  and  $V_{O_2}$  are the extracted hydrogen and oxygen (L/min),  $T$  is the temperature (°C),  $t$  is the time (min),  $P$  is absolute pressure (atm),  $I$  is the applied current (A),  $R$  is the universal gas constant ( $0.082 \text{ L}\cdot\text{atm}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$ ),

and  $F$  is the Faraday constant ( $96485.33 \text{ sA/mol}$ ). Figure 9 shows the theoretical volume of hydrogen and oxygen gases that can be extracted during the electrolysis process of water, assuming the efficiency of the process is 100% and at standard conditions of temperature and pressure (STP). In the electrolysis of water, the volume of hydrogen doubles the volume of oxygen because the number of mols of hydrogen resulting from the electrolysis is always double, and each mol of gas occupies the same volume. For example, at a current density of 30 A, the volume of liberated oxygen is 0.21 (L/min), while the volume of liberated hydrogen is 0.42 (L/min).

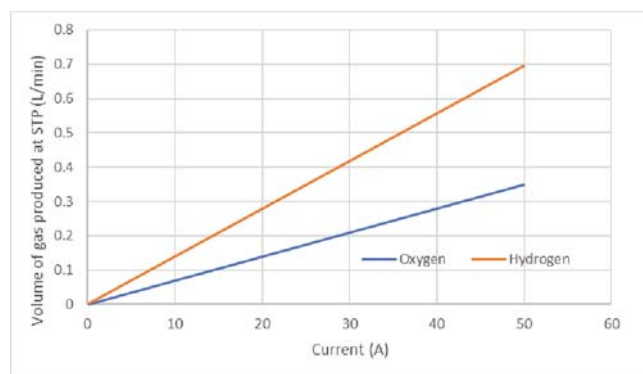


Figure 9. The theoretical volume of hydrogen and oxygen gases during the water electrolysis process

Evaluation of either the oxygen evolution reaction (OER) or the hydrogen evolution reaction (HER) is the method that is utilized to ascertain the effectiveness of the water electrolysis process. Therefore, the efficiency of the electrolysis process might be described as the ratio between the volume of a gas value that was measured experimentally (either oxygen or hydrogen) and the volume of gas value that was calculated theoretically, as demonstrated in the Equation that follows<sup>55, 84, 85</sup>:

$$\eta = \frac{V_{gas}(measured)}{V_{gas}(calculated)} \quad (11)$$

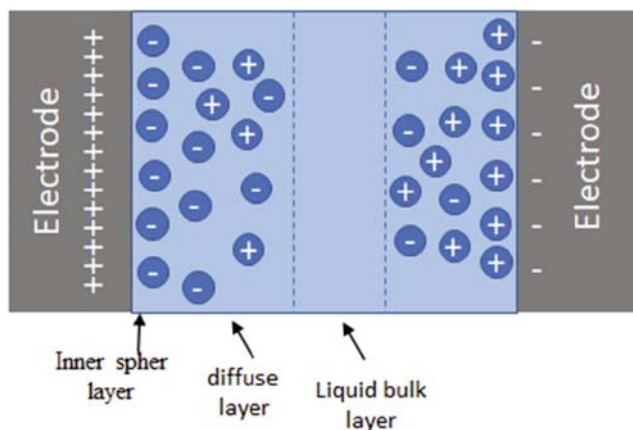
#### CONTROL ON ELECTRON TRANSFER REACTIONS (ET)

The energy provided by an electrochemical reactor is a crucial parameter in electrolysis. It will give the electrons required for the splitting of water. The following steps are involved in an electrolysis process.

- The electroactive solid phase is transferred to the immersed electrode surface in the solution.
- The electroactive particles are adsorbed on the electrode surface.
- Electron transfer occurs between the solution bulk and the electrode surface.
- The reacted particle is either desorbed to the solution bulk or deposited on the electrode surface.

Based on the four steps mentioned above, electron transfer between the solution and electrode interface is crucial in electrochemical reactions since the electrode interface transforms electrical energy into chemical energy. The electric double layer (EDL) is the interfacial area between the electrode and electrolyte that affects the electron transfer process. Figure 10 shows the elec-

tron distribution at the electrode/electrolyte interface. In EDL, the close layer to the electrode surface where the reactant is in direct contact with the electrode surface is named the inner-sphere electron transfer layer. In addition, the electron outer-sphere transfer layer is responsible for the relatively weak connection between the electrode and the reactant. Because the reactant is not directly in contact with the surface of the electrode, the charge on the outer-sphere layer may only sometimes be sufficient to counteract the charges on the metal. As a result, the diffuse layer, which is adjacent to the outer sphere but diminishes away toward the bulk of the solution, is further created. The potential drop appears through the double-layer electric interface with the distance from the electrodes until the potential of the diffuse layer exponentially decays.



**Figure 10.** A schematic diagram of electrochemical electron distribution across the electrode-electrolyte interface

It is possible to use the formula to describe the mass transfer coefficient that occurs in an electrochemical reactor<sup>83, 84</sup>:

$$m = D/\delta \quad (12)$$

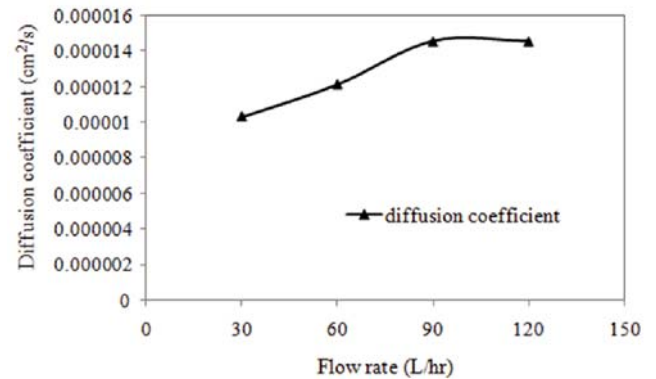
Where  $m$  represents the mass-transfer coefficient in cubic centimeters per second,  $D$  represents the diffusion coefficient in cubic centimeters per second, and  $\delta$  represents the thickness of the diffusion layer in cubic centimeters. At a temperature of 25 degrees Celsius, the Nernst-Haskell equation can be used to determine the total diffusivity of the tracers (NaCl) while they are present in the reactor<sup>85</sup>:

$$D = 8.928 \cdot 10^{-10} \cdot T \cdot \frac{\left(\frac{1}{n_+} + \frac{1}{n_-}\right)}{\left(\frac{1}{\lambda_+} + \frac{1}{\lambda_-}\right)} \quad (13)$$

Given that  $D$  represents the diffusion coefficient in cubic centimeters per second,  $n_+$  represents the valence of the cation and  $n_-$  represents the valence of the anion, the limiting ionic conductance in water is ( $\lambda_+ = 50.1$  and  $\lambda_- = 76.3$ ), where  $A/cm^2$  and  $V/cm$  are measured in gram equivalents per square centimeter, and  $T$  is the temperature in Kelvin. When the reactor's mixing condition is considered, the tracer's diffusion coefficient can be computed. Because the diffusion coefficient is dependent on the flow rate at which the tracer is introduced into the reactor. Since this is the case, Equation (13) can be expressed as follows<sup>83, 84, 85</sup>:

$$D = 8.928 \cdot 10^{-10} \cdot T \cdot \frac{\left(\frac{1}{n_+} + \frac{1}{n_-}\right)}{\left(\frac{1}{\lambda_+} + \frac{1}{\lambda_-}\right)} \cdot \frac{t_p}{\tau} \quad (14)$$

The diffusion coefficient of the tracer is depicted in Figure 11 for every possible flow rate. According to the findings, the diffusion coefficient rises as the flow rate increases, reaching its highest point at 90 liters per hour with the highest possible value. When the flow rate is increased beyond 90 liters per hour, there does not appear to be any discernible improvement in the diffusion coefficient, which could be because raising the flow rate does not create further turbulence.



**Figure 11.** The diffusion coefficient at  $Q = 30, 60, 90$  and  $120$  L/h

Eq. (15) below lists the general equations for the mass transfer-limited currents for tubular cell geometries<sup>40</sup>. Equation (16) can be used to express the limiting current<sup>40, 84, 85</sup>:

$$i = 1.61 \cdot nFCQ^{1/3} \left(\frac{DA}{r}\right)^{2/3} \quad (15)$$

$$i = nFAmC \quad (16)$$

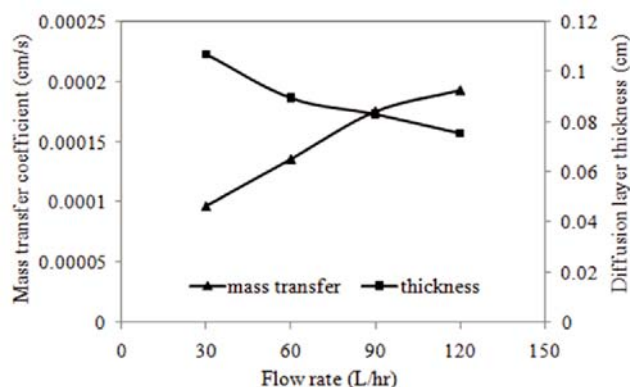
Where  $A$  is an electrode area ( $cm^2$ ),  $C$  is the solution concentration in ( $mol/cm^3$ ),  $D$  is the diffusion coefficient ( $cm^2/sec$ ),  $F$  is the Faraday's constant ( $96500 C mol^{-1}$ ), is the limiting current ( $A$ ),  $m$  is the mass-transfer coefficient ( $cm/sec$ ),  $n$  is the stoichiometric number of electrons involved in an electrode reaction,  $r$  is the tubular electrode radius ( $cm$ ), and  $Q$  is the average volume flow rate ( $cm^3/sec$ ). The diffusion layer thickness, denoted as  $\delta$ , can be obtained by substituting equations (15 and 16) into Equation (12). which allows for the calculation of the distance from the electrode surface, denoted as  $d$ , in centimeters<sup>40, 83, 84, 85</sup>:

$$\delta = 0.62 \cdot (d/t)^{-1/3} r^{2/3} D^{1/3} \quad (17)$$

The inversely proportional between the distance and diffusion layer thickness is shown in Figure 12. According to this figure, increasing the distance between the electrode and the bulk solution will reduce the thickness of the diffusion layer and increase the mass transfer coefficient<sup>86</sup>. It is possible to utilize the concentration gradient layer to describe how the mass transfer coefficient affects the distance between electrodes. When the distance between electrodes grows, the concentration gradient layer close to the electrode surface becomes thinner, increasing the responding ion's transport force. The transport force of the responding ion will grow as the diffusion layer becomes thinner when the concentration difference remains the same. As a result, the mass transfer coefficient will also.

The energy formed will cause hydrogen to appear in the cathode, while oxygen will appear in the anode. The



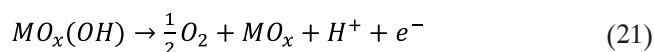
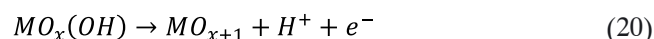
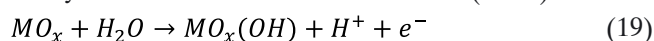


**Figure 12.** Diffusion layer thickness and mass transfer coefficient as a function of flow rate  $Q = 30, 60, 90, 120$  L/h

movement of electrons caused by the electrical source's driving force between the electrodes maintains the current flow in an electrochemical cell. The more unstable electrons will move from the anode electrode to the regions with the fewer electrons and the most stable, which is the cathode electrode; thus, the process of electrolysis of water will be a sustainable process to produce hydrogen and oxygen gases with the availability of electrical energy and electron occurrence. The method in which the cathode gains electrons is called reduction, in contrast to oxidation, which involves the anode losing electrons. The oxidation and reduction reactions (redox reaction) could describe the transferring process of electrons<sup>40, 83</sup>.



Where  $O_x$  is the oxidizing agent (oxidant, oxidizer),  $R_d$  is the reducing agent (reductant or reducer), and  $n_e$  is the number of electrons. The essential roles of catalysts and oxide catalysts are participating in redox reactions and mediating electrochemical electron transfer (ET) reactions. The following equations provide a generic strategy for the electrochemical oxidation reaction on the catalytic anode coated with metal oxide ( $MO_x$ )<sup>40, 83, 84, 85</sup>:



Electron transfer theory in an electrochemical system is a means to determine redox transitions within the solution or to study the properties and potential applicability on the electrode surface to investigate the activation of hydrogen, oxygen, water, and carbon oxide molecules. Equation 21 explains how the adsorbed hydroxyl, also known as physisorbed active oxygen, is created at the electrode surface by hydrolyzing a water molecule. While forming the higher oxide  $MO_{x+1}$  (Equation 22), chemisorbed active oxygen, the adsorbed hydroxyl produced interacts with the oxygen already in the oxide anode. The chemisorption amount is inversely related to the density of states in the electrode material and reflects its electronic structure; electrical interactions in chemisorption cause the binding between the reactant molecules to break.

## CONCLUSIONS AND REMARKS

Hydrogen is a resourceful energy source that can assist in overcoming several pressing energy-related problems. Today, hydrogen is mainly used as a renewable energy source, thus responsible for a significant annual reduction of carbon dioxide emissions. Numerous processes could produce hydrogen; water electrolysis is one of these promising methods. This review identifies and categorizes the main methods and material sources used to make green hydrogen. Also, this review focuses on the water electrolysis process as an environmentally friendly green hydrogen production technique that needs to be more economical for large-scale production. The report closed with research and development suggestions. The theoretical volume of gaseous hydrogen and oxygen that could be produced by electrolyzing water under typical temperature and pressure (STP) circumstances, assuming a 100% efficiency rate of the process. Since there are always two moles of hydrogen produced by electrolysis and one mole of gas occupies the same volume, the volume of hydrogen developed from water is twice that of oxygen. The volume of liberated oxygen is 0.21 (L/min), and the volume of liberated hydrogen is 0.42 (L/min) with a current density of 30 A, for instance—the tracer's diffusion coefficient for all conceivable flow rates. A maximum value of 90 liters per hour was determined to be the threshold at which the diffusion coefficient increased with increasing flow rate. It would appear that the diffusion coefficient remains unchanged at flow rates greater than 90 liters per hour.

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## SYMBOLS AND CHARACTERS

- (LEL) – Lower Explosive Limit
- (UEL) – Upper Explosive Limit
- ( $\Delta H$ ) – Enthalpy
- ( $\Delta S$ ) – Entropy
- ( $\Delta G$ ) – Free energy
- (DC) – direct electric current
- $E_0$  – standard cell potential(V)
- $n$  – number of electrons
- $F$  – Faraday constant (96485.33 sA/mol)
- (OER) – oxygen evolution reaction
- ( $ClO^-$ ) – hypochlorite ions
- ( $RuO_2$ ) – ruthenium oxide
- ( $PtO_2$ ) – platinum oxide
- (DFT) – density functional theory
- ( $R_{ct}$ ) – charge transfer resistance

$V_{H_2}$  and  $V_{O_2}$  – the extracted hydrogen and oxygen (L/min)  
 R – universal gas constant ( $0.082L \cdot atm \cdot K^{-1} \cdot mol^{-1}$ ),  
 (STP) – standard conditions of temperature and pressure  
 (ET) – Electron Transfer Reactions  
 (EDL) – electric double layer.

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