

Volume 7, Issue 2, 415-424



# **Green Hydrogen Synthesis from Human Urine as Sustainable Bioenergy Resources**

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*Abstract: With the earths cry for help as pollution rate increases, researchers are faced with a common task of tackling pollution resulting from dependence on fossil fuel as well as delivering sustainable energy. Renewable energy resources such as solar, wind, hydro to mention a few are currently finding applications within the world energy mix but some limitations which range from meteorology of locations to expected maximum energy output attainable. Hydrogen, the most abundant element in the world stands chance of abating this problem. However conventional method of its producing, poses severe treat to the atmospheric environment with the release of oxides of carbon hence, referred as blue hydrogen. Contrarily, green hydrogen from human urine stands a more sustainable and environmentally friendly energy resource. This study was aimed to empirically model the synthesis of green hydrogen from urea in human urine by an electrolytic process. The synthesized hydrogen was characterized on physiochemical properties of conductivity, turbidity, pH, specific gravity and colour, while the precursor urine characterized on gender, exposure duration and storage temperature. The synthesis process was modelled using Microsoft excel solver for the overall cell energy or polarization curve model, the Faraday's efficiency model and gas purity model at electrolyte concentrations of 25 wt./wt., 30 wt./wt. and 35 wt./wt. of potassium oxide (buffer} to urea over a five-temperature interval range of 45 to 85 <sup>o</sup>C. Findings revealed that the gas produced was 99.88% hydrogen at the cathode. Also, hydrogen produced increased with increase in electrolyte concentration and moderate temperature with optimal conditions at 35 w/w electrolyte concentration and 65 °C. However, the minimum cell voltage was 2.06 V at 85 <sup>o</sup>C and 35 w/w electrolyte concentration. With an exception of the Faraday's efficiency model at 30 wt./wt. electrolyte concentration across the system's operating temperature range yielding an R<sup>2</sup> value of 0.711, all the models yielded coefficient of determination values in the range of 0.96 and 0.99, indicating good fit for the alkaline urine electrolysis for green hydrogen synthesis from human urine.* 

*Keywords: Human urine, Urea, Electrolysis, Green Hydrogen*

# **1. INTRODUCTION**

The need for reliable and sustainable power sources across the world cannot be over emphasized. Consequently, there is need for more reliable and sustainable for power generation routes the aforementioned sources. Hence alternative energy sources such as solar, wind, hydro, geothermal, fuel cell, have complimented roles in the energy-mix for the attainment of an overall sustainable energy system. Goals numbers seven and thirteen of the United Nations sustainable development goals, which are affordable clean energy and climate action respectively are closely related in energy generation via the none application of fossil fuels. In other words, to conform to the above goals, the use of fossil fuel is diminished or abated completely. Fossil fuels have dominated the world's energy source for decades and still are with about 82% of the global energy supply still coming from it [1]. These fossil fuels when combusted produce greenhouse gases such as carbon monoxide, carbon dioxide, oxides of nitrogen, sulphur dioxide which cause adverse effects on human health and on the atmosphere leading to global warming [2]. Apart from its effect of the environment and human health, fossil fuels are also a limited source of energy which is consumed at a faster pace because of the high energy demands [3]. Hence for a more suitable and environmentally friendly energy resource material, there is the need for other sources without given off harmful gases. Hydrogen the most abundant element on the earth satisfactorily met the above conditions. Hydrogen is characterised by combustion with oxygen to get energy and generates only water vapour as the products of the thermochemical reaction at atmospheric conditions [4]. Hydrogen is non-toxic, odourless, tasteless, and light weight gas with high energy content and it is approximately three times that of gasoline (about 44 MJ/kg) which has led to the

statement "hydrogen; the future of energy" [5]. Due to its low density, it is difficult to be stored and transported across long distances except with proper in-situ energy generation facility [6].

Hydrogen in its stable form is normally attached to another element. Since the world's energy demand is fast increasing, finding sustainable energy resources are paramount and hydrogen as fuel has been noticed to be environmentally friendly and on combustion gives water vapour and energy. Similarly, as feed to fuel cells, which operates in reverse to electrolysis, yields water and electric power. Although hydrogen can be gotten from different sources such as methane and ammonia, most methods of production of hydrogen conventionally to obtain "grey and blue hydrogen" with implications of carbon capture and storage are environmentally unsustainable because these processes, produces greenhouse gases [7-9]. On the other hand, electrolysis of water has been a common practice for generation of hydrogen commonly known as green hydrogen. Although it consumes about 1.23 Volts of electric power to break the hydrogen and oxygen bonds, urea only requires bout 0.37 Volts to achieve same output. The electrolysis of urea produces twice the amount of hydrogen gotten from water. The hydrogen generated can later be used in fuel cell to generate electricity [10][11]. Urine, which is abundant in the earth as it can be gotten from both animals and humans, contains urea which can be electrolyzed to generate hydrogen.

Human urine is a mixture that comprises of electrolytes, nitrogenous compounds, vitamins, hormones, organic acids, and miscellaneous organic compounds. It contains chemical compounds such as water, ammonia, urea, sulphate, sodium, uric acid [12]. An average human discharges about 1.42 litres/day [13]. It is abundant produced by every living human and animal on earth. Urine has its negative impact on the environment when not properly disposed, but when in used via electrolytic transformations, yields "green hydrogen" [7]. Human urine as a raw material for the production of green hydrogen via electrolysis to produce cleaner energy and stop air pollution of the environment and not only solves the problem of air pollution caused by poor urine disposal but create a sustainable electric power resource material in fuel cell. This study was aimed at empirical modelling of the synthesis route of hydrogen from the urea of human urine via electrolysis as a sustainable fuel in fuel cells for energy generation. Electrolysis involves passing direct current through conductors, electrodes (anode and cathode) via a solution (electrolyte) given rise to chemical reactions. The alkaline electrolyte electrolytic cell of potassium hydroxide compared to water has been attributed with high yield in hydrogen gas [10]. Electrolytic cell process models include (1) the polarization curve model which predicts the cell potential ( $U_{rev}$ ), is the electric potential difference between the electrodes of the cell. It accounts for the effects of varying temperatures and current densities on the cell potential [14]; (2) the Faraday's efficiency depicts the electric charge utilized by the cell governed by Faraday's law. The amount of electric charge that passes through the cell directly corresponds to the quantity of hydrogen generated. In alkaline electrolysers, number efficiency ranges between 80% and 95% [15][16]; (3) the gas purity model which is a critical operational parameter especially during operation, particularly when an electrolyser is operated by renewable energy sources, also it is a basis for determining shutdown operating conditions in order to avoid explosive of the hydrogen-oxygen mixtures [14].

## **2. MATERIALS AND METHOD**

The materials used included a male and a female human urine obtained from two volunteers' students of the Afe Babalola University. Other chemical reagents used included urea and potassium hydroxide pallets, distilled water.

### **2.1 Sampling**

Human urine was obtained from two volunteers (a male and a female) in good conditions of health. Each sample was kept in sterilized medical laboratory type urine sampling bottles. Both specimens were kept in a refrigerator in the laboratory, in order to avoid microbial degenerative effects on the samples.

### **2.2 Urine Analysis**

Physiochemical analysis was carried on the urine samples for colour, density, pH, conductivity and turbidity at the sampling and storage temperatures as documented elsewhere [17-21]

### **2.3 Experimental Setup of Electrolytic Cell**

The setup consisted of a single cell designed and used to conduct the effects of variations in electrolyte concentrations and systems temperatures on the gas produced at the cathode and a stacked cell designed to obtain model parameters for cell potentials, Faraday's efficiency and hydrogen to oxygen gas purity for a continuous operation of same system.

### **2.3.1 Single cell design**

The electrolytic cell was made using a 600 ml beaker, two 1.5 cm by 16 cm test tube and two cylindrical stainless-steel rods of 4 mm in diameter and 15 cm in length as electrodes. A 9 Volts DC cell was connected to power both ends of the electrode. An ammeter and voltmeter were connected in series and parallel respectively to the electrolyser to measure the current and voltage passing through to the system. Both electrodes were kept at the opposite sides of the electrolytic tank. The gases produced at the anode and cathode are collected separately by the two compartments paced on top of the electrodes [1].

### **2.3.2 Stacked Cell Design**

A second set-up electrolytic cell was made out of stainless-steel electrode with a plastic electrolytic tank, a diaphragm and a hose [23]. The stainless steel with a thickness of 1mm, was cut into a rectangle shape with six pieces of size 2cm by

10cm and two pieces of size of 2cm by 14cm to make up the stack of electrodes and connectors respectively. Stainless was sandpapered to increase the surface area. A 1cm drill bit was used to drill a hole through all the stainless-steel electrodes and connected together with screws, nuts and washers. The electrode was at opposite ends of the electrolytic tank and the diaphragm was placed about 5 cm apart. A 0.7 cm hole was drilled on the lid of the electrolytic tank where the diaphragms and hoses came out of both holes.

# **2.4 Production of Green Hydrogen via Electrolysis**

Urine sample was poured into the fabricated spilt electrolytic cell attached with expandable balloons at each end of the electrodes to recover and store the gases produced. Standard solutions of 25 wt.%, 30 wt.% and 35 wt.% KOH were prepared to examine the effect of varying electrolyte concentrations on the gas production rate [24]. For each KOH concentration, 100mls was poured into the cell and stirred for a particular reaction temperature. The alkaline urine electrolytic cell was connected to a 9V battery while an ammeter and multimeter were also connected to observe the system's current and voltage respectively. The process was continued until the balloon of the cathode was filled with no obvious change in volume. The pop sound, flame test was carried out on the cathode exit gas collected [25]. The process was repeated to confirm the observations and findings.

### **2.5 Effect of Temperature and Electrolyte Concentration on Hydrogen Production**

In parameterizing the urine electrolytic process for hydrogen production, the effect of varying temperature on the cell potential, Faraday's efficiency and gas purity models was carried out between 45 °C and 85 °C, while maintaining constant residence time, particular electrolyte concentration, current and voltage. Similar to the effect varying temperature approach, the effect of varying electrolyte concentration was examined by varying standard prepared concentrations of potassium hydroxide of 25 wt.%, 30 wt.% and 35 wt.%, while keeping residence time, current, voltage and temperature constant [15]. The absorbance and concentrations of urea in urine samples were initially quantified using the uv-vis spectrometer at 280nm as discussed elsewhere [26]. Thereafter, a standard solution of urea in the vicinity of the uv-vis spectrometer outcome was prepared for the study. The standard KOH solutions were each mixed with the prepared urea solution in the ratio of 4:1 and introduced as the electrolyte into the electrolytic cell placed in a heated water bath maintained at the desired temperature. The mixture was stirred for 10 seconds, then the cell was then charged with a 9V battery for 15 minutes. Then the volume of gas produced at the cathode, the cell voltage and current measured as previously [27].

#### **2.6 Model Development**

Theoretically, the polarization curve model or cell potential model is commonly modelled using Nernst model Equation (1).

$$
U_{\text{rev}} = U_{\text{rev}}^0 + \left(\frac{RT}{2F}\right) \ln \left(\frac{\left(P_0 - P_{\text{urea/KOH}}\right)^{1.5}}{\left(\frac{P_{\text{urea/KOH}}}{P_{\text{H}_2O}^0}\right)}\right)
$$
(1)

On the other hand, the model can be parameterised using temperature and current densities with Equations (2) and (3) [14].

$$
U_{rev}^{0} = 1.5184 - (Tx10^{-3}) x [1.5421 + (9.523x10^{-2} x Ln {T}) + (9.84x10^{-5} x T^{2})]
$$
\n(2)

$$
U_{rev} = U_{rev}^0 + (r_1 + r_2) \times i + s \times \log \left( i \times \left( t_1 + \frac{t_2}{T} + \frac{t_3}{T^2} \right) + 1 \right) \tag{3}
$$

Where T is operating temperature ( $^{\circ}$ C) and *i* is the current density (A/cm<sup>2</sup>). Using the Microsoft Excel Solver, the constants, *r*, *s* and *t* in equations (2) and (3) are computed for the operating temperatures, T (45  $^{\circ}$ C to 85  $^{\circ}$ C) and measured current densities, *i*. The current density is the current per unit area. It is a function of the electrolyte concentration (25 wt.%, 30 wt.%) and 35 wt.% KOH) which influenced by the conductivity of electrolyte. It was obtained from the measured current divided by the cross-sectional area of the stacked electrode. Faraday's efficiency model is given by the ratio of volume of gas produced at a particular time ( $V_{Exp}$ ) to the theoretical volume that should have been produced at the same time ( $V_{Th}$ ) given by Equations  $(4)$  and  $(5)$   $[28]$ .

$$
N_F = \frac{V_{Exp.}}{V_{Th.}}\tag{4}
$$

$$
V_{Th.} = \frac{i \times V_M \times t}{2 \times F} \tag{5}
$$

Where *t* is time (s),  $V_M$  is the molar volume of gas under standard conditions (cm<sup>3</sup>/mol) and F is the Faraday's number. Conversely, the efficiency can be parameterised for temperature and current densities using a five-parameter model shown in equation (6) [14].

$$
N_F = B_1 + B_2 \times \exp\left(\frac{B_3 + B_4 T + B_5 T^2}{i}\right)
$$
 (6)

In alkaline-water electrolyzer, the hydrogen – oxygen product gases can be contaminated by their respective counterparts. This is referred as gas crossover. In addition, the dissolution of some hydrogen and oxygen gases in the electrolyte can as well contaminate both streams to become saturated with the respective gases. Thus, the need to ascertain the hydrogen to oxygen (HTO) contents as expressed in equation (7) [29].

$$
HTO = C_1 + C_2T + C_3T^2 + \left[ (C_4 + C_5T + C_6T^2) \times \exp\left(\frac{C_7 + C_8T + C_9T^2}{i}\right) \right]
$$
\n(7)

### **3. RESULTS AND DISCUSSION**





#### **3.1 Physiochemical Property Characterization of Human Urine**

The physiochemical properties analysed for the various urine samples were analysed were colour, density, pH, turbidity and conductivity (Table 1). Through visual inspection on all samples, it was observed that the colour of female urine was amber and that of male was greenish yellow which indicated a high level of urobilin. Urobilin is the chemical compound in urine responsible for the yellowish colouration. The average density of male urine samples was  $1.134 \text{g/cm}^3$  while that of female urine samples was 1.136g/cm<sup>3</sup>. Although the values are approximately equal, they are greater than that of water. This may be attributed to dissolved solid particulate matter contained. In the case of pH, the observations in both male and female urine samples closely approximate each other as well as that of water. This implies the presence of alkali and acids as in ammonia, uric and other organic acids. In comparison with the turbidity of water, which is less than 1.0 NTU, the observed values of both the male and female urine samples were exceptionally high. Although it agrees with literatures [30][31], it indicate the presence of particles sediments with time. The conductivity of both urine samples appears higher than that of water. This is in agreement with turbidity observations of suspended particles presence. It also affirms the higher affinity for conduction of electricity.

### **3.2 Test on Hydrogen Gas Produced**

The gas collected in balloons at the cathode outlet was tested using a flame to confirm the presence of hydrogen gas. On exposure to a flame, pop sounds were noticed indicating that the container gas was hydrogen [25].



Figure 1: Volume of gas produced at cathode versus temperature at different concentrations of electrolyte

#### **3.3 Effect of Temperature and Electrolyte Concentration on Volume of Produced Hydrogen Gas**

The effects of varying temperature and electrolyte concentration on the volume of hydrogen gas produced at the cathode are shown in Figure 1. In all three different concentrations of KOH, the volume of gas generated at the cathode increased with as the temperature rise. Among the electrolyte concentrations, the solution with 35 wt.% KOH gave the best outcome throughout the range of operating temperature. This may be attributed to conductance of the electrodes and the concentration of the electrolyte which determines the rate of flowing current with consequent increase in effective ion collision rate [22].

### **3.4 Effect of Temperature and Electrolyte Concentration on Cell Voltage**

The relationship between observed electrolyser cell voltage, the operating temperature and electrolyte concentration is shown in Figure 2.



Figure 2: Cell voltage versus temperature at different concentrations of electrolyte

Apart from the slight deviation on that pattern at 75  $^{\circ}$ C, when the cell voltage at 30% wt. of KOH dropped 0.01V below that observed for 35% wt. of KOH. There is distinct decline in cell voltages observed with increasing temperature and electrolyte concentration. This may be attributed to enhance reaction kinetics and reduction in reversible voltage, causing the required energy to decrease as temperature rises. In addition, as conductivity increases, resistances reduces and consequently reduction in cell voltages [32]. Since low energy demands are advantageous, the electrolyte concentration at 35% wt. KOH was best yielding a cell voltage of  $2.06V$  at  $85^{\circ}$ C.

#### **3.5 Effect of Temperature and Electrolyte Concentration on Faraday's Efficiency**

The Faraday's efficiency which describes the potential of a system with respect to the amount of current entering into the system is shown in Figure 3.



Figure 3: Faraday's efficiency versus temperature at different concentrations of electrolyte

Apart from the observations at 30 wt.% KOH with a steep decline pattern, all the electrolyte concentrations exhibited a decline in Faraday number efficiency with increasing temperature. Although the Faraday's efficiency and temperature showed a defined inverse relationship. However, with electrolyte concentrations 25 wt.% and 35 wt.% of KOH, there is a clear indication of increasing Faraday's efficiency with increasing electrolyte concentration. Based on literatures, the electrolyte concentrations 30 wt.% and 35 wt.% of KOH 45 °C adequately agrees with expectations of alkaline electrolysers [15].

# **3.6 Effect of Temperature and Electrolyte Concentration on Gas Purity**

The effect of temperature and electrolyte concentration on the purity of hydrogen gas produced at the cathode against oxygen gas contaminations is shown in Figure 4. An increase in temperature increases HTO which implies purer hydrogen production. This may be attributed to the natural flow recirculation rate of hydrogen having a lower vapour density and higher average kinetic energy to oxygen. Also, with lower solubility of oxygen gas in KOH solution hydrogen diffusivity is greater [33][15] On the other hand, HTO increases with decreasing electrolyte concentration due to salting-out effect. A decline in gas solubility, increases salt-induced precipitation [29].



Figure 4: Hydrogen to oxygen (HTO) versus temperature at different concentrations of electrolyte

## **3.7 Polarization Curve or Cell Voltage Model**

The polarization curve or cell potential difference defines the observed consumption by the cell during operation measure between the anode and cathode electrodes. The semiempirical model constants for the alkaline-urine electrolysis study with 25 wt.%, 30 wt.% and 35 wt.% KOH in urea electrolyte using Equations (2) and (3) are provided in Table 2.

Constants	25 wt.% KOH	30 wt.% KOH	35 wt.% KOH
$r_1$	$-3.585279 \times 10^{-3}$	$-2.323957 \times 10^{-3}$	$-7.0426 \times 10^{-3}$
r <sub>2</sub>	$-1.463 \times 10^{-5}$	$-9.96349 \times 10^{-6}$	$6.94452 \times 10^{-6}$
S	0.39127026	0.267562817	0.553189321
$t_{1}$	148.1063025	$-180.0491364$	57.71302527
$t_2$	126.6450162	147219.258	21.66627452
$t_3$	1.792343528	27.56527982	1.769794443

Table 2: Parameterised cell voltage model constant at varying electrolyte concentrations

### **3.8 Polarization curve model validation**

Figures 5, displays the observed and calculated cell voltage values in a view to compare observations against model derivative values under operating temperatures of 45 to 85  $^{\circ}$ C and electrolyte concentrations of 25 wt.% KOH, 30 wt.% KOH and 35 wt.% KOH. In the range of operating temperatures and at 25 wt.% KOH electrolyte concentration, the model adequately reproduced the cell voltage shape of the alkaline electrolytic cell with a coefficient of determination  $(R^2)$  of 0.9977 which indicate that the model was a good fit. Similarly, at the same temperature conditions and at 30 wt.% KOH electrolyte concentration, an  $R^2$  of 0.986 was obtained specifying a good fit. Equally, at the same temperature conditions but with 35 wt.% KOH electrolyte concentration, an  $R^2$  of 0.998 was achieved also indicating a good fit.

### **3.9 Faraday's Efficiency Model**

The parameterised Faraday's efficiency model constants for this alkaline-urine electrolysis with 25 wt.%, 30 wt.% and 35 wt.% KOH electrolyte concentrations determined using Equation (6), are given in Table 3.



Figure 5: Comparison between modelled and experimental cell voltage at varying KOH concentrations in the electrolyte





#### **3.10 Faraday's Efficiency Model Validation**

Figures 6, shows the measured and simulated values for the Faraday's efficiency at temperatures of 45 to 85 °C and electrolyte concentrations of 25 wt.% KOH, 30 wt.% KOH and 35 wt.% KOH. Within the abovementioned range of conditions, the model adequately reproduced the Faraday's efficiency pattern of this alkaline electrolytic cell with a coefficient of determination  $(R^2)$  of 0.974. On the contrary, at the same temperature conditions but at 30 wt.% KOH electrolyte concentration, the model gave an  $\mathbb{R}^2$  of 0.711 which was not a good fit. However, at the same temperature conditions but with 35 wt.% KOH electrolyte concentration, an  $R^2$  of 0.9998 was achieved also indicating a good fit. Therefore, the likelihood of a better prediction of the Faraday's efficiency number is at elevated alkali levels in the electrolyte.



Figure 6: Comparison between modelled and experimental Faraday's efficiency at varying KOH concentrations in the electrolyte

#### **3.11 Gas Purity Model**

The gas purity model constants computed from Equation (7), for this study alkaline-urine electrolysis with 25 wt.%, 30 wt.% and 35 wt.% KOH electrolyte concentrations are shown in Table 4.





## **3.12 Gas Purity Model Validation**

Figures 7, demonstrations the measured and simulated values for the gas purity at temperatures of 45 to 85  $^{\circ}$ C and electrolyte concentrations of 25 wt.% KOH, 30 wt.% KOH and 35 wt.% KOH. In the range of operating temperatures and electrolyte concentrations of 25 wt.% KOH, the model significantly replicated the behaviour of the alkaline electrolysis with  $R^2$  value of 0.96 which indicate that the model is a good fit. Under the same temperature conditions but at 30 wt.% KOH electrolyte concentration, the model gave an outstanding  $R^2$  value of 0.995. Then with same temperature conditions but at 35 wt.% KOH electrolyte concentration, an  $\mathbb{R}^2$  value of 0.984 was obtained. All three analyses revealed that the model effectively predicted the purity of the hydrogen gas produced.



Figure 7: Comparison between modelled and experimental gas purity at varying KOH concentrations in the electrolyte

# **4. CONCLUSIONS**

The dissociation of urea in human urine through an alkaline electrolytic process was used to generate hydrogen gas. This paper has established empirical models for predicting the electrolytic cell voltage requirement for the process over feasible operation temperature ranges. In addition, volume of gas produced and purity prediction models were also developed using Faraday's efficiency approach for urea-alkaline electrolyte buffered by 25 wt.%, 30 wt.% and 35 wt.% concentrated potassium oxide solution. The following from among the objectives were noted: the male and female urine samples obtained displayed closely related physiochemical characteristics, but distinctly off compared to distilled water especially on colour, turbidity, conductivity, and density. The gas produced at the cathode was hydrogen based on the pop sound ignition test; the volume of hydrogen produced increases with increase in electrolyte concentration. The maximum production was at 35 wt.% of potassium oxide. The actual cell voltage and Faraday's efficiency properties varied inversely with temperature, while the gas purity varied proportionally with temperature. On the other hand, cell voltage and gas purity properties varied inversely with electrolyte concentration, while the Faraday's efficiency varied proportionally with electrolyte concentration; the minimum or lowest of cell voltage was 2.06 V at 85 oC with 35 wt.% of KOH for 15 minutes. While at the same condition Faraday's efficiency of about 60% and gas purity HTO about 2% indicated a little above average volume of gas produced and less purified gas. Although with increased residence time, the outcome is most likely to be of advantage; except for the gas purity model with 30 wt.% of KOH yielding coefficient of determination of 0.72, all the developed models attained simulated outcomes compared to experimental observations yielded coefficients of determination within the range of 0.96-0.99. It indicated that the various models adequately fit and are appropriate to

represent the alkaline urine electrolysis for hydrogen generation. Thus urine-alkaline electrolysis adequately produced pure hydrogen gas with as low as a 3 volts power source.

## **Abbreviations**

Urev: Cell potential U<sub>rev</sub>: Standard cell potential  $P_{H2O}^{0}$ : Water vapour pressure Purea/KOH : partial pressure of urea-KOH mixture P0 : atmospheric pressure *i*: current density  $V_M$ : Molar volume  $V_{Exp}$ : Measured volume  $V_{\text{Th}}$ : Theoretical volume  $N_F$ : Faraday's efficiency HTO: Cathode gas hydrogen to oxygen ratio V: Volt R: Gas constant F: Faraday's number A: Ampere DC: Direct current KOH: potassium hydroxide wt.: weight

## **ACKNOWLEDGEMENTS**

The founder of Afe Babalola university, Nigeria, Aare Afe Babalola for providing a conducive environment and facilities for advanced studies, and the entire staff of the department of chemical and petroleum engineering and the college of engineering workshop, and the technologist of chemical and water resources laboratories engineering, Afe Babalola University.

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