



Photoelectrosplitting water for hydrogen production using illumination of indoor lights

Rahadian Zainul¹, Admin Alif², Hermansyah Aziz², Syukri Arief², Syukri²
and Arief Yasthopi³

¹Laboratory of Computational and Electrophotochemical Chemistry, State University of Padang, Air Tawar, Padang

²Laboratory of Electrophotochemical dan Nanomaterial Chemistry, Andalas University, Limau Manis, Padang

³Faculty of Education and Teaching, University of Riau, Pekanbaru

ABSTRACT

This research aims to study process and mechanism of water splitting by photoelectrochemistry. Water splitting to produce hydrogen was initiated by photocatalysis on semiconductor of photovoltaic cell to growth the sufficient voltage so can be used for water electrolysis system by using tandem PV-EC cell. Visualization of water splitting has been monitoring with high resolution CMOS camera, 13 MPixel of OPPO X9006. This visualization has been modeling for hydrogen gas formation mechanism at carbon electrode (graphite) surface. PV Cell use $\text{Cu}_2\text{O}/\text{Al}$ as electrode with 0.003711 m^2 surface area. Among ten PV cell series arrangement (surface area = 0.03711 m^2), produce voltage between 3.01 V (room lights) ~ 3.43 V (neon lights) (this voltage was exceed minimum voltage for water splitting with voltage 1,47V) and current 509.8 μA and 438.7 μA . The process of water splitting observed at initiation of formation H_2 gas and H_2 release at carbon surface. Rate of H_2 gas formation in the first 10 minutes is $1.72 \times 10^{-5} \text{ ml/min}$, and stable with rate $1.17 \times 10^{-5} \text{ mL/min}$ after 1 hour and 50 minutes. H_2 gas volume produced reach 0.00281 mL after 5 hours 45 minutes.

Keywords : Photoelectrochemical, Photovoltaic, Indoor Lights

INTRODUCTION

Sunlight is one of renewable energy resource with abundant stock. Its potential energy reaches $1000\text{-}1369 \text{ Watt/m}^2$ or about $3.9 \times 10^6 \text{ EJ}$ ($1 \text{ EJ} = 10^{18} \text{ J}$) from one year total energy (1; 2) and only about 5-12 % (3). We reutilized by humans through photovoltaic technology. In addition, the energy of sunlight does not have negative impacts like fossil fuel. The process of converting sun's energy was not have waste product so it is one of clean energy resource. Therefore, solar energy has great potential to become the future energy resource, with abundant stock and environmentally friendly(4).

Photovoltaic technology has growing rapidly with the utilization direct sunlight. Ranging from the use of silicon, organic, DSSC, until the polymer has been developed and investigated as a filler material of the solar cell(5). Development in reactor engineering photo cell is also have been studied, for example, to design a reactor container, reflector for light collectors, absorbers reflection or anti reflector, n-p junction connecting systems, and solar panels as a sandwich layer and electrodes used models. All these efforts are intended to improve the conversion of photovoltaic cells(5; 6).

So far photocell research emphasizes the utilization of direct sunlight that has a high intensity. The reactor was placed in a position perpendicular to the direction of the sun coming, according to the zenith position and the light coming. In the tropics, this position is known as AM1, where as the subtropics area AM1.5. The reactor was placed in an open space and designed to be able to interact with the maximum of Solar Cells reactor. Meanwhile, the reactor that can work in room light has not been widely studied. This is because room light has relatively low light energy and solar panels that can work effectively is still not developed. Another factor is the difficulty to directly transform the low-intensity light energy to commercial energy and direct storage such as batteries.

Development of photocells reactor that can use energy from room light with low intensity to another intermediate energy forms as a carrier, in the formation of hydrogen gas continuously, it becomes an attractive option. Room light was used is sunlight coming into the room and the irradiation from lamp, like a neon (7). The conversion process can be done by making a tandem photovoltaic cells and electrolysis cells(PV-EC) to transform indoor light energy into electrical energy that adequate for the electrolysis of water (1,47 V) into hydrogen gases(8; 9). In this study conducted a study on the process of water splitting into hydrogen gas was observed with a high resolution camera on the Oppo X9009 and modeled through calculation assumptions hydrogen gas bubbles in scale to capture images on the surface of the carbon electrode.

EXPERIMENTAL SECTION

Materials and tools

The tools was used in this research are multimeter (Heles), Lightmeter, SEM-EDX (Hitachi S-3400N), XRD, neon Lamp (Philip 10 watt), paper, carbon paper, Furnace, analytical balance, and glass tools.

Materials was used in this research are glass (PT Asahimas), glass glue, Cu plate (PT Metalindo Sejahtera), Al Plate, Natrium sulfat (Na_2SO_4) (Merck), gelatin, chloroform (Merck) and aquades.

Method

Preparation of Copper Oxide electrode

Copper Oxide electrode was prepared by calcinating Cu plate on various temperature 300, 350, 400, 450 and 500°C, for 1 hour. The resulting Copper Oxide plate was characterized with SEM EDX and XRD.

Preparation of photovoltaic cell

Photovoltaic cell was prepared with design like figure 1.

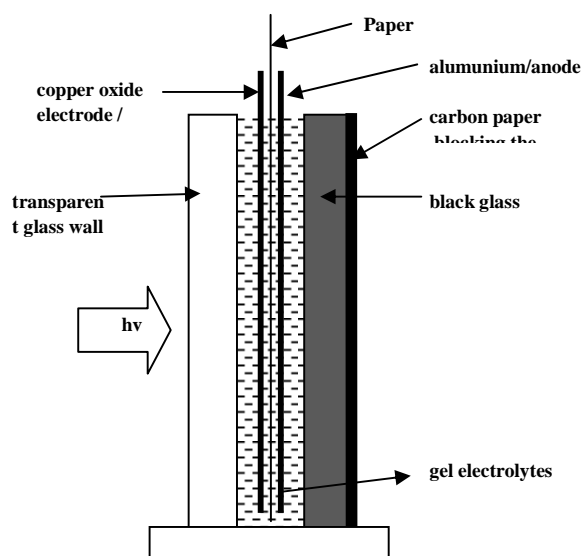


Figure 1. Scheme of design PV Cell

Preparation of Natrium Sulphate (Na_2SO_4) gelatin electrolyte

3,6 gram Na_2SO_4 was diluted with 100 mL water. Then, the solution was added 0,5 gram gelatin powder. The mixture was stirred and heated until boiling and become clean. After that was added some drops of chloroform and then solution was filled to cells directly.

Measurement current and voltage of PV cells

Each PV cell was filled by natrium sulfate gelatin, then illumination under room lights and neon lights. Current and voltage from cells was measured with multimeter.

Preparation PV-EC Tandem Reactor

PV-EC tandem cell was designed like scheme on picture 2.

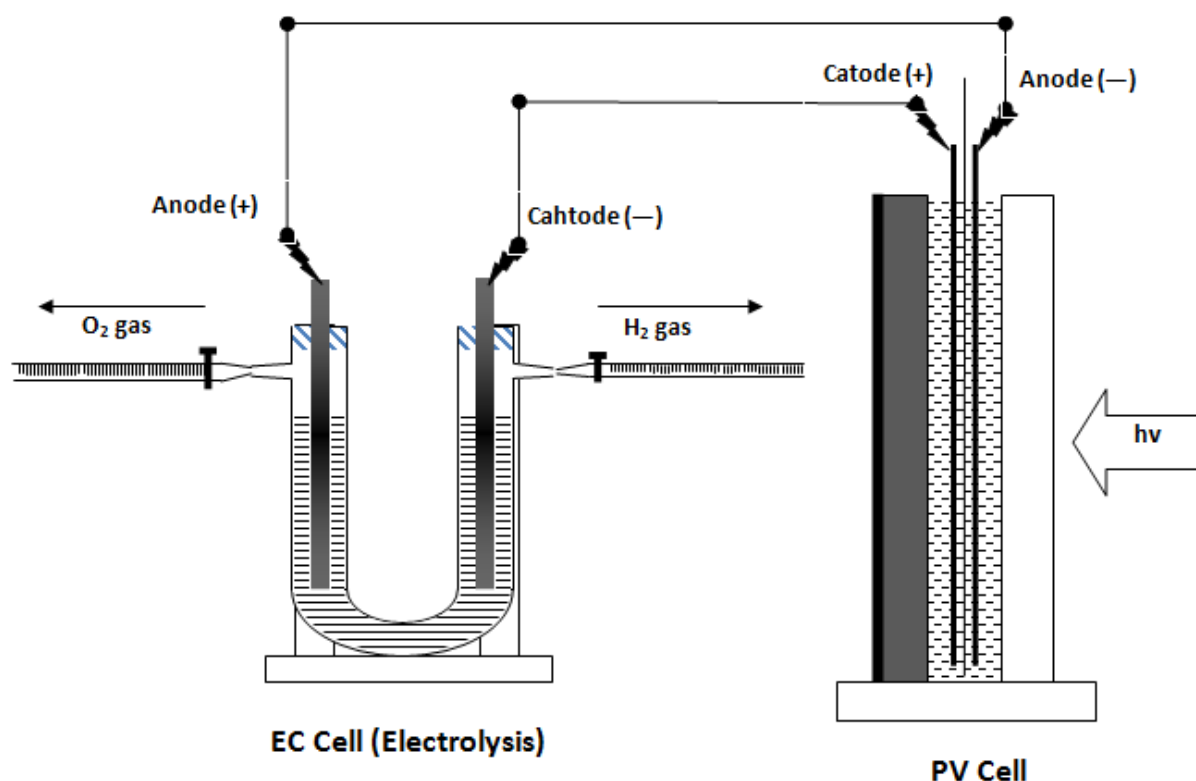


Figure 2. Scheme of design Photovoltaic and Electrolysis (PV-EC) tandem reactor

Image (Photo) Capturing and Calculation Model of Gas Bubble

Hydrogen gas bubble formation process at cathode in electrolysis cell was captured using high resolution camera CMOS 13 megapixel Oppo X9006. Calculation was done by using 50 time zooming for initial capture and record the mobility of bubble was observed with video capturing at surface of carbon electrode during splitting water into hydrogen takes place.

RESULTS AND DISCUSSION**Assembling of PV Cell****The Making of Electrode at PV Cell and Characterization by SEM-EDX-XRD**

Copper plate with specification (thickness 0,27mm, and size 36,5 cm x 120 cm, and weight 1,2 kg) was cut with size 4 cm x 12 cm. Plate was calcinated at 400 and 500°C. The best performance was obtained with plate after calcinate at 400°C. Copper oxide plate was used as cathode in PV cell. Meanwhile, for anode was used alluminium plate.

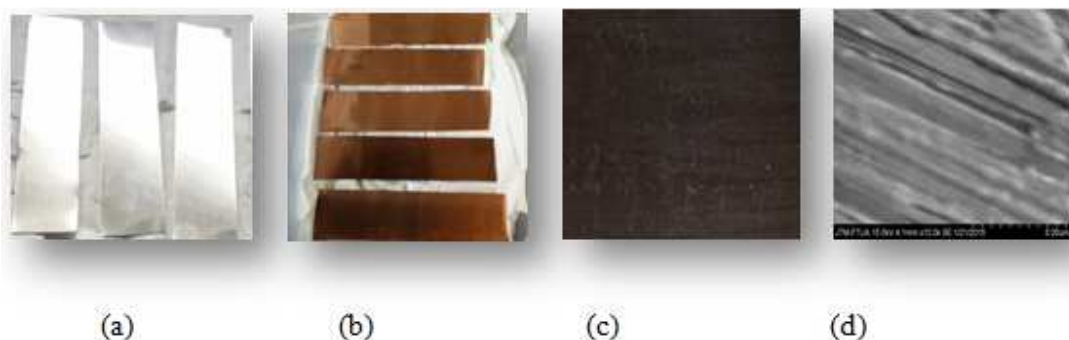


Figure 3. Photo of electrode plate (a) Aluminium (b) Copper (c) Surface of copper plat using Oppo X9009 camera and (d) SEM image of copper at 10000x enlargement

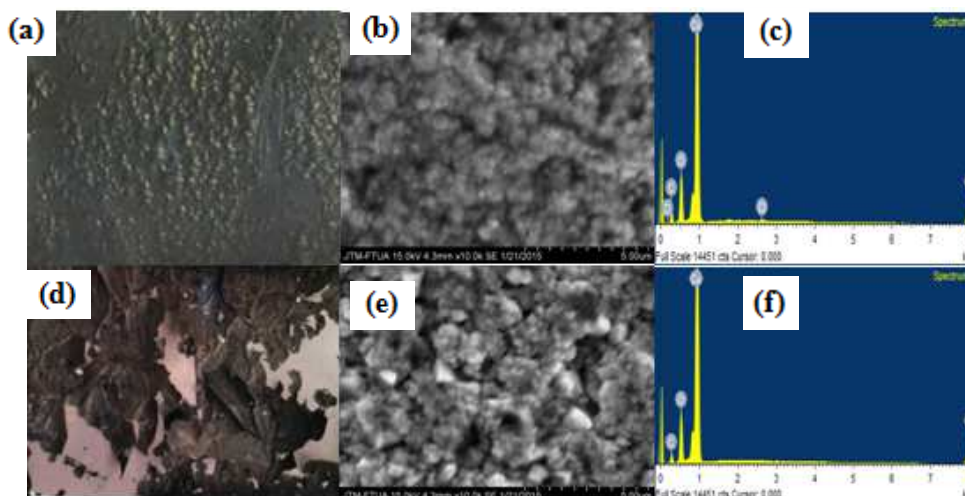


Figure 4. Photo of Copper Oxide plate surface at 400°C calcinations (a) CMOS Camera (b) SEM with 10.000 times enlargement (c) EDX ; and d, e, f for 500°C calcinations temperature

Calcinating copper plate causes the formation of oxides on the surface as shown in Figure 3 and 4. The higher of calcination temperature, the oxide layer is formed more and more as shown in figure 5. This is due to the increasing number of reaction between oxygen atoms at the surface of the copper plate. From the camera catches Oppo X9009, visible changes on the surface of the copper plate before and after calcination.

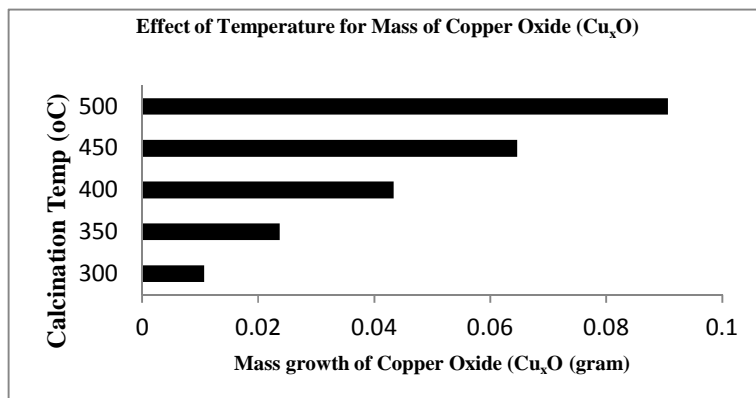


Figure 5. Effect Calcination Temperatur towards Mass growth of Copper Oxide

At the time of PV Cells modified by replacing the anode (Cu plate) with plate Al, an increase in power PV cells significantly as shown in Table 1. Increasing the ability of PV cells is because the nature of aluminum plates such as n-type junction that provides electron more than plates Cu that are p-type junction(12). Therefore, plate Al causes a potential difference greater PV cell so as to produce greater power.

Table 1. PV Cell Power of Cu₂O/Al at indoor lights from sunlights entering the room and from illumination of neon lamp

PV Cell (Cu ₂ O/Al)	Sunlights entering the room (Intensity = 71.91 ftc, fluk = 774)			Illumination of Neon Lights (Intensity = 184.75 ftc, flux = 1989.5)		
	Current (μA)	Volt (mV)	Power (μWatt/m ²)	Current (μA)	Volt (mV)	Power (μWatt/m ²)
average 10 PV Cell	337.2	509.8	46322.97	318.3	438.7	37628.19
Seri 10 PV Cell	497	3010	40311.78	517	3430	47785.23

PV cells Cu₂O/Al is used in tandem with the electrolysis cell to produce hydrogen gases from splitting of water. Splitting of water process on the surface of the carbon in the electrolysis cells (EC) was observed with 13 Mpixel CMOS camera Oppo X9009, as shown in Figure 8. Formation of gas bubbles of H₂ occur on the surface of the carbon electrodes and marked on the 8 point Hydrogen gas bubble formation. Each H₂ gas bubble nucleation point is observed and measured by capturing image scale method by comparing the size of the carbon electrodes used in EC Cell.

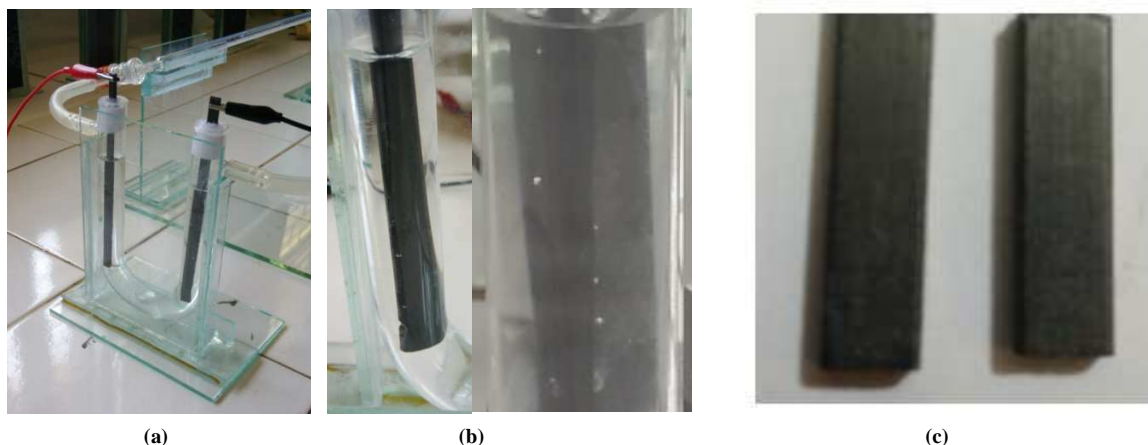


Figure 8. Electrolysis Cell using Carbon bar at cathode (a) and nucleation point of gas bubbles at Carbon electrode surface (b), sectional Carbon electrode (c)

Analysis of Capturing Image Scale Measurement

Carbon electrode of photo images taken with 13 Mpixel CMOS Oppo F7a X9009 done capturing image magnification and printed with HP Laser Jet printer. Size magnification to capture images was measured by comparing the scale of the actual size of the carbon electrode as a benchmark to get the actual size of the gas bubbles.

Results of measurement of the cross section of carbon electrode obtained the following results. Height/thickness of the carbon electrode (graphite) is 2 mm, a width of 5 mm and height of 140 mm. Measurement scale hydrogen gas bubbles using a cross-sectional measurements in the vertical position on the wide position electrode C is 5 mm. Photos printed electrode interface and conducted comparative measurement scale with the size of the cross section of carbon electrodes.

Table 2. Results of bubbles scale measurement for gas H₂ gas (Big = x B, Medium = x S, and Small = x K)

H ₂ gas Sizes	Image Capturing		Real		H ₂ diameter bubbles (mm)
	x (mm)	y (mm)	x (mm)	y (mm)	
Big	3	22	x B	5	0.68182
Medium	2	22	x S	5	0.45455
Small	1	22	x K	5	0.22727

Based on the measurement scale camera capturing, hydrogen gas bubbles have formed classified into three groups, i.e., large bubble (x B), medium bubble (x S) and small bubble (x K), with the size of each bubble are 0.68182 mm, 0.45455 mm and 0.22727 mm. The formation of gas bubbles are monitored by camera catches, and shift of bubble in buret scale. However, the formation of H₂ gas bubbles growth slightly, the method of measurement was done with a video recording on the surface of the carbon electrode for 5 hours and 45 minutes. Results recorded video capture on the surface of the carbon electrode was analyzed to get accurate results about the mechanism of formation of H₂ gas bubbles.

Analysis of Video Capturing at Carbon Electrode Surface

Capturing video observations for 5 hours 45 minutes reported by calculating the scale on the image 13 MP (Scheider certified professional camera)/50 Mega Pixel Photo Impressive Capturing from Oppo F7a X9006, when gas bubbles are formed and obtained by the real size scale comparators in image capturing. In this study actually gained diameter of each is 0.681818 mm for large size, 0.454545 mm for medium-size and 0.227273 mm for the small size.

Bubble formation occurs at minute 10, characterized by the formation of small bubbles (NBT) and the same time the formation of large bubbles (NBT). After 20 minutes, a bubble is formed again 1 large bubble (NBT) and 1 medium bubble (NST). Meanwhile, the release of gas bubbles occurred after 50 minutes of the release of 2 large bubbles (NBL). 8 minutes later, one huge bubble of H₂ gas (NBL) was released from surface of electrode. The counting process can be seen in Table 3.

The process of the formation and transport of gas takes place at the time to 39:34 (39 minutes 34 seconds) is the No. 3 gas bubbles smaller gas bubbles move closer No. 4 larger. In the 45th minute, H₂ gas bubbles in point 4 was released from electrode surface. H₂ gas bubble migration reaction was observed in the recording surface of the Oppo F7a. 26 seconds later, the initiation point reappear in the same location, namely point 4. H₂ gas bubble nucleation No. 4 getting bigger and the same size as the gas bubbles No. 3 at minute 53. Both of these gas bubbles is approximately 5 mm and engaged with each other approaching at minute 53, second to 13.

Table 3. The formation H₂ gas bubbles at the cathode, NBT = number of large-size H₂ bubbles formed, NBL = number of H₂ large gas bubbles escaping from the cathode surface, S = medium, K = small, t = formed, L = apart

time	Minute	N Bt	N BL	N St	N SL	N Kt	N KL	Σ bubbles	Total H ₂ Volume
9:15	0:00	0	0	0	0	0	0	0	0
9:25	0:10	1	0	0	0	1	0	2	0.000172
9:35	0:20	2	0	1	0	1	0	4	0.000387
9:45	0:30	4	0	1	0	1	0	6	0.000719
9:55	0:40	4	0	2	0	2	0	8	0.000775
10:00	0:45	4	0	2	0	3	0	9	0.000781
10:05	0:50	4	2	1	0	2	0	9	0.001058
10:13	0:58	4	3	2	0	2	0	11	0.001273
10:25	1:10	4	3	3	0	1	0	11	0.001316
10:31	1:16	3	4	4	0	0	0	11	0.001359
10:36	1:21	3	4	4	0	1	0	12	0.001365
11:00	1:45	3	4	4	0	1	0	12	0.001365
11:15	2:00	3	4	5	0	0	0	12	0.001408
11:30	2:15	3	5	4	0	0	0	12	0.001525
11:40	2:25	3	6	3	0	0	0	12	0.001642
11:50	2:35	3	6	3	0	2	0	14	0.001654
12:00	2:45	3	7	3	0	1	0	14	0.001814
12:25	3:10	3	8	2	0	1	0	14	0.001931
12:45	3:30	3	8	3	0	2	0	16	0.001986
13:00	3:45	3	9	3	0	1	0	16	0.002146
13:25	4:10	3	9	3	0	2	0	17	0.002152
13:30	4:15	3	9	3	0	4	0	19	0.002164
14:00	4:45	3	9	4	0	3	0	19	0.002207
14:20	5:05	2	12	4	0	1	0	19	0.002527
14:35	5:20	0	14	4	0	1	0	19	0.002527
14:45	5:30	0	14	4	0	2	0	20	0.002533
15:00	5:45	0	16	3	0	1	0	20	0.00281

At the time of 01:10:57 (1 hour: 10 minutes: 57 seconds), both the bubble (No. 3 and 4) has migrated to the surface of the electrolyte from the electrode surface. 4 minutes later, point 3 and 4 re-emerged, and the process of formation of H₂ gas re-occur. This process was observed for 5 hours 45 minutes of 0915 until 15:00 pm. The formation of gas

bubbles as tabulated in Table 3. The term NBT, NST, HCV, respectively explain the large number of gas bubbles formed to size Large, medium and small. The term L, for the bubbles apart.

From Table 3 have seen that the formation of gas bubbles occur is continuous for 5 hours and 45 minutes. Hydrogen gas bubbles after the point is established, then the bubble is enlarged on the surface of the electrode (cathode) and finally detached from the cathode surface to the water surface.

Nucleation point H₂ gas bubbles begin to form after the tandem PV-EC work for 10 minutes 5 seconds. Based on the observations, H₂ growing gas bubbles with a diameter of 0.68 mm as shown in Figure 9. Determination of H₂ gas volume is formed by the following formula (assuming a spherical bubble of H₂ gas). The volume of gas bubbles H₂ = $V = \frac{4}{3}r^3$. Where r = radius of H₂ gas bubbles ($r = \frac{1}{2}$ diameter). Hydrogen gas bubbles are large in diameter 0.681818 mm, then his fingers can be calculated, ie $r = \frac{1}{2}$ mm x 0.681818 = 0.340909 mm. Thus, the volume of H₂ gas bubbles are generated is 0167mm³.

Table 4. Sizes and bubbles model of H₂ gas

Bubbles	d (mm)	r (mm)	V (mm ³)	V(cm ³)
Big	0.681818	0.340909	0.166027	0.000166
Medium	0.454545	0.227273	0.049193	4.92E-05
Small	0.227273	0.113637	0.006149	6.15E-06

On the Figure 9 have seen that H₂ gas bubbles is formed with variation sizes. There is three variations sizes, that small, medium and big, depend on H₂ gas bubbles diameter on sectional electrode surface.

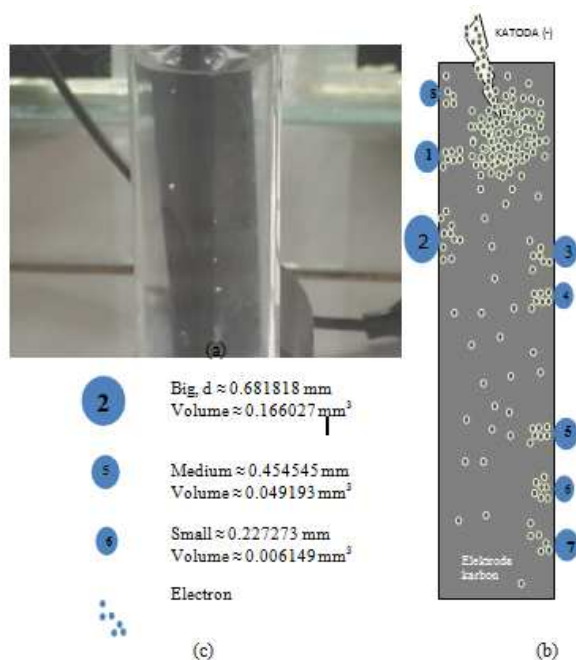
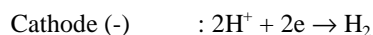


Figure 9. Gases bubbles image and models, (a) at carbon surface with 13 MPixel/50 time enlargement, (b) illustration of Hydrogen gas bubbles has formed in interface of Carbon electrode depend on electron distribution theory and (c) representation of H₂ gas bubbles has formed

Theory of Hydrogen Gas Bubbles Formation

Process of H₂ bubbles formation on reaction taking place in water *splitting* at cathode surface.



Analysis of the formation of hydrogen gas on the surface of elektroda. Tahapannya is convection, migration and diffusion. The movement of electrons in the inner electrode is a process of convection currents generated from the electrolyte galvanic cell. In the electrolysis cell, the process of convection is the movement of electrons occurs towards the electrode surface. After the formation of hydrogen gas electrochemically, the movement of gases on the surface of the electrode is a migration process in translation. Gas will be shifted and eventually leave the surface of the electrode as the process of migrating from the liquid phase to the surface of the electrolyte solution. Finally, the movement of gas through the electrolyte to diffuse from the surface of the output pipe, toward the end of the gas storage.

Various factors affect the electrochemical transport period is a surface electrode, electrolyte environmental conditions, in addition to the main factor is the current and potential. The type of electrolyte used very effectively influence the migration process. Migration in acidic, alkaline and salt will have differences. Because of differences in the atmosphere of the electrolyte, affecting the conductivity of the solution. On the electrode surface, convection process is highly dependent on the structure of the electrode surface, which raises the style of style to the style of convection and gas formation on the electrode surface. Surface electrodes that are not symmetrical cause polarization on the electrode surface, as illustrated in Figure 10.

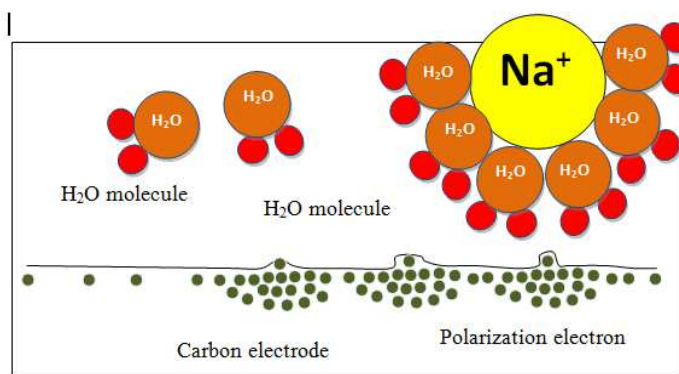
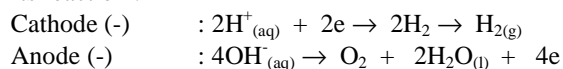


Figure 10. Schematic of electron polarization on carbon electrode interface

The phenomenon of the formation of hydrogen gas at the electrode surface was observed with the following stages. Initiation stage, which is the starting point of the formation of hydrogen gas. This point occurs on the surface of the effective where the convection of electrons on the surface of the electrode is more optimum and at this point there is also an effective collision of H₂O with the active C interface electrode surface.

Reactions that occur at the initiation stage is the culmination point with the achievement of the activation energy so that the current that flowed on the surface of the carbon electrode (C), allows for the course of the electrochemical reaction of the hydrogen atoms that exist in H₂O in the electrolyte solution. The electrochemical process, is a process of reduction at the cathode where the flow of electrons from the electrode surface to the hole point of the reactant species. At the same time, the oxidation reaction occurs at the anode where the reactant species that carry electrons give electrons to the hole area (+) on the surface of the C electrode (anode).

Its reaction :



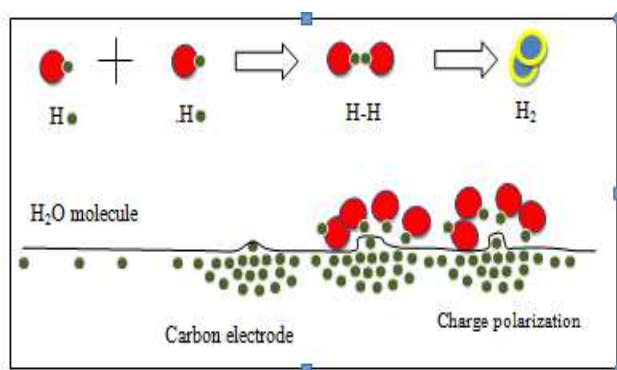


Figure 11. Scheme of H₂ gas bubbles formation on C electrode surface

The second stage is the formation of gas bubbles on the surface of the carbon electrode on the active side. This process was observed by the formation of small dots on the surface of the electrode that eventually become small bubble size diameter of 0.2 mm to 0.67 mm. The starting point of the formation of gas bubbles called nucleation sites on the electrode surface. This gas bubble formation will inhibit the electrochemical processes at the electrode surface until H₂ gas bubbles regardless of nucleation points. Phenomenon that occurs in the formation of H₂ gas bubbles are:

1. The spontaneous formation of gas bubbles at nucleation sites. After the gas bubble diameter of 0.6 mm, the bubbles is separated from the surface so that the electrochemical processes can walk back. During the nucleation process until the moment the release of H₂ gas bubbles, the electrode surface has blocked for core nucleation reaction of H₂ gas.

2. The movement of the electrode surface after nucleation of H₂ gas formed at the adjacent position (about 1-3 mm) with some movement patterns. The movement of the point of H₂ gas bubble size is very small tend to be attracted or moving closer to larger gas bubbles. The second movement of the other is moving closer to each other bubbles to form larger bubbles. The process of movement on the surface of the electrode runs translational and when the bubble is getting bigger, the next process is the process of release of H₂ gas bubbles from the electrode surface.

On the electrode surface nucleation sites that are far away from each other, point 7 and 8 in the scheme of H₂ gas bubble formation, the H₂ gas discharge becomes difficult to occur. This can be overcome with the vibration of the electrode so as to increase the momentum of H₂ gas bubbles and the gas transport leaving the electrode surface.

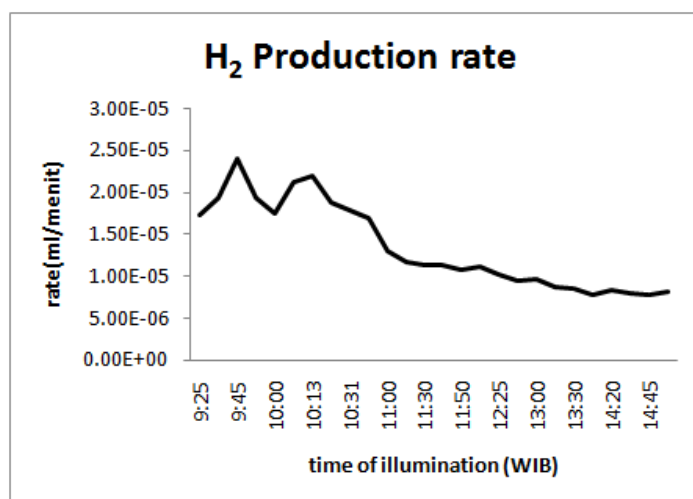


Figure 12. Hydrogen gas bubbles production rate

Based on Figure 12, rate of H₂ gas production at cathode is 1.72 x 10⁻⁵ ml/minute in time range of first 10 minute, and its will increase in 1 hours after that, about 2.19 x 10⁻⁵ mL/minute, thus finally decrease until 1.17 x 10⁻⁵ mL/minute after 1 hours 50 minute. From table 3, has been showed that after 6 hours, Hidrogen gas was achievely produced 0.00281 mL.

CONCLUSION

Photoelectrospitting water for H₂ gas production has taken place at the Carbon electrode surface with initiation process by nucleation point under illumination indoor lights. We can make tandem electrolysis-photovoltaic (PV-EC) reactor cell with 3010 mV voltage (room lights) and 3430 mV voltage (neon light). Both of them can produce H₂ gas bubbles with 2 step, which spontaneously bubble formation and nucleation-accumulation bubble formation. Visualization of H₂ production mechanism has monitored and recorded by image and video capturing with high resolution camera. Rate of H₂ production is 1.17 x 10⁻⁵ mL/minute, and the future research can be increased by modified at electrode surface of electrolysis cell.

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