

Hydrogen Production via Ice Electrolysis

by

Muhammad Anas Bin Zainal Abidin

Dissertation submitted in partial fulfillment of
the requirements for the
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(Mechanical Engineering)

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CERTIFICATION OF APPROVAL

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A project dissertation submitted to the
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Approved:

(AP. Dr. Bambang Ari-Wahjoedi)

UNIVERSITI TEKNOLOGI PETRONAS

TRONOH, PERAK

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CERTIFICATION OF ORIGINALITY

This is to certify that I am responsible for the work submitted in this project, that the original work is my own except as specified in the references and acknowledgements, and that the original work contained herein have not been undertaken or done by unspecified sources or persons.

(MUHAMMAD ANAS BIN ZAINAL ABIDIN)

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ABSTRACT

Achieving a sustainable energy system obviously is an important goal of all societies. However, achieving that goal is complicated by multiple players with divergent interests promoting their views in the context of numerous complex technological considerations. This report basically discusses the project research done and basic understanding of the chosen topic, which is **Hydrogen Production via Ice Electrolysis**. The objective of the project is to do a research and verify that ice electrolysis is a more economic approach or method to produce and obtain hydrogen for multipurpose. The challenge of this project is to generate and separate all the gasses from the ice using electrolysis system which is to obtain oxygen and also hydrogen. The separation using electrolysis is more difficult when the medium is water instead of ice cube which it will reduce the voltage or current used while electrolyzing to produce hydrogen gas. When the electrolysis is in process, the voltmeter will show the usage of the voltage while electrolyzing the ice cube which will verify the topic of the project. As shown in the results, the level of pressure of hydrogen increases as water level increases which means that hydrogen can be produced more using ice electrolysis.

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CHAPTER 1

INTRODUCTION

1.1 BACKGROUND OF STUDY

Historically, the first known electrolysis of water was done by William Nicholson and Anthony Carlisle in about 1800. One important use of electrolysis of water is to produce hydrogen. Of the various procedures for the production of hydrogen from water, electrolysis is presently, and for the foreseeable future, the only one of practical importance. Water electrolysis in its conventional form, alkaline electrolysis, has been in commercial use for over 80 years. Electrolysis of water can be observed by passing direct current from a battery or other DC power supply through a cup of water (in practice a salt water solution increases the reaction intensity making it easier to observe). Using platinum electrodes, hydrogen gas will be seen to bubble up at the cathode, and oxygen will bubble at the anode. About four percent of hydrogen gas produced worldwide is created by electrolysis, and normally used onsite. Because electrolytically produced hydrogen is created indirectly via the energy carrier 'electricity', this process is considered as one of the expensive type of ways to produce hydrogen.

The main reasons to produce hydrogen can be summarized as follows:

1. Hydrogen is widely seen as a future transport fuel, but that future is probably further off than popularly perceived.
2. The use of hydrogen in the production of transport fuels from crude oil is increasing rapidly and is vital where tar sands are the source.
3. The energy demand for hydrogen production could exceed that for electricity production today.

1.2 PROBLEM STATEMENT

Hydrogen is abundant in nature, but not as a free element. It is bound to other atoms in water or organic material. Therefore, to produce hydrogen, another energy source is required to separate it from the atoms to which it is attached, which makes it an energy carrier, instead of an energy source. Production methods for hydrogen vary from advanced technologies to those that are still in the research and development phase. Any source of energy, fossil or renewable may be used for the production process. Once generated, hydrogen may be utilized in every component of our energy system – as a fuel for transportation, a source for electricity or heating.

World energy infrastructure has been in place long enough to establish market conditions that are favorable to fossil energy sources. In contrast the envisioned hydrogen energy system is still largely in a conceptual phase, with many unknowns and concerns. Even though a hydrogen-based energy system offers many advantages as demonstrated by pilot applications, questions and criticisms remain. Some concerns are based on the unknowns inherent in the technologies, while others are due to misconceptions and lack of information. These factors give rise to an atmosphere that may hinder development or result in sub-optimal decisions and less favorable circumstances for both individual investors in hydrogen production facilities and society as a whole. A structured decision-aiding process that would help facilitate the objective consideration of all factors and interests of all involved parties may substantially assist the transition to a national hydrogen energy system in the world.

Nowadays, hydrogen production by electrolyzing water uses a lot of power i.e. electricity which cause another problem focusing on generating electricity. Water electrolysis consume a lot of power supply mainly voltage energy from either batteries or hydro system for the process of separating gases molecules from the water source. The decomposition of water is consists of two partial reactions that take place at the two electrodes.

Therefore, an alternative way to produce hydrogen also via electrolysis is design by using ice as the medium in which will essentially reduce the energy consumption i.e. voltage energy from the power source. This will decrease the cost of other power generation such as hydro system or batteries and also enhance the ability to produce hydrogen in mass production.

1.3 OBJECTIVE AND SCOPE OF STUDY

The objectives of this research are:

1. To experiment the reaction of ice cube according to voltage consumption when electrolyzing.
2. To establish the relationship between amounts of voltage used in electrolysis process with arrangement of water molecule in liquid and solid forms.
3. To compare and prove via economic analysis that ice electrolysis is a more economical approach to produce hydrogen.

The scope of study for this project is to investigate and verify that by using ice as the medium to perform electrolysis will basically uses less amount of voltage energy rather that electrolysis using water as the base medium. When the water is in a solid state, the bonding of water molecule has decrease in strength which can lead to a less amount of energy required to break the bond thus producing hydrogen faster.

CHAPTER 2

LITERATURE REVIEW

2.1 ELECTROLYSIS

In light of recent hydrocarbon shortage concerns, hydrogen is receiving increased attention from the scientific community and the media for its potential role in a sustainable energy system. Hydrogen, like electricity, is an energy carrier and not an energy source, and significant research is underway to test the feasibility of a future transition to a total hydrogen energy economy. To understand the implications of such an economy, the Iowa Energy Center funded an extensive literature search over the summer of 2006. This search included approximately 130 research reports, case studies and other esteemed publications having to do with important aspects of the hydrogen economy (i.e. production, efficiency, electrochemical conversion, etc.). Findings of the search are focused on hydrogen production by electrolysis, several storage and delivery methods, electrochemical conversion to electricity in fuel cells, and process efficiencies (refer Figure 1).

Because hydrogen is a chemical energy carrier (unlike electricity, which is a current of electrons), it is potentially more effective as a storage medium than other technologies like batteries, especially for use in renewable energy systems such as wind or solar power. Research efforts are currently being focused on optimizing the entire hydrogen production-to-consumption process with increased interest in renewable energy applications. When derived from renewable resources such as wind or solar energy, hydrogen can be produced and utilized free of carbon emissions. Research efforts are being directed toward the transition to a sustainable

hydrogen-based economy, which is a carbon-free energy system in which hydrogen is the only energy carrier.

Hydrogen is nearly unavailable in its molecular form on earth. A number of production methods including electrolysis, steam reformation of natural gas, and coal gasification are the foci of widespread production research; but electrolysis currently offers the greatest potential for a sustainable hydrogen economy. Water electrolysis is a technique that utilizes a direct current to split water into protons, electrons, and gaseous oxygen at the anode (positive electrode) in the electrolyzer. Protons pass through an electrolyte such as a proton exchange membrane (PEM) and recombine with electrons at the cathode (negative electrode) to form diatomic hydrogen (H_2). The minimum potential difference between the cathode and anode must be near 1.5 V for efficient electrolysis. Electrolysis is not yet economically feasible; this is mostly due to high material costs of the catalysts and electrolytes. As a result of high material costs, a significant amount of research is being performed to find cheaper, more efficient materials for use in electrolyzers. If the electrolyzer's input electricity is generated by renewable energy alternatives, renewable-to-hydrogen systems can be fully-sustainable; a number of case studies report that renewable-to-hydrogen technology is available and ready to implement today.

Electrolysis is a proven method for producing hydrogen (or oxygen) from water in solid or liquid state with electricity. This process is enhanced by the addition of electrolyte to the water as well as by using certain electrode materials. Gravitational, as well as "centrifugal" force can have an effect on electrolysis performance.

Electrolysis takes place when H_2O , i.e. water, reacts with energy input, in the form of electricity, to create H_2 and O_2 . Hydrogen is evolved at the cathode and oxygen at the anode.

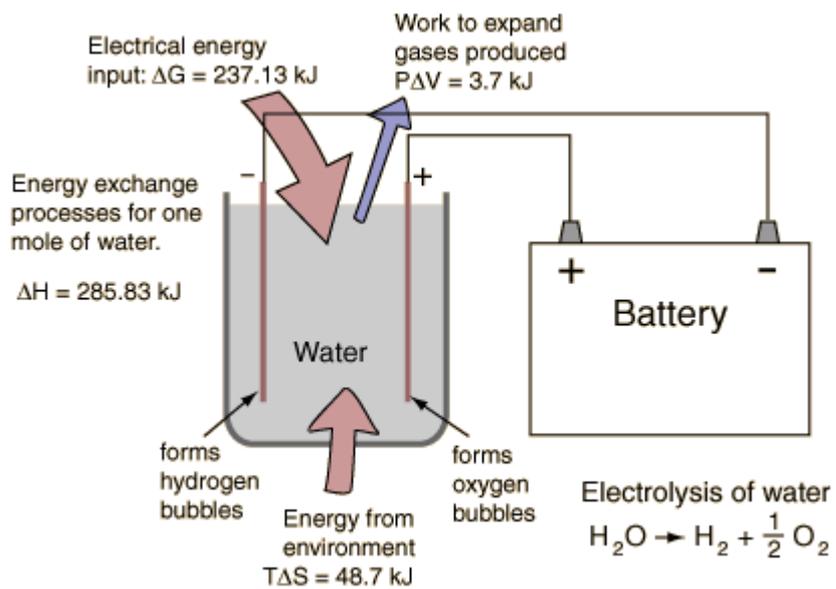


Figure 1: Simple Electrolysis
 (C.R Nave, Hyperphysics , 97)

In an experiment conducted by researcher, it was shown that electrolytic cell voltage could be reduced by more than 0.5 volt by placing the cell under an increased centrifugal force. The cell voltage is reduced because the increased force causes the gas bubbles in the cell to separate from the electrodes more quickly, thus reducing resistance in the cell.

Sodium sulfate and sulfuric acid are two common electrolytes used to increase the rate at which water can be electrolyzed. This happens because the electrolytes increase the conductivity of the water and therefore facilitate the transfer of hydrogen and oxygen ions in the water. Any substance that increases the conductivity of the electrolytic solution will increase the rate of electrolysis, including salts, strong acids, and strong bases.

In addition to the electrolyte, the electrode material has a large effect on the electrolysis process. Nickel, as well as nickel-iron alloys, are good electrode materials, with the ability to decrease electrode potentials by as much as 0.6 volts and therefore decrease the power necessary for electrolysis to take place. Austenitic stainless steels, such as grade 304, have substantial nickel and chromium content making them highly corrosion resistant and very desirable as an electrode material. Typically, the less reactive the material, the better suited it is for electrolysis since the electrode itself will not undergo chemical decomposition due to electrolysis, and all energy input will go into electrolyzing the water.

A study done by researcher demonstrated a way of analyzing electrolysis efficiency on the basis of voltage drop through the cell, as well as a simple method of estimating cell current based on voltage drop across a known inline resistance. Ohm's Law, in the form $I=V/R$, is applied to determine this current.

For this project, equivalent whole process of electrolysis will be carried out using ice cube or water ice which is water in solid state as medium instead of using water as mentioned above.

2.2 THE STRUCTURE OF ICE (S)

Ice possesses 12 different crystal structures, plus two amorphous states. At ordinary (low) pressures the stable phase is termed ice I. There are two closely related variants: hexagonal ice I_h, whose crystal symmetry is reflected in the shape of snowflakes, and cubic ice I_c. Ice I_h is obtained by freezing water; ice I_c is formed by depositing vapor at low temperatures (-130°C). Amorphous ice can be obtained by depositing vapor at still lower temperatures and by compressing ice I_h at liquid nitrogen temperature. In addition to the elemental phases are clathrate hydrates. These are crystalline compounds composed of a large H₂O cage in which Xe, Ar, or CH₄, for instance, is entrapped.

If water vapor is condensed on a cold substrate between -80 C and 130 C, a cubic modification, ice I_c, is formed. Ice I_c is related to ice I_h in the same way as cubic diamond is related to hexagonal diamond, the cubic and hexagonal forms having almost the same density.

The peculiarity of the H₂O molecule lies in the presence of four sites to establish H-bonds that are partitioned into two donor sites and two acceptor sites. An H₂O molecule is thus able to establish four H-bonds around it. This is what it does surrounded by other H₂O molecules and thus gives a unique species where the *number of H-bonds is then equal to that of covalent bonds*, a really exceptional property. It happens in ice but this will be seen to be also the case of liquid water. In ice, H₂O molecules build highly ordered arrangements that are such that the two H atoms of each H₂O molecule establish two H-bonds on neighbour H₂O molecules, while the two lone-pairs of this same molecule accepts two H₂O molecule are consequently positioned in a tetrahedral arrangement around it (Figure 2, lower drawing). This is possible at the price of a small distortion of the H-bonds: the angle H-O-H of individual H₂O molecules is equal to 104.5° in vapour. In ordinary ice, obtained by freezing liquid water or condensing water vapour at ambient pressure and temperature below 0°C, the value of the H-O-H angle falls in the vicinity of 106°, which allows accommodating the tetrahedral angle of 109.5° of the O-atoms with such a slight distortion of H-bonds.

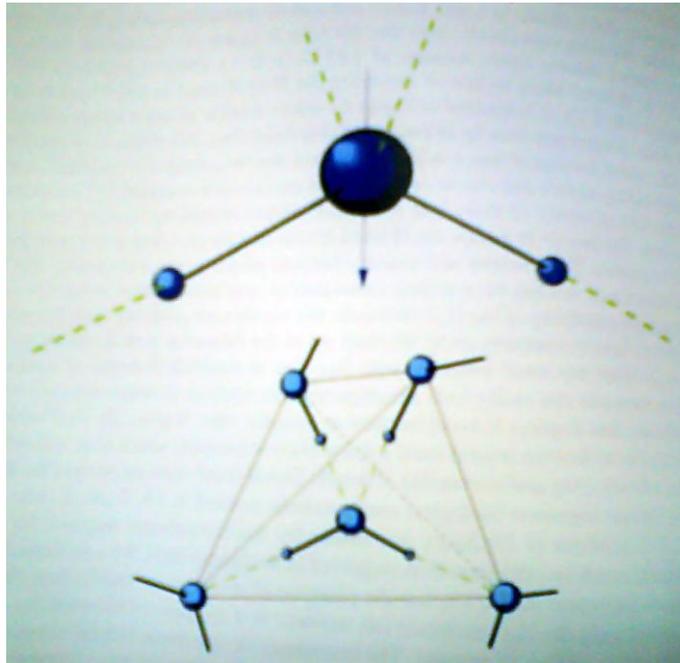


Figure 2: The molecule diagram¹⁰

- Water molecule (upper drawing) and its tetrahedral configuration in ice (lower drawing)

Under artificial laboratory conditions of very high pressures and low temperatures, ice can be forced to crystallize in a number of allotropic forms that are stable only under those particular conditions. Crystallization can occur in these laboratory situations in one of several non-hexagonal forms. This is similar to the way that carbon atoms may crystallize to form graphite or, under more extreme conditions, diamond. The conditions under which the alternate forms might be created do not occur naturally on Earth. They may, however, be present on other bodies in space.

The crystalline structure of ice may be deformed by stress, such as the weight of overlying ice on the deeper portions of a glacier. One type of deformation involves shearing of the crystal lattice along parallel planes. Recrystallization, on the other hand, entails the change in the shape and orientation of crystals within the solid. Both of these processes produce the phenomenon known as creep, responsible for the flowing motion of massive ice bodies such as glaciers.

2.2.1 Crystal Structures

2.2.1.1 Hexagonal Ice (Ih)

Ordinary ice is called ice Ih for hexagonal ice. It is the only form of ice that is found in natural conditions with maybe an exception mentioned below. It is the form of snow crystals, ice of glaciers, ice cubes that come from refrigerators, etc. Its structure is drawn in Figure 3. The O-atoms are found on summits of nonplanar hexagons having a chair form. Projection of these hexagons on a plane perpendicular to axis *c* gives regular hexagons (lower drawing). Between two adjacent O-atoms on a same nonplanar hexagon lies in a single H-atom, covalently bonded to one of these two O-atoms and establishing an H-bond energy of formation E_{HB} of these H-bonds as being equal to some 23 kJ mol⁻¹. Each O-atom is in addition alternatively linked to the O-atom of a hexagon either of the upper layer or of the lower layer. This link is of the form O-H...O or O...H-O. The O-atoms in arrangement is not so much usual. It is however, encountered also in the case of silica, where the Si-O-Si motif replaces the O-H...O motif of ice Ih. Let us note that the electric dipole moment of individual H₂O molecules in ice Ih is the order of 3.1D, that is 1.7D greater than that of isolated H₂O molecules in vapour, which we have seen to be of 1.83D at the beginning. This is a nice illustration of the cooperativity of H-bonds we defined previously.

In position to O-atoms, H-atoms are only partially ordered. They are found between two adjacent O-atoms, closer from one of them than from the other one. Their distribution between these two possible positions is not completely random, but obeys the “ice rule”, which states that each O-atom is covalently bound to two H-atoms and at the same time accepts on its lone-pair electrons two H-bonds from two neighbour O-H groups. As many configurations of H-atoms can fulfill this ice-rule, the H-atoms are somewhat disordered. It means that the ground state of ice, the only one populated at 0 K, is degenerate, consisting of numerous states with same energy, which correspond to the numerous possible positions of the H-atoms. This is a situation which is scarcely encountered and is at the origin of a residual entropy at 0 K, which reflects the disorder of H-atoms at this temperature.

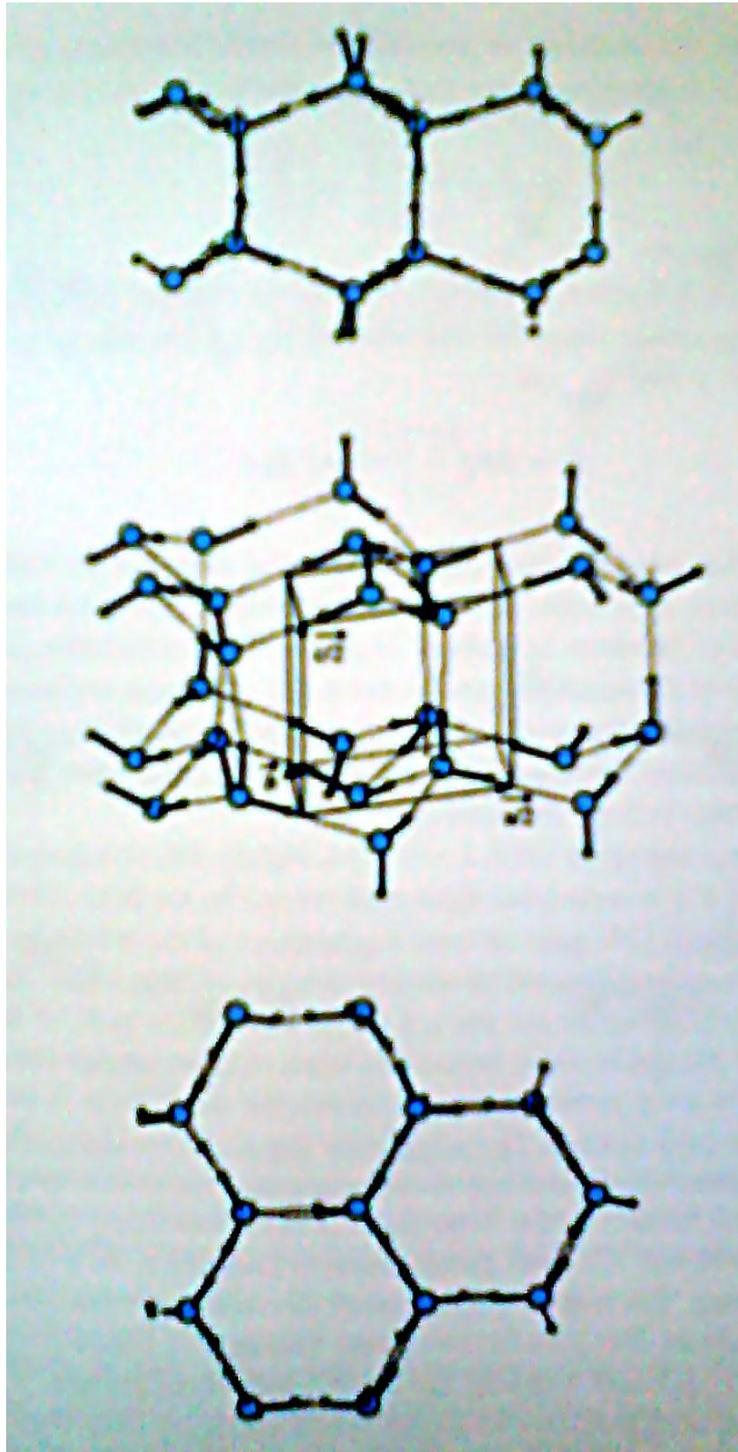


Figure 3: Hexagonal ice Ih¹⁰

- Projection on the a,c plane (upper drawing) and on the a,b plane (lower drawing), where the hexagons are apparent. The middle drawing is an intermediate projection derived from the upper drawing by a rotation around a followed by a small rotation around c .

2.2.1.2 Cubic Ice (Ic)

It is natural to wonder if a structure like ordinary ice, but based on a cubic close packing arrangement, is possible. It is. The structure is shown below (Figure 4).

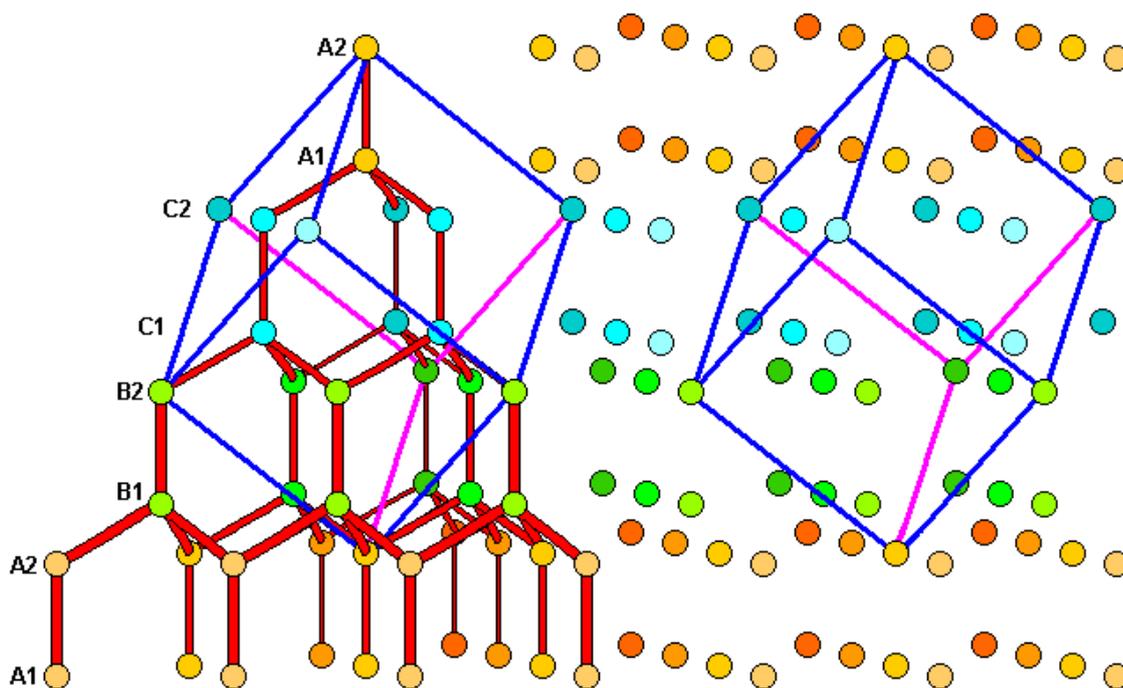


Figure 4: Cubic Ice Ic¹³

The oxygen atoms have the same arrangement as the carbon atoms in diamond. This form of ice is called Ice Ic. At above is a cubic unit cell of Ice Ic, with only the oxygens shown. O-H-O links are in red/blue. The diagram also shows the relationship of the cubic unit cell to the close packing layers. Ice Ic forms from the vapor below about -80 C and appears to be a metastable form of ice, although it has almost exactly the same density as Ice Ih. Ice Ih does not change to Ice Ic at very low temperatures but Ice Ic reverts readily to Ice Ih when warmed above -80 C. Ice Ic may form in extremely high clouds and some halo features not readily explainable in terms of hexagonal ice have been attributed to Ice Ic.

CHAPTER 3

METHODOLOGY

3.1 PROJECT IDENTIFICATION

This project will be done by using normal electrolysis process which needs two electrodes, ice cube, voltmeter and batteries 9.0 V as shown in Figure 5 below.

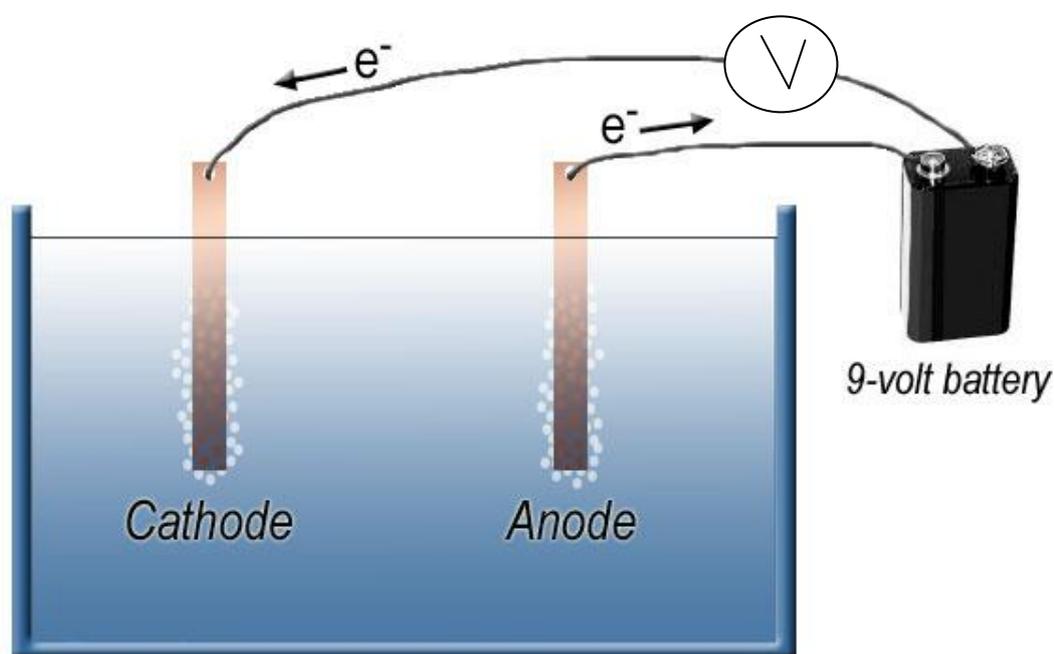


Figure 5: Set-up for electrolysis experiment

Prepare a "burning" wood splint to test for the hydrogen gas. The hydrogen gas produced at the cathode electrode will be trapped in a case or small tube which will be tested after several minutes after the process starts.

An observation will be made to see the amount of voltage used in the process of ice electrolysis compared to water electrolysis.

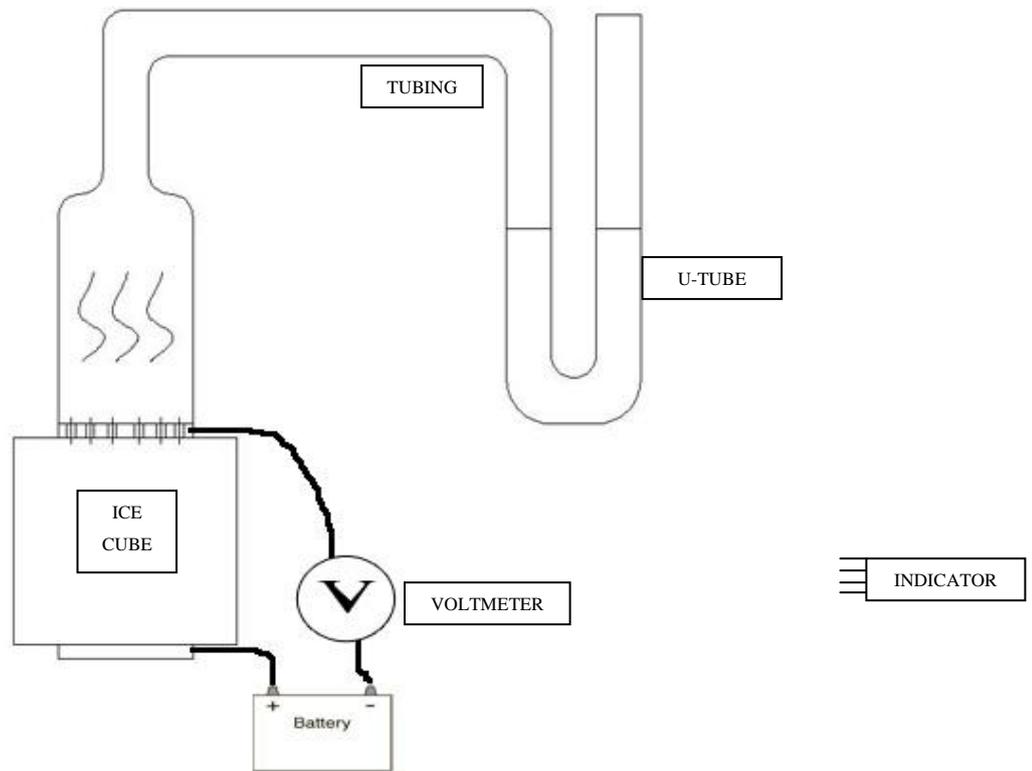


Figure 6: Ice Electrolysis Process

From previous explanation is only to show the absence of both gasses which is the oxygen and hydrogen. Therefore experiments apparatus will be set up according to Figure 6 for the measuring and to calculate thus clarify the objective of the project of which can be made by details below:

- a) Body – Plexiglas or Plastic
- b) Electrode – Nickel (50cent Coin)
- c) Ice Cube
- d) Voltmeter
- e) Battery or PSU (Power Source Unit) variable voltage
- f) U-Tube – (Use tubing for connection)
- g) Stop Watch

For the body, the Plexiglas or plastic will be cut and made into a model as shown in Figure 5. Then, a 50cent coin will be used for the electrode. This is because 50cent coin is being made from the same material as Nickel. Therefore it can be used and it is actually the best electrode for electrolysis rather than carbon. But the 50cent coin must be grinded until the surface is truly flat before it is used as the electrode and several holes will be drilled to it for the hydrogen gas to pass through. The 50cent coin will be put on top of the ice cube so that when the ice cube shrinks, the coin will naturally be moved downward together as it is pulled by the gravity. To have a better and persistent result, a hand gentle press is required to push the case to make the reaction more accurate. The tubing will be connected to the body at which it is suitable for the process to occur smoothly.

After setting the apparatus accordingly, the first experiment will be conducted using water as the medium as shown example in Figure 5. The gasses released will be pushed the water level inside the U-Tube as shown in Figure 6 which later the water level difference will be taken and compared by using a stop watch. The only gas that have to focus is the Hydrogen, thus have to make sure that the measurement taken by observing the level of water inside the trap is precise. After several experiments done, all the data can be compiled and another set of experiments will be conducted using ice as the medium. The procedure will be the same as by using water, but only the medium will change. Then the measurement of each experiment will be compared by the time taken for each medium. Below is the table for comparison of the experiments.

3.2 ECONOMIC ANALYSIS

By electrolyzing water and ice, the experiments consume a significant amount of energy used which in this case is electricity. The amount of electricity used can be distinguished either by water or ice respectively. Below are the analyses for both electrolysis using water and ice.

$$\alpha = [\text{kW} \times (\text{RM}/ \text{kWh})] / m$$

where, α = estimating energy value for water electrolysis

kW = power used in process

RM/kWh = rate of economic value, cost

m = mass of medium used

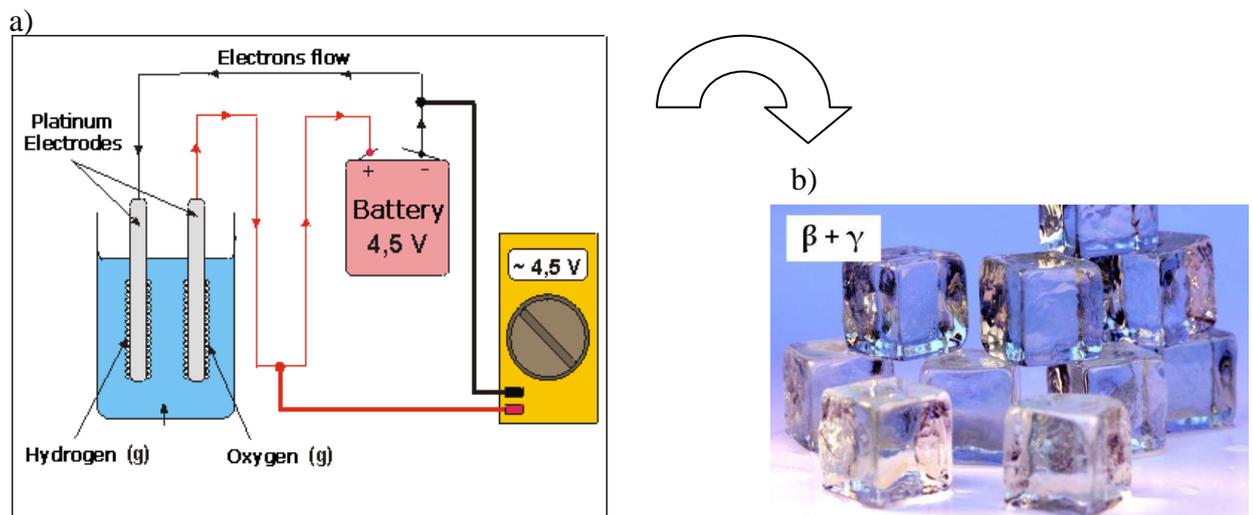


Figure 7: a) Voltage use of 4.5V in water electrolysis shown in the voltmeter.

b) Energy usage to form ice cubes which is $\beta + \gamma$.

The result must prove that energy used when electrolyzing ice uses less energy than at when electrolyzing water such as stated below:

$$\beta + \gamma \leq \alpha \quad , \quad \text{where } \gamma = \text{energy used to form ice from water}$$

$$\beta = \text{energy used when electrolyzing ice cube}$$

Calculations:

(a) Water electrolysis

$$\alpha = [\text{kW} \times (\text{RM/ kWh})] / m$$

Data obtained,

Power used in process, kW = 6 kW

Rate of economic value (cost), RM/kWh = 0.38

Mass of medium used, m = 0.3 kg

Therefore, $\alpha = [6 \times (0.38)] / 0.3$

$$\alpha = 7.6$$

(b) Ice electrolysis

Data obtained,

Freezing point, $T_1 = 273 \text{ K}$ (actual freezing)

Cooling point, $T_2 = 255 \text{ K}$

Enthalpy of ice, $h = 333,55 \text{ J/g}$ (¹³Crystallography of Ice)

Changing state from liquid to solid,

$$300 \times 333.55 = 100050 \text{ J}$$

Water ice has lower heat capacity, $C = 2.050 \text{ J/ (K.g)}$

$$(273 - 255) \times 300 \times 2.050 = 11070 \text{ J}$$

Therefore, $\text{Total} = 100050 + 11070 = 111135 \text{ J}$

$$1 \text{ kWh} = 3.6 \text{ MJ}, \quad 111135 \text{ J} = 0.0309 \text{ kWh}$$

γ = energy used to form ice from water

$$\gamma = 0.0309 \text{ kWh}$$

The energy used when electrolyzing ice cube is as the same when the experiment done when electrolyzing water which is **6 kW**

Therefore,

Energy when electrolyzing ice cube, $\beta = 6 \text{ kW}$

So,

$$\beta + \gamma = 6 + 0.0309$$

$$= 6.00309 \text{ kWh}$$

$$\alpha = 7.6 \text{ kWh}$$

we get , **$\beta + \gamma \leq \alpha$**

From the above equation, it shows that in terms of energy usage, the electrolysis done by using ice is more economically cost saving with compare to the electrolysis done by using water as the medium to produce hydrogen.

CHAPTER 4

RESULT AND DISCUSSION

4.1 EXPERIMENTAL RESULT

For the first half of the project, researches were done and theoretically it has been proven that by literature review and some calculations. Now, for the second half of the project, experiments were carried out to confirm the theory which was done on the first half of the project's schedule.

Below is the experiments result on both water electrolysis and ice electrolysis which is to compare with the level of water arises in the tubing using consistent amount of voltage.

Table 1: Ice Electrolysis

No. of Exp.	Voltage (V)	Water Level (mm)	Time Taken (s)	P_{H_2} (Pa)
1	6	0.5	60	0.49
2	9	0.75	60	0.735

Table 2: Water Electrolysis

No. of Exp.	Voltage (V)	Water Level (mm)	Time Taken (s)	P_{H_2} (Pa)
1	6	0.5	90	0.49
2	9	0.75	90	0.735

4.2 DISCUSSION

From Table 1, we can see that when using Ice Electrolysis, to get the water level arises to 0.5 mm would acquire only about 60 minutes of time and to arise to 0.75 mm of displacement, it takes with the same amount of time which is 60 minutes or one hour. To have the displacement of water in the tubing, the experiment used battery energy of 6V for the first experiment and 9V for the second experiment respectively.

The angle H-O-H of individual H₂O molecules is equal to 104.5° in liquid and 109.5° in solid form(ice). Shorter length giving stronger hydrogen bonding.

Theoretically proven that by using ice, hydrogen can be produce easier as the bonding of ice is much more fragile which compare to bonding of molecule in water or liquid form.

Calculation for Pressure of Hydrogen (Figure 8):

$$P_{\text{air}} + P_{\text{H}_2} = P_{\text{water}} + P_{\text{air}}$$

P_{air} is same on both sides can be cancelled out,

Therefore for $\Delta h = 0.5 \text{ mm}$,

$$\begin{aligned} P_{\text{H}_2} &= P_{\text{water}} \\ &= \rho_{\text{water}} \times \Delta h \times g \\ &= 1000 \text{ kg/m}^3 \times (0.5/1000) \text{ m} \times 0.98 \text{ m/s}^{-2} \end{aligned}$$

$$P_{\text{H}_2} = \mathbf{0.49 \text{ Pa}}$$

For $\Delta h = 0.75 \text{ mm}$,

$$P_{\text{H}_2} = \mathbf{0.735 \text{ Pa}}$$

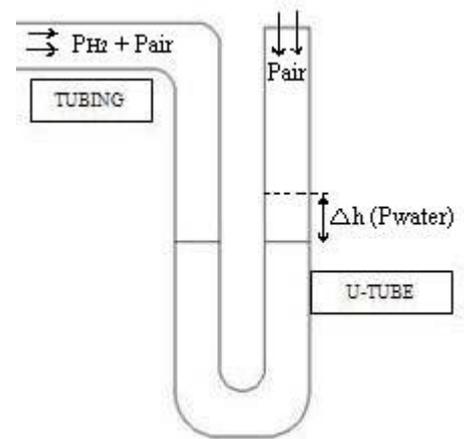


Figure 8: Indication of pressures in tubing and U-tube

CHAPTER 5

CONCLUSION

For the conclusion, the methodology which is used in this project can support the objectives in the project which is to compare that ice electrolysis will produce hydrogen with less amount use of voltage energy with compare to electrolysis of water. Ice or water ice is water in solid state which has less bonding strength and can be separated easier which compare to water in terms of molecule in liquid state. Therefore less energy required to break the bonds and can produce hydrogen more efficiently. Also when consuming less amount of energy to produce hydrogen, it shows that economically, ice electrolysis is more convenient than water electrolysis.

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APPENDICES

APPENDIX 1 – Project Gantt Chart

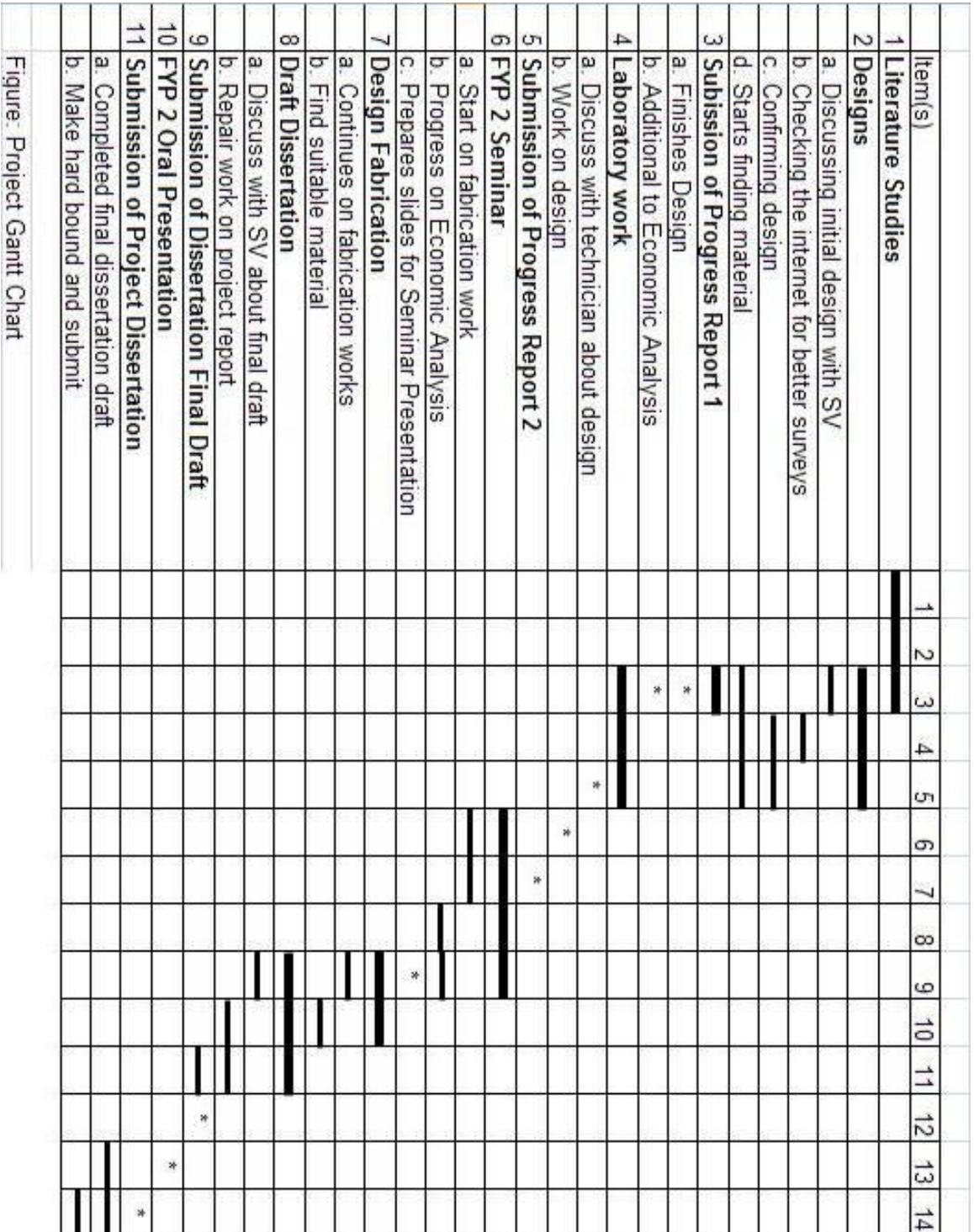


Figure: Project Gantt Chart

APPENDIX 2 – Experiment Works

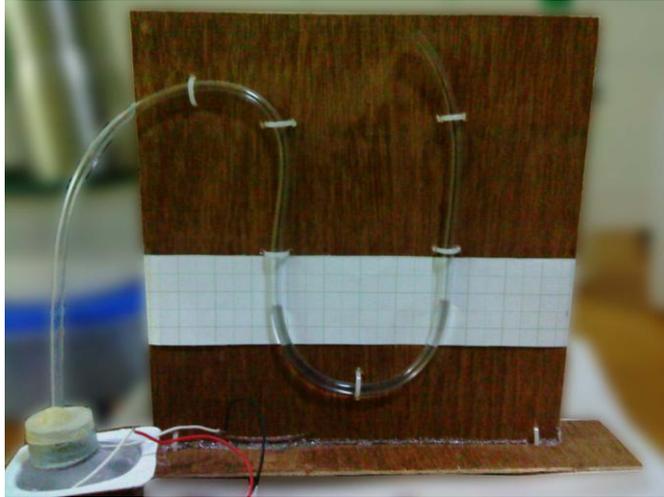


Figure 9: Apparatus setup for Ice Electrolysis

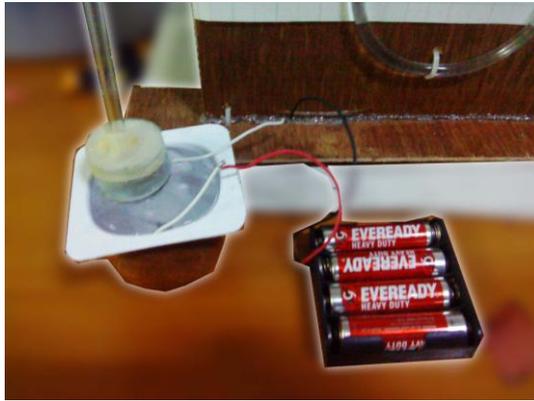


Figure 10: Electrodes placement by cathode (hydrogen produced) and anode (batteries)

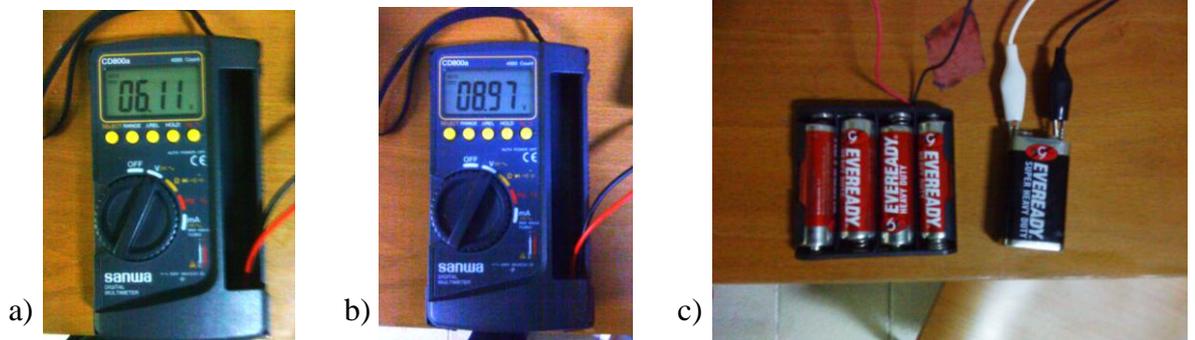


Figure 11: a) Value of voltage use in experiment 1. b) Value of voltage used in experiment 2
c) Types of batteries used in the experiments