A Precursor Study for Modification of Hydrogen Production by Electrolysis

Relebohile Mokete^{1*}, Frantisek Miksik², Nobuo Takata¹, Kyaw Thu^{1,2}, Takahiko Miyazaki^{1,2}

1 Department of Energy and Environmental Engineering, Interdisciplinary Graduate School of Engineering Sciences,

Kyushu University, 6-1 Kasuga-koen, Kasuga-shi, Fukuoka 816-8580, Japan

2 Research Center for Next Generation Refrigerant Properties (NEXT-RP),

International Institute of Carbon-Neutral Energy Research (I2CNER), Kyushu University

744 Motooka, Nishi-ku, Fukuoka 819-0395, Japan

ABSTRACT

Various technologies for renewable energy need to be employed for sustainability and the hydrogen production through water electrolysis (WE) is one of the green energy approaches. In this study, solar energy was used for splitting sodium chloride solution into hydrogen gas using an experimental electrolyzer, while the hydrogen production and the performance of the PV cell were evaluated. The incoming solar radiation ranged from 810.1 W/m² to 637.8 W/m² whereas the respective atmospheric temperature increased, and humidity subsequently decreased. The efficiency of WE (η_F) was 61.8% and the PV cell efficiency (η_{SP} ; at temperature; 25.5°C, humidity; 42.2% and I_R; 810.1 810.1 W/m²) was 12.7%. The H₂ production was coupled with voltage drop whose minimization needs to be addressed in future research along with improvement of efficiency and costeffectiveness.

Keywords: renewable energy, water electrolysis, salt electrolysis, hydrogen gas, proton exchange membrane, solar energy

NONMENCLATURE

Abbreviations	
WE	Water Electrolysis
PEM	Proton Exchange Membrane
DI	Deionized
SE	Salt Electrolysis
IEM	Ion Exchange Membrane

PV	Photovoltaic
CA	Cell Area
out	Output
in	Input
max	Maximum
cum.	Cumulative
non-cum.	Non-cumulative
Symbols	
Р	Power
I _R	Irradiance
η _{sp}	PV cell efficiency
η _F	WE efficiency
V_{H_2real}	Real H ₂ volume
$V_{H_2 ideal}$	Ideal H ₂ volume
I	Current
t	Time
F	Faraday's constant
α	Number of electrons

1. INTRODUCTION

The energy demand has led to the high usage of fuel sources that negatively affect the environment. The fossil fuels result in greenhouse gas emissions that lead to climate change and the examples of such include coal which emits carbon dioxide gas among others [1]. The use of fossil fuels has been notable since the 18th century and this usage is subject to human development [2]. It is therefore a global concern to minimize the pollution by resorting to renewable energy forms to ensure sustainable energy systems [3]. Green energy includes,

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amongst others, the main renewable sources namely wind, hydro and solar. However, all these systems are affected by weather conditions and require storage due to their intermitted nature [4].

Hydrogen is a very promising energy form since it can be used directly as a fuel as well as a storage system [5]. WE is a process that produces hydrogen as a renewable energy form and it is simply related to the splitting of water into hydrogen (H_2) and oxygen (O_2) gases under the influence of electricity [3, 6]. When the electricity is applied, water splits to oxygen in the anode chamber along with generation of protons and electrons. The electrons produced in the anode chamber go through an external electron path to the cathode. Meanwhile, the protons travel through a PEM to combine with electrons in the cathode thus interacting to form hydrogen gas [7-8].

Although WE is suitable in pure water applications, the vast forms of available water sources have led to the exploration of various modifications of water commercialization of PEM electrolyzers but research has contributed in slowly availing the WE technology. In their study, Feng et al [11] recovered salt from hydrazine hydrate (N₂H₂) to produce NaOH through IEM electrolysis and they successfully removed other impurities that affect the electrolysis at a reasonable cost. Accordingly, in desalination systems, the emphasis on solar energy technology has been attributed towards the electricity generation but the research that focuses on desalination and hydrogen production also requires more attention [12]. The aim of this research is to use salt solution electrolysis in order to understand the underlying principles of H₂ production via WE and to form a baseline reference of improving the WE system. Also, the incoming solar radiation that initiates electrolysis has been measured.

2. MATERIAL AND METHODS

2.1 Materials



Fig. 1. Hydrogen generation through electrolysis of Salt water

experimentally, particularly to improve the conductivity such as by using acid/alkaline media or salt addition to DI water [9]. This, therefore, makes the WE to be widely applicable in desalination systems, for instance, and it is coupled with hydrogen gas generation [10]. The WE process slightly changes upon the addition of salt to water (also known as SE) and application of the electrical energy whereby chlorine and hydrogen gases are produced in the cathode and anode chambers respectively [11]. The representative schematic diagram for the SE process is shown in Fig 1.

Ferriday et al. [1] indicated that the cost of a PEM applied for WE had been a major limitation for the

The DI water and table salt (NaCl) were used as the main materials for SE. The used electrolyzer was composed of an IEM and electrodes. The cathode and anode as per the manufacturer's specifications were metals that include titanium, ruthenium and platinum. The rubber stoppers were used for closing the electrolyzer whereas the backflow prevention valves were used for the connection of the electrolyzer with the gas storage system. Current, voltage, and temperature were recorded using the multimeter (BTMETERBT-42B, Japan) whereas the hydrogen volume was measured using gas storage tank (Fuel Cell Store, USA) which uses the principle of water volume displacement. The power source used was a 5W PV cell with the area of 19.5cm × 25cm and the incident angle was around 90°C. Figure 2 shows the pictorial view of the experimental unit highlighting the PV cell and the electrolyzer. The pyranometer (EKO, Japan) was used for determination of incident solar radiation whereas the temperature and humidity were measured with a digital sensor (SHT, Japan).



Fig. 2. Hydrogen generation through electrolysis of Salt water

2.2 Procedure

The cathode and anode chambers were filled with water (150ml) where 1g of NaCl was added on the anode chamber. The system was then connected to the PV cell. The values of the current, voltage, H_2 volume and temperature were recorded. The overall time for the experiment was 1 hour 15 minutes and the results were recorded every 15 minutes. Within the same time interval, the hydrogen production with respect to received solar radiation was recorded.

2.3 Theory/calculation

With reference to section 1, the overall concept of electrolysis is represented in equations (1-3) [11]:

(1

Anode	<i>reaction</i> : H	$l_2 0 \rightarrow$	1/2 0₂ + 2H [°]	+ + 2e ⁻ (2)

Overall reaction: $H_2O \rightarrow H_2 + 1/2 O_2$ (3)	(3))
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The SE, which slightly differs from the WE, follows equations (4-6). Simply, H_2 and Cl_2 are generated at the cathode and anode respectively when the NaCl solution experiences electrical energy and another product that is formed is NaOH.

Cathode reaction:
$$2 H_2O + 2e^- \rightarrow H_2 + 2OH^-$$
 (4)

Anode reaction:
$$2CI \rightarrow Cl_2 + 2e^-$$
 (5)
Overall reaction: $2NaCl + H_2O \xrightarrow{electrolysis}$
 $2NaOH + H_2 + Cl_2$ (6)

Additionally, the ratio of the cell's power output (P_{out}) also known as maximum power output (P_{max}) to that of the power input (P_{in}) was used to define the PV cell efficiency (Π_{SP} , equation 7) where P_{in} is mainly the product of irradiance ($I_R = 810.1 \text{ W/m}^2$) and cell area (CA; m²) [13]. For Π_{SP} , the calculations were based on actual measurements instead of standard values. Furthermore, the WE efficiency (Π_F) is expressed in relation to Faraday's law and it is given as the real H₂ volume to the ideal H₂ volume ratio as shown in equation 8. Equation 9 shows ideal H₂ volume where I, t, V_M, α and F represent current (mA), time (sec), molar volume of ideal gas in standard conditions (24 L/mol), number of electrons and Faraday's constant (96 498.3 C/mol), respectively [14].

$$\begin{aligned} \eta_{SP} &= \frac{P_{out}}{P_{in}} = \frac{P_{max}}{P_{in}} = \frac{P_{max}}{P_{in}} = \frac{P_{max}}{I_R * CA} \times \end{aligned} \tag{7} \\ 100$$

$$\Pi_E = \frac{V_{H_2real}}{V_{H_3ideal}} \times 100$$
⁽⁸⁾

$$V_{H_2ideal} = \frac{I \times t \times V_M}{2 \times F}$$
(9)

3. RESULTS AND DISCUSSIONS

Both the changes in voltage and current over time are reported in Fig. 3.a whereas the cumulative and noncumulative H₂ volume (cm³) as well as the temperature change over time are presented in Fig. 3.b and c, correspondingly. From Fig.3.a, it is noted that the current and voltage increased in the first 30 minutes after which the voltage sharply decreased whereas the current slightly increased although it was generally low (0.306A). This is attributable to various factors such as the thermal losses in the PV cell that increase with increasing solar intensities [15]. Accordingly, as heat is absorbed by the electrolyte, the reaction kinetics are enhanced leading to more efficient hydrogen production, but this is accompanied by the generation of waste heat that affects the system hence cooling methods have been suggested as a counter solution [16]. This therefore validates the H₂ production that was observable within the first hour of the reaction followed by a slight decrease and this is almost the similar trend to that of temperature (Fig. 3.c).



Fig. 3. Voltage and current results (a.) along with H₂ volume (b) and temperature change (c)

The slight temperature decrease maybe subject to waste heat as well as solar intensity fluctuation. The reversible degradation plays a role in increased current densities and it is attributed to ohmic resistance hence ohmic voltage drop or mass transport which are evident [17]. Also, the formation of bubbles result in energy loss and the factors that affect the ionic transfer within the electrolyte include electrolyte concentration and membrane state [18]. The voltage drop is attributed to the adsorption of ions on the membrane and the presence of organic impurities hence this affects the membrane's overall performance [11]. Therefore, changing the electrolyte concentration or replacing the membrane as well as adding appropriate additives may improve the conductivity [18]. Table 1 lists the respective average efficiency of WE which is 61.8% whereas the PV cell efficiency (Π_{SP} ;) at temperature; 25.5°C, humidity; 42.2% and I_R ; 810.1 W/m² was 12.7%. Also, the generated cumulative H_2 was 89 cm³ (Fig. 3b).

The H_2 production was determined with respect to received solar radiation which is representative of the incident solar radiation, while the corresponding

temperature and humidity were recorded (Fig. 4). The initial solar radiation received was 810.1 W/m^2 but slowly decreased to 637.8 W/m^2 after 1 hour 15 minutes (Fig. 4.a).

Table 1 Efficienc	y and H ₂	production
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Parameters	Values	-
Ŋ _{SP} (%)	12.7	-
Ŋ _F (%)	61.8	

These conditions yielded slow but gradual production of H_2 of 1 cm³ after 15 minutes and a maximum of 18 cm³ after 1 hour and 15 minutes (Fig. 4.b). The reaction and membrane activation explain the production observed in the beginning. Consequently, the outside temperature (Fig. 4.c) and humidity (Fig.4.d) graphs show that as temperature increases, humidity relatively decreases respectively. However, factors such as cloud cover and season change may disturb incoming



Fig. 4. Solar radiation (a) and hydrogen generation (b) along with atmospheric temperature (c) and humidity (d)

solar radiation. In general, high solar radiation led to an increase in temperature which contributed to increasing H_2 production with time. From the results, there is a verification that H_2 is indeed produced (via equation 6) from water splitting by solar energy which is a renewable energy system. Although the WE has drawn a lot of research interest, there is a requirement for further research to help understand and improve the WE research as a whole. The future research is expected to focus on improving efficiency and electrolyte conductivity as well as determining the cost-effective means of H_2 production.

4. CONCLUSIONS

Solar powered WE is a renewable approach of hydrogen production. The solar energy harnessed by the PV cell is responsible for the splitting of NaCl solution into H₂. The produced H₂ gas over a 1 hour 15 minutes period was 89 cm³ whereas the respective PV cell efficiency (η_{SP} ; at temperature; 25.5°C, humidity; 42.2% and I_R; 810.1 W/m²) was 12.7%. Additionally, the electrolysis efficiency (η_{F}) was 61.8%. The ohmic potential drop experienced over time is due to bubbles' formation and waste heat generation. Furthermore, the received solar

radiation ranged from 810.1 W/m² to 637.8 W/m². This study verifies that an alternative means of obtaining H_2 gas is through the electrolysis of salt water, and it can be a reference study used to assess the underlying principles of electrolysis. Future research should address the cost-effectiveness, efficiency as well as conductive electrolytes as the key parameters for H_2 production systems through WE.

REFERENCE

[1] Ferriday T, Middleton PH. Experimental analysis of materials in proton exchange membrane electrolysis cells. International journal of hydrogen energy 2019;44:27656-27663.

[2] Yu J, Jung G, Su Y, Yeh C, Kan M, Lee C, Lai C. Proton exchange membrane water electrolysis system-

membrane electrode assembly with additive. International Journal of Hydrogen Energy 2019;44:15721-15726.

[3] Sanchez-Molina M, Amores E, Rojas N, Kunowsky M. Additive manufacturing of bipolar plates for hydrogen production in proton exchange membrane water electrolysis cells. (In press). [4] Lamy C, Jaubert T, Baranton S, Coutanceau C. Clean hydrogen generation through the electrocatalytic oxidation of ethanol in a Proton Exchange Membrane Electrolysis Cell (PEMEC): Effect of the nature and structure of the catalytic anode. Journal of Power Sources 2014;245:927-936.

[5] Kopp M, Coleman D, Stiller C, Scheffer K, Aichinger J, Scheppat B. Energiepark mainz: technical and economic analysis of the worldwide largest power-to-gas plant with PEM electrolysis. Int J Hydrogen Energy 2017;42:13311-20.

[6] Park J E, Kim J, Han J, Kim K, Park S, Kim S, Park HS, Yong-Hun Cho Y, Lee J, Sung Y. High-performance protonexchange membrane water electrolysis using a sulfonated poly(arylene ether sulfone) membrane and ionomer. Journal of Membrane Science 2021;620:118871.

[7] Santos DMF, Sequeira CAC, Figueiredo JL. Hydrogen Production by Water Electrolysis. Quim. Nova 2013;36:1176-1193.

[8] Ito H, Miyazaki N, Ishida M, Nakano A. Stack Performance of Proton Exchange Membrane Based Unitized Reversible Fuel Cells. Int. J. Microgravity Sci. Appl., 2016;33:330305.

[9] Wu Y, Ji S, Wang H, Pollet BG, Wang X, Wang R. A highly efficient water electrolyser cell assembled by asymmetric array electrodes based on Co, Fe-doped Ni(OH)₂ nanosheets. Applied Surface Science 2020;528: 146972.

[10] Bourounia IS, Chaibib MT, Tadrist L. Water desalination by humidification and dehumidification of air: state of the art. Desalination 2001;137: 167-176.

[11] Feng L, Tian B, Wang B, Yang M. Purification of hydrazine hydrate waste salt using a water washing based integrated process for the production of sodium hydrate via ion-exchange membrane electrolysis. Journal of Cleaner Production 2021;319:128626

[12] Ali A, Tufa RA, Macedonio F, Curcio E, Drioli E. Membrane technology in renewable-energy-driven desalination. Renewable and Sustainable Energy Reviews 2018;81:1-21.

[13] Martinez R, Forero E. Estimation of energy efficiency in solar photovoltaic panels considering environmental variables. IOP Conf. Series: Materials Science and Engineering 2018;437:012008.

[14] Papagiannakis I. Studying and improving the efficiency of water electrolysis using a proton exchange membrane electrolyser. Strathclyde University: 2005, p 57-68.

[15] Nafchi FM, Baniasadi E, Ebrahim Afshari E, Javani N. International journal of hydrogen energy 2018;43:5820-5831.

[16] Oruc ME, Desai AV, Kenis PJA, Nuzzo RG. Comprehensive energy analysis of a photovoltaic thermal water Electrolyzer. Applied Energy 164 (2016) 294–302

[17] Rakousky C, Reimer U, Wippermann K, Carmo M, Lueke W, Stolten D. An analysis of degradation phenomena in polymer electrolyte membrane water electrolysis. Journal of Power Sources 2016;326:120-128.
[18] Diogo M. F. Santos* and César A. C. Sequeira. Hydrogen production by alkaline water electrolysis. Quim. Nova 2013;36:1176-1193.