FABRICATION AND CHARACTERIZATION OF PHOTOELECTROCHEMICAL SOLAR CELL USING COPPER (I) SULPHIDE SEMICONDUCTOR ELECTRODE

BY

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NOVEMBER, 2016.

DECLARATION

I hereby declare that this work is my product of research efforts undertaken under the supervision of Dr. Abdu Yunusa and has not been presented anywhere for the award of a degree certificate. All sources have been duly acknowledged.

________________________ ________________________

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CERTIFICATION

This is to certify that the research work on the Fabrication and Characterization of Photo-electrochemical Solar Cell using Copper (I) Sulphide Semiconductor Electrode was conducted by Yusuf Umar SPS/1/MPY/00020 and wholly supervised by Dr. Abdu Yunusa of the Department of Physics, Faculty of Science, Bayero University Kano.

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This is to certify that this Dissertation has been examined and approved for the award of the degree of Master of Science in Physics (M.Sc. Physics)

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DEDICATION

This research work is dedicated to victims of Boko Haram Insurgency in the Northeast, Nigeria.

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ABSTRACT

In order to address the increasing public concerns of carbon dioxide emissions and enhanced depletion of fossil fuel reserves motivates the development of technology based on alternative energy sources. This work presents results of fabrication and characterization of Photo-electrochemical solar cell (PEC) using p-type (Cu_2S) semiconductor electrode device. The p-type semiconductor was produced using modified electroless deposition method. When tested under illumination, the PEC solar cell was found to have an open circuit voltage, V_{oc}, of 235mV, and a short circuit current I_{sc} of 2.11mA, fill factor (FF) of 0.85, maximum power density (P_{max}) of $46.9x10^{-2}Wm^{-2}$ and efficiency (η) of 0.09%.

CHAPTER ONE

INTRODUCTION

1.0 GENERAL INTRODUCTION

The depletion of petroleum resources in this century and raising awareness of environmental change caused by the combustion of fossil fuels make nations and public reconsider the development of technology based on alternative energy sources, such as solar energy (Xin, 2014). While silicon-based technologies have been developed to harness solar energy efficiently, they are not yet competitive with fossil fuels mainly due to the high production costs. It is an urgent task to develop much cheaper photovoltaic devices with reasonable efficiency for widespread application of photovoltaic technology (Fujishima, 1972). An electrochemical approach (PEC cells) of trapping the solar energy has been the subject of intensive research today because of its economic viability and processing simplicity (Chandra, 1985). PEC solar cells are the most efficient chemical means known for converting solar energy. These devices are simple to construct and often consist of nothing more than two electrodes, one metallic and one semiconducting, that are immersed into a liquid (electrolyte) and exposed to sunlight. The semiconducting electrode can efficiently absorb sunlight, create delocalized charges, effect the separation of these charges with high yield, and produce an electrical current that leads to energy conversion (Minx, 1994). However, most work on PEC solar cell has been concentrated on n-type semiconductors. The best efficiency reported to date is approximately 12% at bell laboratory in Murray Hill, New Jersey, USA, using an n-GaAs single-crystal electrode (Musa and Abdu, 2013).

These conversion cells have such potential advantages as, a) easy method of fabrication, b) no problem of lattice mismatch, c) no need for antireflection coatings, d) with proper choice of an electrolyte redox couple, the Fermi level of an electrolyte could be adjusted to a desired level etc, over the conventional devices (Chandra, 1985). Again, one of the major early setbacks for PEC cells has been corrosion of the electrode surface during operation; however it has been reported that this problem is almost entirely eliminated where a p-type semiconductor is used (Minx, 1994). Although, the best result has been obtained using a single-crystal electrodes with efficiency of approximately 8% have been obtained with polycrystalline CdSe0.65T0.35 electrode (Musa and Abdu, 2013).In photo-electrochemical (PEC) solar cells, light energy is converted into electrical and/or chemical energy (Figure 1.1). The performance and effectiveness of a solar cell device mainly depend upon its design and the properties of the photovoltaic materials used especially the light absorbers and their connections to the external circuit (. The choice of the charge mediator involved may also be crucial.Light can be pictured as a stream of photons, energy packages of definite size or quantum of electromagnetic wave energy. Whenever light is absorbed by matter, photons transfer their energy and electrons in the materials so bombarded are excited to higher energy states, usually followed by relaxation to their ground state. In a photovoltaic device, the relaxation may be avoided as the energy stored in the excited electrons is quickly transferred to an external circuit, in order to do electrical work. In 1972, Honda and Fujishima managed to split water into hydrogen and oxygen by illuminating titanium dioxide semiconductor electrodes (Honda, 1972). Since titanium dioxide absorbs light mainly in the ultraviolet (UV) wavelength region, the efficiency in converting light energy to chemical and electrical energy is low. In order to form an efficient solar energy converter the semiconductor should have an energy band gap optimized for the spectral distribution of solar radiation and also exhibit chemical resistance against corrosion and dissolution (Heléne, 2005). One way to increase the spectral response is to sensitize the semiconductor material with dye molecules.

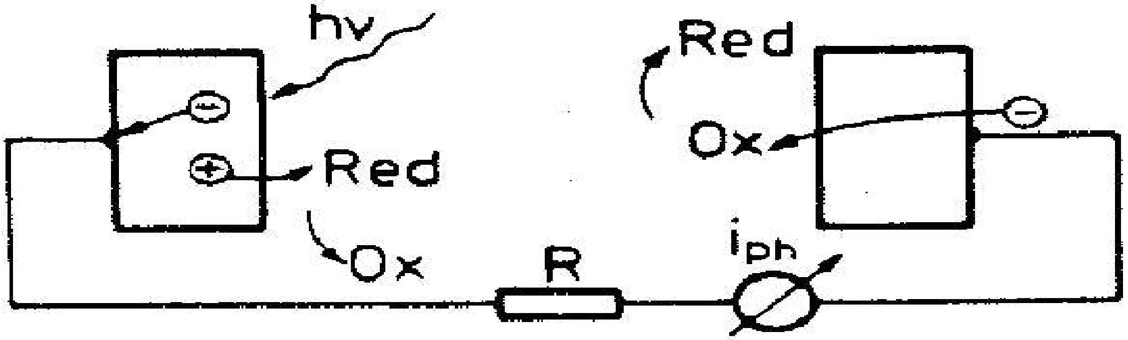


Figure 1.1: Conversion of Light to Electrical Energy in Photo-electrochemical Solar Cell

The figure 1.1 above show the process of light-to-electrical energy conversion in a photo-electrochemical (PEC) solar cell, where Red and Ox are the reduced and the oxidized species, respectively, in the electrolyte and R represents the resistance in the external circuit or load.The most successful thin film solar cell belong to the following material families: (i) CIGS (Copper indium gallium selenite) family, where the absorption semiconductor consist of CulnSe_2 or related material or alloy, such as CulnS_2, Cu(ln, Ga)Se_2 or even Cu(ln, Ga)(Se, S); (ii) the CdTe family; and (iii) the silicon family, consisting of an amorphous silicon-hydrogen alloy (a-Si:H or u.a-Si:H) or related alloy such as a-SiGe:H or a-SiC: H (Honda, 1972)

Chalcopyrite-type semiconductor like Cu(ln,Ga)S_2 or Cu (ln,Ga)Se_2 have very beneficial properties for photovoltaic applications, which lead to a strong scientific interest in thin-film solar cells based on these materials, however gallium and indium used for the preparation of active layer are very rare and expansive elements. This could lead to shortage in the supply of these elements and would inhibit a cost-effective large-scale production (Grätzel, 2001).

Silicon is the most commonly used material for the manufacturing of solar cells due to its direct band gap and low absorption coefficient Si-based cells are typically very thick leading to very significant increase in module cost (Longcheng, 2007). Therefore it is highly desirable to develop low-cost photovoltaic materials with high absorption efficiency. Despites these several progresses made researches are still ongoing to determine a suitable solution to the problems of some of the cells mentioned above. Thus, leading to the departing completely from the classical solid-state junction device, by replacing the phase in contact with the semiconductor by an electrolyte (liquid, gel or organic solid), thereby forming a photo-electrochemical device (Heléne, 2005).

1.1 STATEMENT OF THE PROBLEM

With 120 PW of solar energy striking the surface of the earth at any given moment, the challenge in converting sunlight into electricity via photovoltaic solar cells is to reduce dramatically the cost per watt of delivered solar electricity[2, 3].An electrochemical approach (PEC cells) of trapping the solar energy has been the subject of intensive research today because of its economic viability and processing simplicity (Chandra, 1985). However, most work on PEC solar cell has been concentrated on n-type semiconductors. The best efficiency reported to date is approximately 12% at bell laboratory in Murray Hill, New Jersey, USA, using an n-GaAs single-crystal electrode (Musa and Abdu, 2013). While, one of the major early setbacks for PEC cells has been corrosion of the electrode surface during operation; however it has been reported that this problem is almost entirely eliminated where a p-type semiconductor is used (Minx, 1994). Therefore, this study also aims at fabrication of p-type semiconductor device for PEC solar cell application.

1.2 AIM AND OBJECTIVES

The main objective of this study is to fabricate and characterize small-scale photo-electrochemical solar cells using p-type semiconductor (Cu_2S) device. The major contributions of this work is the fabrication of copper (I) sulphide (Cu_2S) p-type semiconductor device for photo-electrochemical solar cell application, produced via modified electroless deposition method (Yunusa, *et al.*, 2012).

1.3 SCOPE

In this work, photo-electrochemical solar cell was fabricated and characterized using p-type (Cu_2S) semiconductor electrode device.The p-type semiconductor was produced using modified electroless deposition method(Yunusa, *et al.*, 2012) andused as the photo-anode in photo-electrochemical solar cell.

CHAPTER TWO
LITERATURE REVIEW

2.0 INTRODUCTION

Mankind has regarded SUN as the biggest source of energy. Solar energy coming down to the earth's surface per year is approximately ten thousand times the worldwide energy consumption per year. Harnessing solar energy has therefore attracted the attention of the scientists, technologists, economists, sociologists and politicians. Many efforts have been directed towards developing new and better solar energy conversion devices (Patel, 2002).

A high degree of sophistication has been achieved in the fabrication of p-n junction solar cells. However, a challenging problem in solar energy research is solar energy storage. In 1970s, an alternative strategy was suggested in which a solid-liquid junction was used. In 1972, Fujishima and Honda used this junction to photo-electrolyte water and thus obtain hydrogen, which is a transportable form of energy. In 1975, Gerischer used this junction for direct conversion of solar energy into electricity. In this thesis, use of solid-liquid junction has been made to take up the strategy adopted by Gerischer i.e. direct conversion of solar energy into electricity. The photo-electrochemical conversion of energy is attractive because there is an opportunity of solar energy storage in the form of fuel, which is easily transportable. A photo-electrochemical cell isgenerally referred as a PEC cell (Patel, 2002).

A photo-electrochemical (PEC) solar cell is defined as a cell in which the irradiation by light of appropriate frequency on an electrode in contact with a suitable electrolyte produces a change in the electrode potential with respect to reference electrode under open circuit, conditions or produces a change in the current flowing in the galvanic cell containing the electrode, under short circuit conditions (Wei, 2007).

Number of research articles has been written on the field of photo-electrochemical conversion of solar energy. In the present decade two monograms one on PEC cells and the other on photo-electrochemistry and photovoltaics of layered semiconductorshave been published (Wei, 2007). First monogram introduces the subject of PEC conversion of energy from fundamentals and deals with all the recent development in the field whereas second describes various aspects of the layered semiconductors, e.g. their interfacial characteristics, optical to electrical (chemical) conversion parameters, photo-conversion and surface modification, surface electronic properties, quantum size effects and material preparation (Chandra, 1985).

In 1991, Grätzel and O'Regan presented an efficient dye-sensitized PEC cell containing a highly porous nanocrystalline titanium dioxide electrode sensitized with a monolayer of a ruthenium complex (Heléne, 2005). By this invention, high light absorption was achieved in the visible part of the solar spectrum. The working electrode consisted of nanometer-sized, interconnected titanium dioxide particles, which formed a three-dimensional network. In comparison to planar, single-crystal or polycrystalline films, they provided great advantages such as a large surface area, high porosity and enhanced light-harvesting capacity of the adsorbed dye, resulting in improved electrical and optical properties. The three-dimensional, nanoporous morphology facilitates the penetration of the electrolyte through the film down to the supporting conducting substrate and thus enables every single particle to be in contact with the electrolyte.

Dye-sensitized, nanocrystalline solar cells (nc-DSCs), also known as Grätzel cells, have obtained overall light-to-electricity conversion efficiencies of about 12% in diffuse daylight. At a light intensity of 1 sun (1,000 W m^{-2} 25ºC) providing a global AM1.5 spectrum, efficiencies of 11 % have been achieved while illuminating an area < 0.2 cm^2 and 10 % for an area > 1 cm^2(Grätzel, 2001). The choice of electrolyte material and its composition is crucial in the efforts to obtain optimized overall efficiencies of nc-DSCs. For long-term operation the usage of liquid electrolytes containing organic solvents is sensitive to negative stability effects, caused by evaporation or decomposition. Several attempts have been made to find substitutes for the liquid electrolyte by introducing hole-transporting materials, polymers, and p-type semiconductors (Musa, 2010). Room-temperature molten salts, also called ionic liquids, display qualities that make them attractive and suitable as potential alternative electrolytes. Desirable features such as a high electrical conductivity, non-volatility, good ionic mobility and electrochemical stability make them preferable to organic solvent-based electrolytes. Quasi-solid state electrolytes containing liquid dialkylimidazolium salts with additional polymer gels have also been successfully used in solar cells (Helene, 2005). Alternative redox mediators to the ubiquitous iodide/triodide couple have been introduced based on series of modified cobalt complexes. Several nc-DSCs incorporating these components have reached overall efficiencies of 8% (in $100Wm^{-2}$, AM1.5), certainly highlighting promising candidates for further investigation (Nura, 2014). Also other halide/polyhalide and corresponding pseudo halide systems have been tested with good results (Helene, 2005).In long-term measurements performed under different conditions regarding acceleration of the ageing process, organic imidazolium or nitrile based solar cells showed persistently good stabilities. The most critical feature was elevated temperatures. However, after about 1,000 h solar cell efficiencies of 5% were achieved at 45^oC and 1,000 Wm^{-2} illumination, and even 8% at 85^oC and darkness. Improved stability against UV radiation was obtained by the addition of magnesium iodide or by the modification of the TiO_2 surface by insulating oxide layers (Helene, 2005).

2.1 PHOTO-CONVERSION

Photons are the quanta of electromagnetic radiation. Traditionally, photo conversion is taken as a process through which the visibleelectromagnetic radiation is converted into electrical energy. In general, the photo conversion process involves interaction of these photons with materials, which give rise to:

1. Photoemission from metallic surfaces and

2. Photoeffects in semiconductors

Upon photoirradiation of semiconducting material and subsequent absorption of this radiation in the semiconductor, following processes may result:

1. Excitation of electrons from valance band to the conduction band.
2. Excitation of electrons from and to the impurity atoms.
3. Excitation of electrons to higher energy states in the same band.
4. Excitation of excitonic states.
5. Excitation of phonons.

With one or more of the above kind of processes occurring, two kinds of photoeffects; namely, photoconductive and photovoltaic have generally been recognized. It may be pointed out that it is the photovoltaic effect, which is at the root of the liquid junction solar cells.

2. 2 SEMICONDUCTOR-ELECTROLYTE INTERFACE

The electronic energy levels in a semiconductor can be described by using a band structure model, arising from combinations of the atomic energy levels. In large crystallites, the energy levels lie close enough to essentially form continuous bands. Valence electrons fill the valence band (VB) of the solid completely. They can be thermally excited into the conduction band (CB), thus producing vacancies (positive holes) in the VB. A presence of electron rich dopants gives rise to donor levels (donators of electrons) in the band gap and results in an n-type extrinsic semiconductor.

The electronic and optical properties of a solid material depend on the size of the energy band gap, between the top of the VB and the bottom of the CB. The Fermi distribution function, F(E), expresses the probability of an energy level E being occupied by an electron:

$$F(E)=\left[1+\exp\left[\frac{E-E_f}{kT}\right]\right]^{-1} \qquad (2.2)$$

Where E*f* is the Fermi energy, k is Boltzmann's constant and T is the absolute temperature. The Fermi energy is the electrochemical potential of the electrons in a solid, also described as the energy level where the probability of being occupied by an electron is ½. The Fermi level can also be defined as the highest occupied molecular or crystal orbital (HOMO). For metals, the valence band is only partly filled with electrons. In semiconductors, all bands are either completely filled or empty (disregarding thermal excitations), and therefore the Fermi level is placed in the band gap between VB and CB, and the conducting ability is low. For solar cells, the size of the band gap will affect the upper limitations for their conversion efficiencies. In case the band gap is very large, only light of short wavelengths will be absorbed, resulting in low photocurrents. If too small, the chances for large photocurrents are increased, but probably in combination with small voltages and low efficiency results.

In PEC cells, the electrolyte contains cations and anions for ionic conduction as well as a redox couple. A distribution of energy levels in a solution is shown in Figure 2. The probability of electron transfer between theelectrode and the electrolyte depends on the energy levels of the species involved at the instant of the charge transfer process. The probability that the energy of a component of the redox couple has changed to another level, due to thermal fluctuations in the polarization, is represented by the function W(V). The most probable energy levels of an oxidized agent (electronacceptor) and a reduced agent (electron donor) are qV_{ox} and qV_{red},respectively, where q is the charge. The intersection point of the distributionof oxidized and reduced species in the electrolyte, assuming equalconcentrations, can be interpreted as the electrochemical potential, qV_{redox}, orthe Fermi level of the electron in the liquid phase, where

$$qV_{redox} = (V_{ox} + V_{red})q/2 \qquad (2.3)$$

The redox potential of the electrolyte, V_{redox}, is determined by

$$V_{redox} = V^{0}_{redox} + \frac{R_g T}{nF} ln \frac{\{ox\}^{V_{ox}}}{\{red\}^{V_{red}}} \qquad (2.4)$$

Where V^0redox is the standard redox potential, Rg is the common gas constantand n is the number of electrons transferred. The chemical activities of theoxidized and reduced species in equilibrium are represented as {ox} and{red}, respectively, whereas ox and red are their stoichiometric factors. Inelectrochemical measurements the normal hydrogen electrode (NHE) isdefined as a reference point at certain standard conditions, while insemiconductor crystals the vacuum level is taken as the zero point.

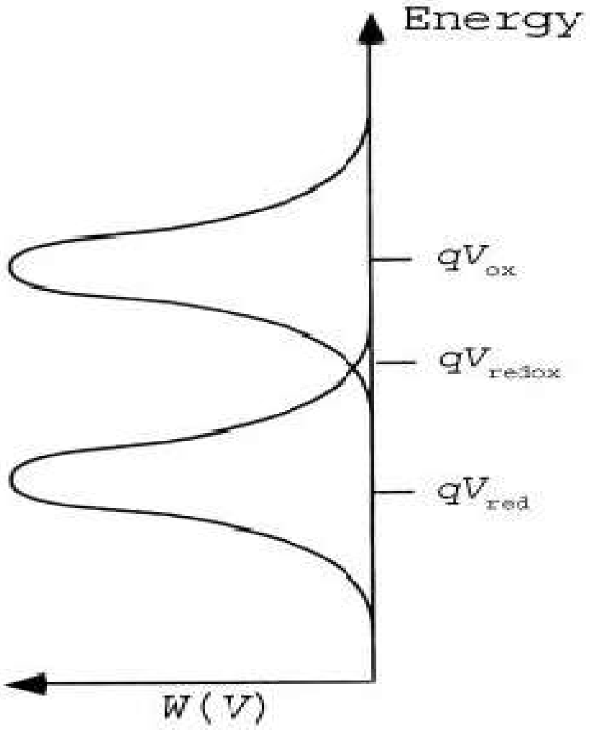


Figure 2.1: Energy levels of redox species in an electrolyte. W(V) represents the probabilityof finding a species with energy qV at a certain energy level, thus showing the distributionof filled and vacant levels in the solution.

2.3 SEMICONDUCTOR-ELECTROLYTE INTERFACE UNDER ILLUMINATION

When the semiconductor electrode is illuminated, an incident photon of energy greater than the band gap ($hv \geq E_g$) can be absorbed and excites an electron from the valence band to the conduction band, leaving a hole behind in the valence band. The optically generated electron-hole pairs in the depletion region are separated by the built-in electric field across the interface and swept away to opposite directions. The direction of the built-in electric field determines that the majority carriers move towards the bulk of the semiconductor and the minority carriers move towards the semiconductor-electrolyte interface. Because of the separation of these excess charge carriers, an electric field of the opposite direction of the original one is formed and partially compensates the magnitude of the original one. As a result, band bending is reduced and the Fermi level of the semiconductor and the electrolyte is no longer aligned (Figure 3). A photopotential V_{ph} is obtained at open circuit. If a counter electrode is provided and the two electrodes are connected through an external circuit with a load, then a photocurrent can be measured.

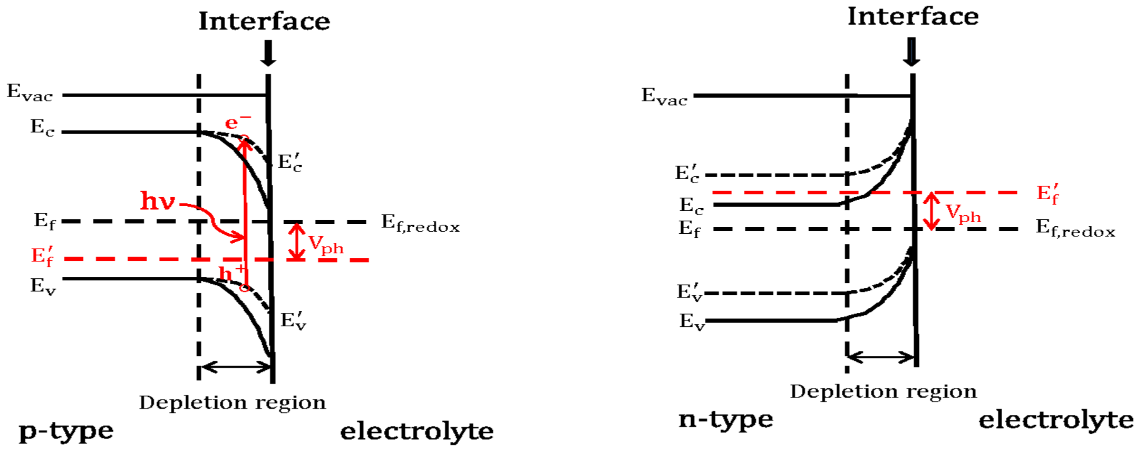


Figure 2.2: The band bending of a semiconductor in contact with a redox electrolyte under illumination V_{ph} is the photo-potential.

Based on the knowledge of the semiconductor-electrolyte junction discussed above, the existence of the built-in electric field across the junction is a necessary condition for the PEC solar cell to function properly because it separates the photogenerated charge carriers. The formation of the depletion region at equilibrium requires a suitable combination of the semiconductor and the redox electrolyte—the Fermi levels of the two materials must be different in a certain way for a p-type semiconductor as photoelectrode, the Fermi level of the redox electrolyte should be higher than the Fermi level of the semiconductor, while for n-type semiconductor, the Fermi level of the redox electrolyte should be lower. However, when the Fermi levels of the two materials are equal, no electron flow will occur across the interface and therefore no depletion layer will be formed. In such a case, the redox potential of the electrolyte is called "the flat band potential", because no band bending occurs. The flat band situation is not favorable for the purpose of fabricating a PEC solar cell.

At the illuminated semiconductor-liquid interface, electric fields (the space charge layer) occurs concurrent with charge-ion redistribution at the interface (Licht, 2012). The charge energy distribution in the semiconductor may be approximated by the Boltzmann function,

$$n_e \approx N_o exp\left[\ \frac{E_o - E_F}{KT}\right] \qquad (2.5)$$

Creating a space charge region

Where N_0 = constant ($N_C N_V$) effective density of state (in cm), E_0 = (E_c or E_v) energy at lower edge and upper edge of conduction band and valence band respectively, E_F = Fermi energy and K= Boltzmann constant.

$$ni^2 \approx N_o exp\left[\ \ \frac{E_c - E_v}{KT}\right] \qquad (2.6)$$

$$ni^2 \approx N_o exp\left[\ \ \frac{E_g}{KT}\right] \qquad (2.7)$$

On photo-generation of electron-hole pairs, this electric field impedes recombinative processes by oppositely accelerating and separating these charges, resulting in minority carrier injection into the electrolytic redox couple. Thus, free electrons are generated in the conduction band and free holes in the valence band.

$$2\ \ v = 2e^- + 2\ \ ^+ \qquad (2.8)$$

The electrons and holes are separated due to the potential generated at the interface of the semiconductor-electrolyte due to band bending. Since the semiconductor is p-type, it will act as the photo cathode thus, the electrons in the conduction band move to the interface toward the electrolyte, where they participate in reduction process i.e electrochemically react with the redox electrolyte. The transport has to switch from electronic to ionic and vice versa, where they are reduce to

$$Ox + e = Red$$

$$e.g\ F_e^{3+} + e = F_e^{2+} \qquad (2.9)$$

The holes in the valence bond participate in an oxidation reaction F_e^{2+} is oxidized to F_e^{3+}

i.e $Red + \quad = Ox$

$$e.g\ F_e^{2+} + \quad = F_e^{3+} \qquad (2.10)$$

2.4 ADVANTAGES OF PEC SOLAR CELLS OVER THE SOLID STATE PHOTOVOLTAIC CELLS

The important advantages of a PEC solar cell over the solid state cells in general can be summarized as follows:

1. The great ease with which the semiconductor/liquid junction can beformed.
2. Since the photosensitive junction in a PEC is extremely abruptcompared to the solid state counterpart and one side of the junctionis practically transparent to the solar spectrum, more of theincident light is absorbedwithin the region of high electric field atthe interface where charge carriers are more efficiently separatedand collected.
3. The simple formation and the abruptness of the photosensitivesemiconductor/liquid junction make the use of polycrystallinematerial in PECs feasible (Patel, 2002),
4. Many processing steps required for solid state solar cells e.g. (p-njunction) are either simplified or completely eliminated. The fabricationsteps, which would be eliminated for a PEC device, are as follows;
    a) deposition of the grid structure
    b) deposition of an antireflection coating
    c) high temperature processing of the semiconductor substrate forjunction formation by doping

Additional steps required in a PEC cell fabrication sequence relative to p-n junction devices are the following;

   a) injection of an electrolyte containing suitable redox species
   b) fabrication of counter electrodes
   c) insulation of the back surface of the photo electrode

5. In situ energy storage is possible with some PEC cells and thuscan accomplish in one stage, which the photovoltaic cell/storagebattery combination can accomplish in two stages (Pandey, 1996)
6. In an electrochemical photovoltaic cell, the band bending may beincreased by adjusting the redox potential of the electrolyte, thusincreasing the attainable open circuit voltage. In comparison, theopen circuit voltage (barrier height) in a Schottky type cell isgenerally independent of the metal work function because of the Fermi-level pinning (Pleskov, 1984).
7. It has been elegantly shown that significant reduction in costfor the fabrication of a PEC device (relative to solid cells) areexpected in spite of the additional processing steps outlined in (4)above (Patel, 2002).

2.5 CURRENT-VOLTAGE CHARACTERISTICS AND PARAMETERS OF A SOLAR CELL

The main electrical parameters of a solar cell can be analyzed by studying its current-voltage characteristics under illumination and in dark. These parameters are as follows: (1) short circuit current density (J_{sc}), (2) open circuit voltage (V_{oc}), (3) fill factor (FF), (4) dark saturation current density (J_o), (5) diode non-ideality factor (A), and (6) the electrical power conversion efficiency (η). These parameters provide the output performance of a solar cell. Because of the barrier layer which is essential for the photovoltaic effect, solar cell has diode characteristic in dark. When illuminated, an additional current component is added which shift the characteristic along the current axis by I_{sc} amount where I_{sc} is the short circuit current density and nearly independent of the voltage.

The fill factor (FF) is the measure of the deviation of I-V characteristic from the ideal one and it's define as the ratio of the maximum output that can be extracted from the cell to the product of I_{sc} and V_{oc} and is a measure of the "squareness" of the I-V curve.

i.e. $$FF = \frac{I_{max}V_{max}}{I_{SC}V_{OC}} \tag{2.11}$$

The electrical power conversion efficiency of solar cell is determined by the ratio of the power output to power input. The efficiency of a solar cell can be determined from its I-V characteristics curve as follows:

$$\eta = \frac{P_{max}}{P_{in}} = \frac{J_{SC}V_{OC}FF}{P_{in}} \tag{2.12}$$

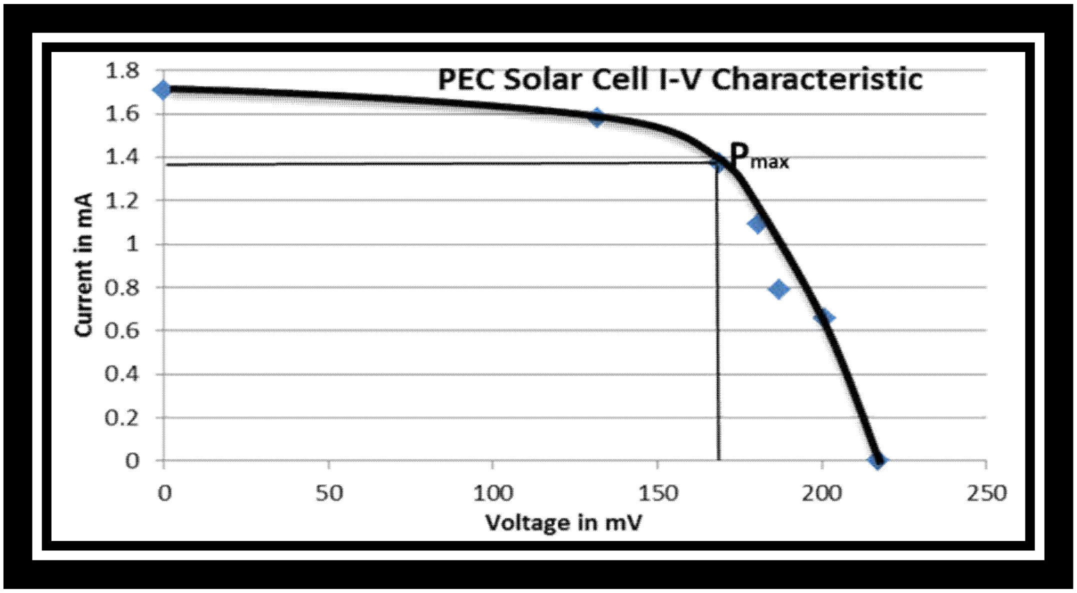


Figure 2.3: shows the *I-V characteristics of the photoelectrochemical solar cell*

The maximum power (P_{max}) is found, where the product of the current and voltage is maximum, since the electrical power is given by current (I) times voltage (V), i.e. $P = IV$**(2.13)**

CHAPTER THREE

MATERIALS AND METHODS

3.0 INTRODUCTION

This chapter describes the procedurefor fabrication of the Cu-Cu_2Sphotoelectrochemical solar cell. Copper preparation, formation of Cu_2O layers, copper sulphide Cu_2S formation, sodium chloride and ferric chloride solution preparation,and determination of electrical parameters of Cu-Cu_2S photo-electrochemical solar cell. Details are given below.

3.1 MATERIALS

Copper sheet (BDH 99.99%), 78HW-1 magnetic heating stirrer, weighting balance (Ohaus AR 2140), sodium sulphide (Na_2S BDH), sodium chloride (NaCl), ferric chloride ($FeCI_{2)}$, copper sulphate (CuSO4), and distilled water.

3.2 COPPER PREPARATION OF Cu_2S

According to an existing procedure for the preparation of quality Cu_2O material, the copper surface is conditioned according to an existing procedure (Musa, et al; 1998). This eliminates any grease or dirt from the surface of the copper foil. High purity copper sheets (0.1mm thickness, and 99.99% purity) were cut into samples of 3 cm x 2 cm size, and were polished afterwards. The copper sheets were then washed in 30%

nitric acid for 20secs, and then later rinsed in distilled water severally and, finally, dried between tissue papers.

3.3 SOLUTION PREPARATION

Anhydrous copper II sulphate of purity 99.0% (BDHGPR) of molecular weight 159.61 was used to prepare the CuSO4 solution of 0.1 M concentration. A Metler B154 analytical balance was used to weigh 15.9610g of the copper II sulphate and dissolved in 1000 cm^3 distilled water.

3.4 GROWTH OF CUPROUS OXIDE(Cu_2O)LAYERS

The deposition of the n-type Cu_2O layer was done by chemical heating method (Abdu, 2012). In this method, 100 cm^3 of CuSO4 solution was taken in a beaker and its pH was measured to be 4.62 ± 1, using TES 1380 pH meter. The beaker containing the solution was heated to 80^0C using 78HW-1 magnetic heating stirrer. Later, one copper foil was dipped into the heated solution and the heating was maintained for 2hrs. The sample was removed at the end of the time, washed in distilled water severally and finally dried between tissue papers.

3.5 COPPER SULPHIDE (Cu_2S) FORMATION

78.04g of Na_2S, was weighted using Ohaus AR2140 balance, and dissolved in 1 liter of distilled water to make 0.05M Na_2S solution (Abdu, 2012). The n-Cu_2O substrate was totally immersed in the Na_2S solution for about 2min then removed and finally dried in the air.

The reaction for this formation is as follows

$Na_2S + H_2O + Cu_2O \rightarrow Cu_2S + 2NaOH$

3.6 SODIUM CHLORIDE SOLUTION PREPARATION

2.922g of NaCI was dissolved in 1ltr of distilled water in a cylindrical transparent container to make 0.05M of NaCl. This process was repeated for 5.844g, 8.766g, 11.688g and 14.610g to make 0.10M, 0.15M, 0.20M and 0.25M of NaCl respectively.

3.7 FERRIC CHLORIDE SOLUTION PREPARATION

19.0125g of $FeCI_2$, was measured and dissolved in 1 liter of distilled water to make 0.15M $FeCl_2$ solution.

3.8 Cu-Cu_2S PHOTO-ELECTROCHEMICAL SOLAR CELL FABRICATION

The cell consists of a photo-anode semiconductor working electrode (Cu_2S) and counter electrode made of Copper metal (Cu). Both electrodes were immersed in electrolyte. The cell was kept under illumination, where the open voltage, V_{oc} and short circuit current, of the cell were measured under no load condition for only the electrolyte and the addition of redox couple into the electrolyte to determine the effect of redox couple in the PEC solar cell. Later different values for the voltage V, and the current I, of the cell were also measured by varying the load

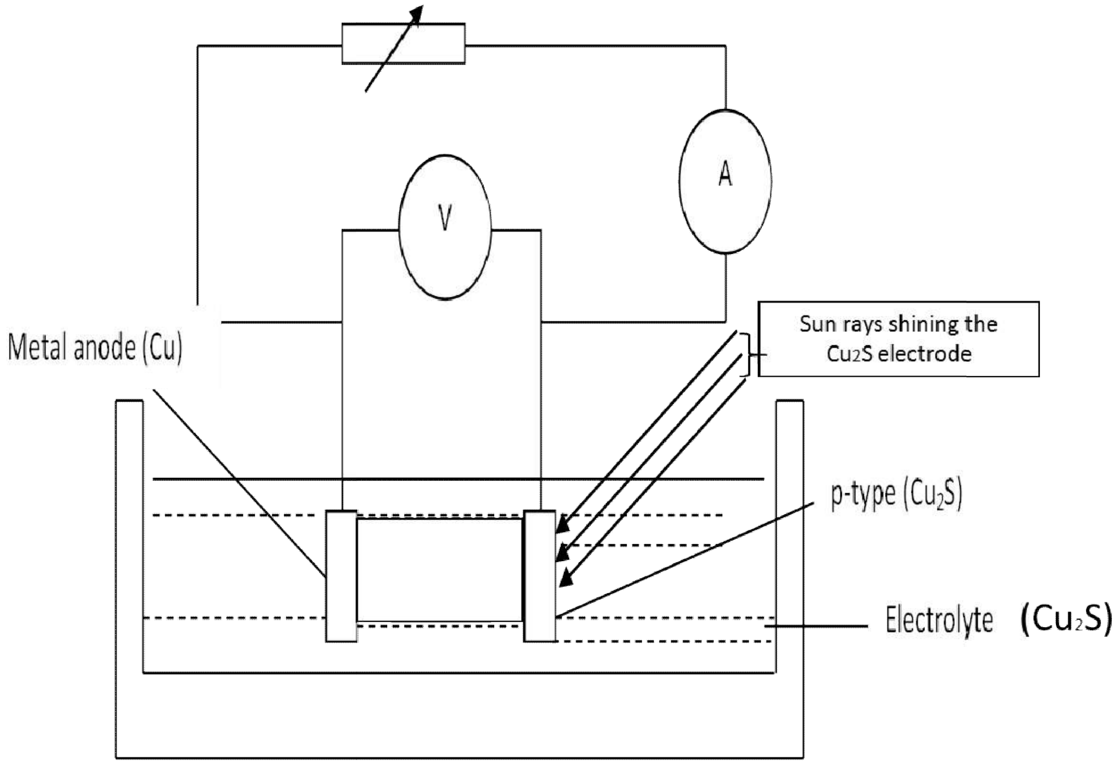


Figure 3.2: Illustration of the fabricated Cu – Cu_2S Photoelectrochemical Solar Cell, under load condition

The figure above shows an idealized diagram of a PEC solar cell in which an aqueous solution of sodium chloride is use as the electrolyte. The Na^+ ions migrate toward the semiconductor electrode and the Cl^- ions migrate toward the metal electrode. But, now there are two substances that can be reduced at the anode: Na^+ ions and water molecules

3.9 REACTION OF THE ELECTROLYTE SOLUTION

$$2NaCl \rightarrow 2Na + Cl_2$$

At the Anode: $Na^+ + e^- \rightarrow Na$

$$2H_2O + 2\,e^- \rightarrow H_2 + 2\,OH^-$$

At the Cathode $2Cl^{-} \rightarrow Cl_2 + 2\ e^{-}$

$$2H_2O \rightarrow O_2 + 4\ H^{+} + 4\ e^{-}$$

The two phenomenons can happen in a semiconductor electrolyte system under photoexcitaion or illumination:

a) The electrolyte species, may be excited to higher energy states or

b) The semiconductor absorbs the photons, which results in theenhancement of charge carriers in it through the generation ofelectron hole pairs.

The first phenomenon leads to photogalvanic cells while the second phenomenon leads to photo-electrochemical cells. It is the second phenomenon, with which we are concerned in the present work. The principle of charge transfer reaction at the semiconductor electrolyte interface forms the basis of various types of photo-electrochemical solar cells. In addition to the semiconductor electrolyte interface, incorporation of a counter electrode in the electrolyte to complete the electrical circuit gives the desired photo-electrochemical solar cell

3.10 CURRENT – VOLTAGE CHARACTERISTICS MEASUREMENT

The constructed Photo-electrochemical solar cell was used for testing current-voltage characteristic measurement under illumination. The open circuit voltage and the short circuit current were measured. Variable load resistance was used to record the current-voltage values. The current-voltage characteristic curve was plotted and used to obtain the solar cell external electrical parameters.

CHAPTER FOUR

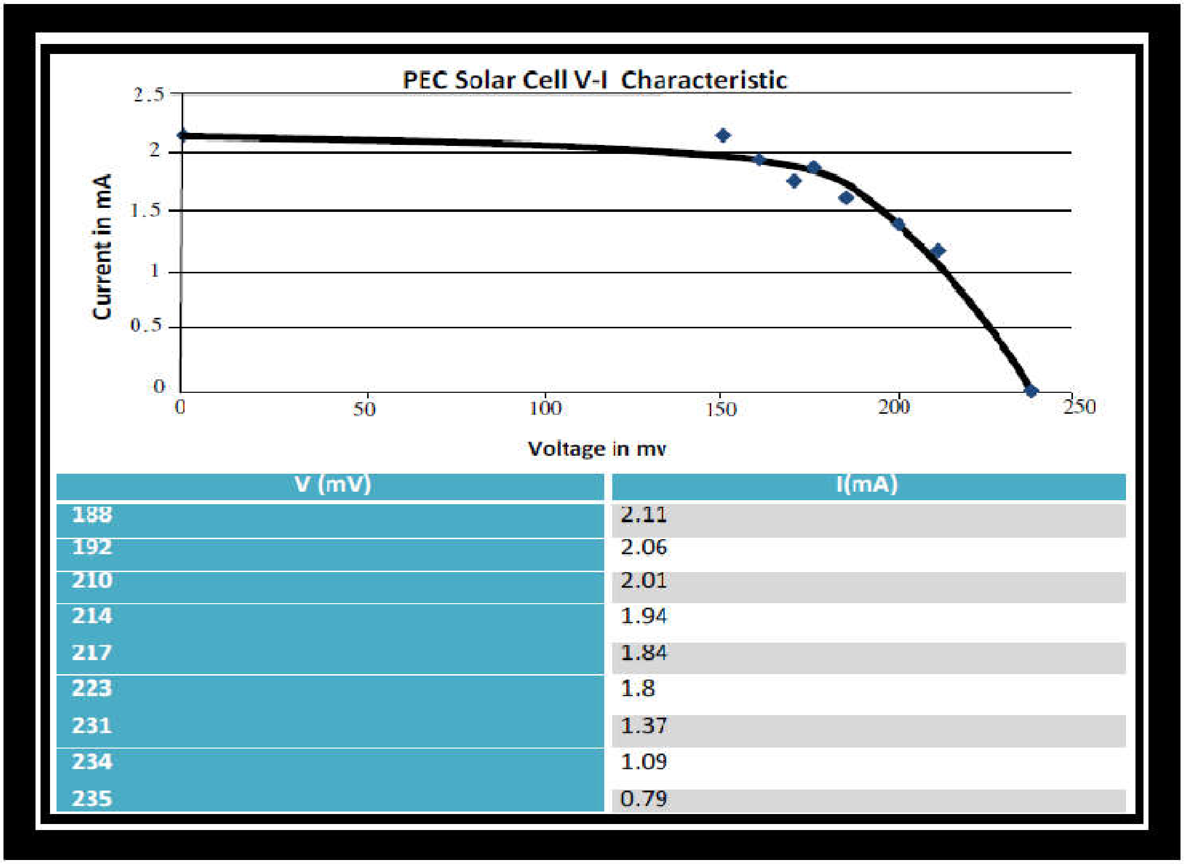
RESULTS AND DISCUSSION

4.0 INTRODUCTION

This chapter presents the experimental results and discussion on the fabricated Cu-Cu_2S photoelectrochemical solar cell.

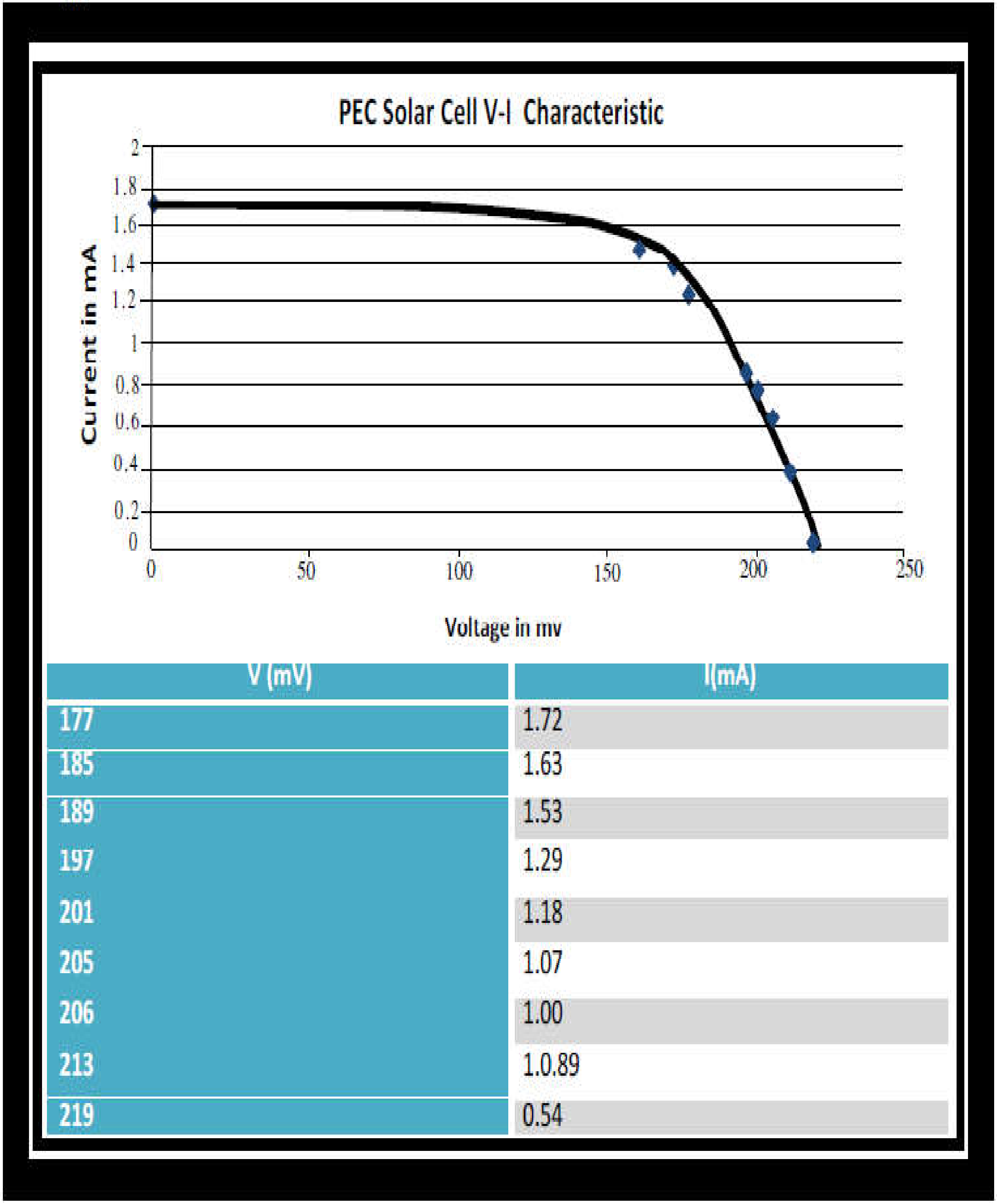
From figure 4.1 to figure 4.5 below, the Photoelectrochemical solar cell performance is better for electrolyte (NaCl) concentration of 0.25M containing redox couple ($FeCl_3$), because of its higher values of the cell efficiency.

4.1 RESULT



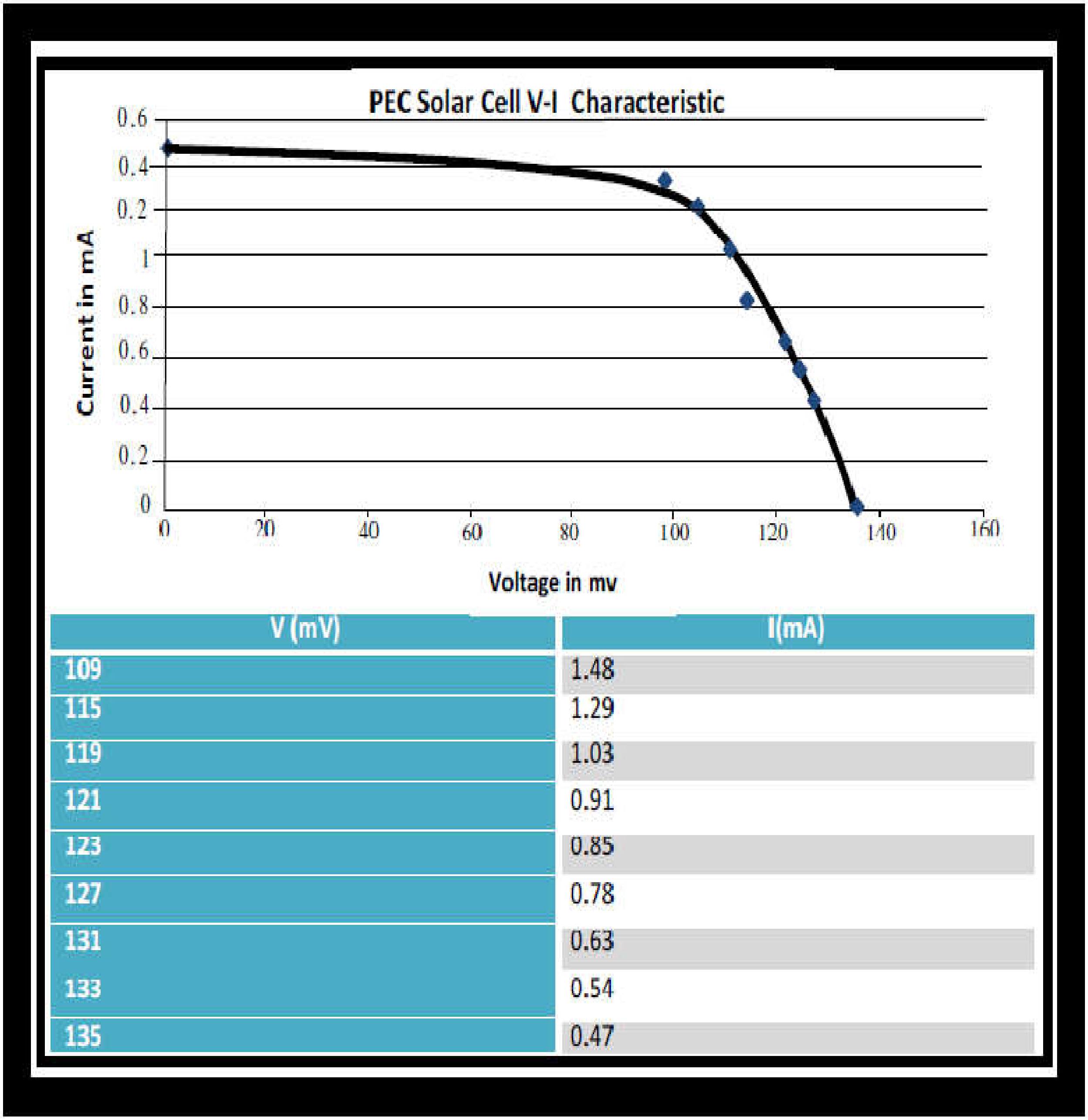
V (mV)	I(mA)
188	2.11
192	2.06
210	2.01
214	1.94
217	1.84
223	1.8
231	1.37
234	1.09
235	0.79

Figure 4.1: Current-Voltage Characteristics of Photo-electrochemical Solar Cell under Illumination with 0.25M NaCl (Electrolyte) with 0.15M Redox Couple ($FeCl_3$)



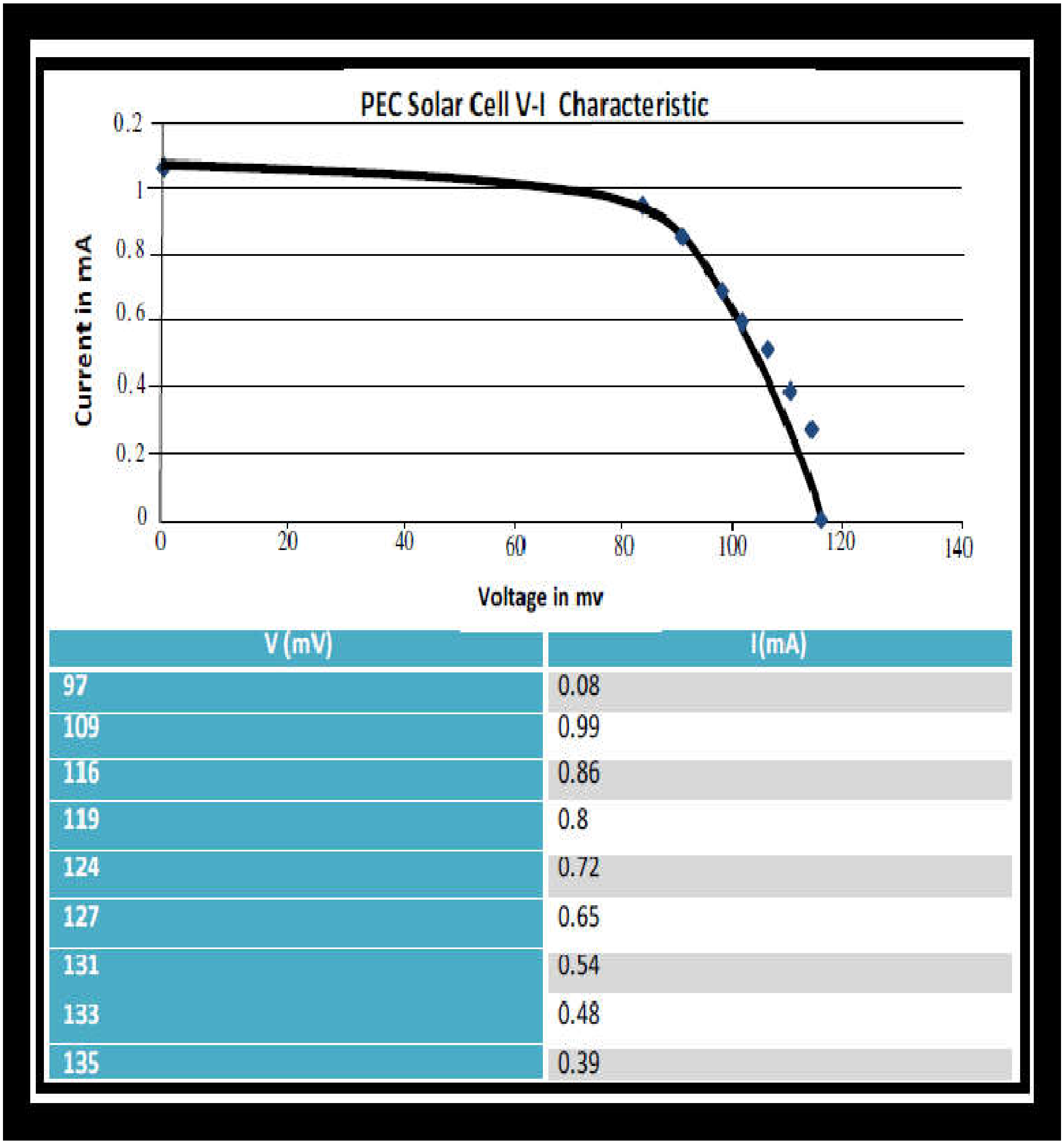
V (mV)	I(mA)
177	1.72
185	1.63
189	1.53
197	1.29
201	1.18
205	1.07
206	1.00
213	1.0.89
219	0.54

Figure 4.2: Current-Voltage Characteristics of Photo-electrochemical Solar Cell under Illumination with 0.20M NaCl (Electrolyte) with 0.15M Redox Couple ($FeCl_3$)



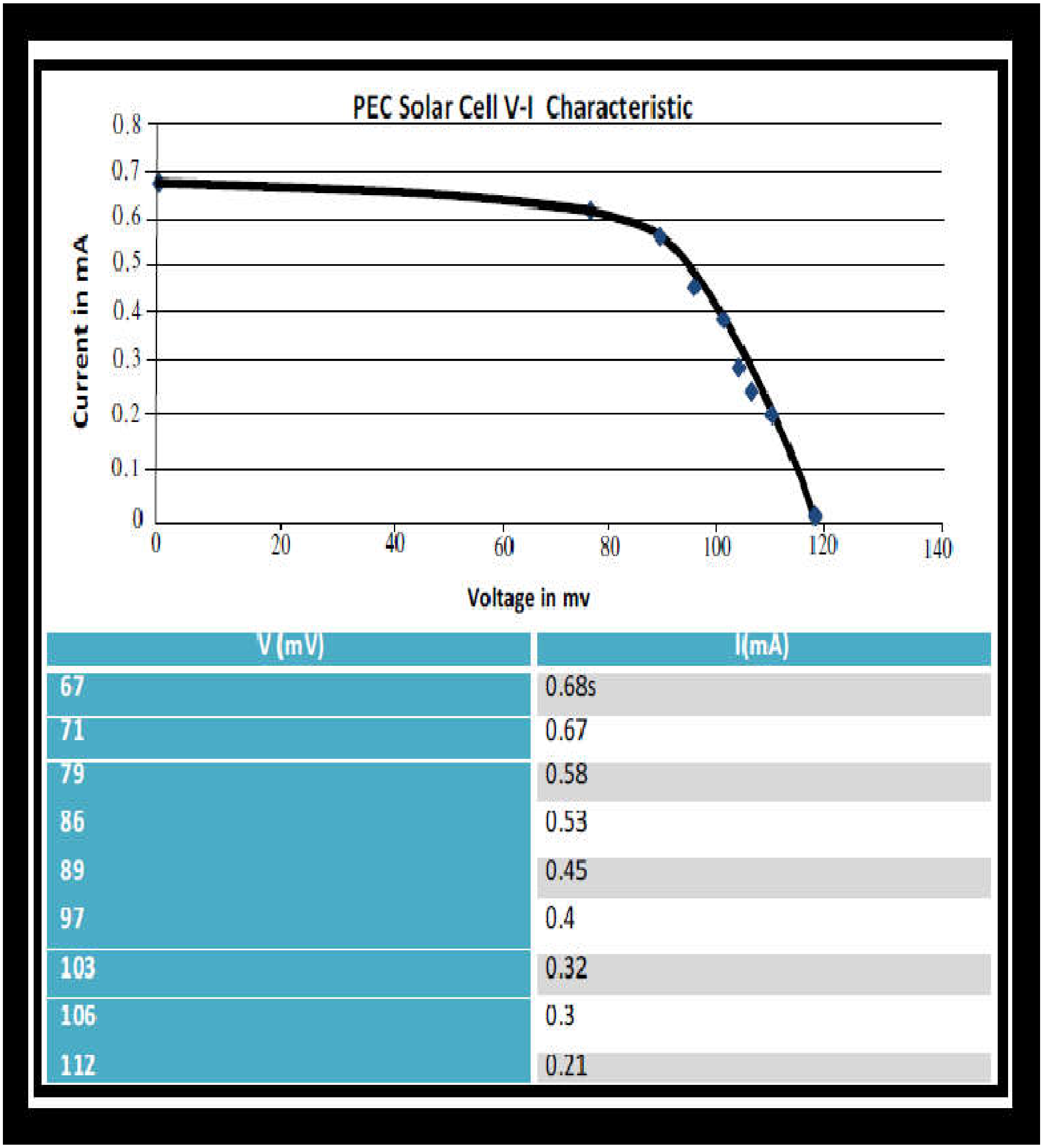
V (mV)	I(mA)
109	1.48
115	1.29
119	1.03
121	0.91
123	0.85
127	0.78
131	0.63
133	0.54
135	0.47

Figure 4.3: Current-Voltage Characteristics of Photo-electrochemical Solar Cell under Illumination with 0.15M NaCl (Electrolyte) with 0.15M Redox Couple ($FeCl_3$)



V (mV)	I(mA)
97	0.08
109	0.99
116	0.86
119	0.8
124	0.72
127	0.65
131	0.54
133	0.48
135	0.39

Figure 4.4: Current-Voltage Characteristics of Photo-electrochemical Solar Cell under Illumination with 0.10M NaCl (Electrolyte) with 0.15M Redox Couple ($FeCl_3$)



V (mV)	I(mA)
67	0.68s
71	0.67
79	0.58
86	0.53
89	0.45
97	0.4
103	0.32
106	0.3
112	0.21

Figure 4.5: Current-Voltage Characteristics of Photo-electrochemical Solar Cell under Illumination with 0.5M NaCl (Electrolyte) with 0.15M Redox Couple ($FeCl_3$)

The current – voltage characteristics of figure 4.1 to figure 4.5 above,is used to study the external parameters of the photo-electrochemical solar cell. The parameters extracted are the short circuit current (I_{sc}), open circuit voltage (V_{oc}), fill factor (FF), the maximum power density (P_{max}) and efficiency (η) as shown in the table 4.1 below.

Table 4.1: Parameters of photo-electrochemical solar cell under different concentrations of sodium chloride solution

Electrolyte (NaCl) + Redox Couple ($FeCl_3$)	**External Parameters of the Photoelectrochemical Solar Cell using different Electrolyte Concentration**				
	V_{oc} (mV)	**I_{sc} (mA)**	**FF**	**Pmax (10^{-2} x Wm^{-2})**	**η (%)**
0.05M	**112**	**0.68**	**0.6246**	**5.2856**	**0.0101**
0.10M	**133**	**1.08**	**0.7513**	**11.9900**	**0.0231**
0.15M	**135**	**1.48**	**0.8074**	**17.9244**	**0.0345**
0.20M	**219**	**1.72**	**0.8082**	**33.8267**	**0.0651**
0.25M	**235**	**2.11**	**0.8501**	**46.9012**	**0.0901**

From the table 4.1 above the PEC solar cell performance is better for electrolyte concentration of 0.25M because of its higher values of short circuit current (I_{sc}), open circuit voltage (V_{oc}), fill factor (FF), the maximum power density (P_{max}) and the electrical power conversion efficiency (η)of the PEC cell.

4.2 DISCUSSION

The current – voltage characteristics of the fabricated photoelectrochemical solar cell tested under different electrolyte concentration as shown in Figure 4.1 to Figure 4.5,was used to study the external parameters of the photoelectrochemical solar cell. The cell performance is better under electrolyte concentration of 0.25M containing redox couple ($FeCl_3$),because of its higher values of short circuit current (I_{sc}) of 2.11mA, open circuit voltage (V_{oc}) of 235mV, fill factor (FF) of 0.85, the maximum power density (P_{max}) of $46.9x10^{-2}Wm^{-2}$ and electrical power conversion efficiency (η) of 0.09%. This value of the electrical power conversion efficiency is higher when compared with that of 0.069% obtained for $Cu-Cu_20$ photo-electrochemical solar cell (Musa and Yunusa, 2013), 0.08% recordedfor Cu/Cu2S (Nura, 2014) and 0.002% obtained for Cu_20-Cu_2S Heterojunction solar cells (Yunusa, 2012).

CHAPTER FIVE

SUMMARY, CONCLUSION AND RECOMMENDATIONS

5.0 SUMMARY OF RESULTS

The successful fabrication of p-Cu_2S semiconductor device for photo-electrochemical solar cell applications was achieved by the sulphidation of n-Cu_2O produce using modified chemical method of heating (Yunusa, 2012).

Photo-electrochemical solar cell was fabricated with p-Cu_2S semiconductor and a metal copper. When tested under illumination, photo-current and photo-voltage were successfully detected in the PEC solar cell, the PEC solar was found to have an open circuit voltage, V_{oc} ,of 217mV, and a short circuit current I_{sc} of 1.71mA, fill factor (FF) of 0.64, maximum power density (P_{max}) of 39.33Wcm^{-2} and efficiency (η) of 0.072%.This is the best result obtained, under electrolyte concentration of 0.25M of NaCl containing 0.15M of Ferric chloride.

5.1 CONCLUSION

The successful fabrication of the p-Cu_2S semiconductor electrode for photo-electrochemical solar cell applications was achieved, using modified electroless deposition method of heating (Yunusa, 2012). When tested under illumination, photo-current and photo-voltage were successfully detected with conversion efficiency (η) of 0.072%. This value represents an improvement over when compared with that of 0.069% obtained for Cu-Cu_2O photoelectrochemical solar cell (Musa and Yunusa, 2013)

5.2 RECOMMENDATIONS

1. Future research in this field should try the use of other metal oxides, chloridesand ionic compounds (NaI, $MgCl_2$, Cu_2SO4 etc.) for possible improvement in the electrical properties of the cell (like I_{sc} and V_{oc})
2. Stability studies should be conducted in future research to test for cell degradation over time

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