Effect of Operating Parameters on Performance of Alkaline Water Electrolysis

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Abstract

In this fundamental research investigation, the simple fundamental experimental design with two platinum wire as anode/cathode electrode and KOH solution as electrolyte were used throughout the experiments. The effect of electrolyte volume and concentration, electrode location and submerged length into the electrolyte, distance between two electrode and operating temperature on efficiency of water electrolysis was investigated. The results showed that the performance of alkaline water electrolysis is significantly affected by distance between electrode, electrolyte concentration and operating temperature. Higher rate of hydrogen production can be possible at smaller gap between electrodes with higher concentration of electrolyte operating at higher temperature.

Keywords:

1. Introduction

Hydrogen is an important energy source for sustainable development[1-5]. Fuel cells use hydrogen to generate power and produce only water [6]. Moreover, hydrogen is believed as safe for commonly used fuels [7]. The large scale hydrogen consumptions requires large scale production. Presently, the hydrogen production is dominated by reforming of natural gas and gasification, which is neither renewable nor clean [6-8].

Hydrogen can be produced from water via different existing technology like photocatalysis, thermochemical cycles, and water electrolysis [6, 8-10]. These methods offer renewable and clean production of hydrogen fuel and, therefore, have attracted increasing research interests in recent years. Among these technologies, water electrolysis is the most promising technology for large-scale hydrogen production [1, 10]. However, a significant challenge exists for water electrolysis, which is to improve its efficiency, which in turn reduces energy consumption at high hydrogen production rate.

The driving force of chemical reactions in water electrolysis is electrical energy. By passing a current through electrodes in a solution of water and electrolytes, water molecules (H_2O) decompose to hydrogen (H_2) and oxygen (O_2) gas through an electrochemical reaction. Typical electrolysis plants with normal or slightly elevated pressure usually operate at electrolyte temperature of 70-90^{0}C, cell voltage of 1.85 - 2.05 V and consume 4-5 KWh of energy for every m^3 of hydrogen generated [11]. There have been various attempts to improve efficiency and reduce energy consumption of water electrolysis process, such as development of new cell geometry, electrocatalytic materials for electrodes, etc [11]. In contrast, a more popular way of improving electrolysis efficiency is increasing the process temperature, which lowers the voltage required to electrolyze the water. At elevated temperature (800 - 900°C), the electric power consumption is expected to be about 3 KWh/$m^3_{hydrogen}$. However, this technology with elevated temperature is still in its developmental stage [11].

In this project, we studied the effects of operating parameters on improving the efficiency of water electrolysis. As alkaline water electrolysis is one of the simplest methods for hydrogen production, this research focused on the study of water electrolysis using potassium hydroxide, KOH, as the electrolyte. The reactions can be written as:

Total reaction:

$$H_2O \rightarrow H_2 + \tfrac{1}{2}O_2 \qquad (1)$$

Anode:

$$2OH^- \rightarrow H_2O + \tfrac{1}{2}O_2 + 2e^- \qquad (2)$$
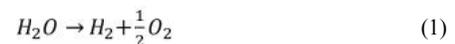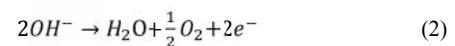
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Cathode:

$$2H_2O + 2e^- \rightarrow H_2 + 2OH^- \qquad (3)$$

The theoretical minimum cell voltage to start water electrolysis, called reversible potential calculated by Gibbs free energy ΔG^o, is $-1.23V_{@25°C}$.

The objective of this research is to demonstrate the effects of operating parameters to increase reaction efficiency by lowering the voltage required for water electrolysis reactions to occur and thus reducing the total energy consumption of the process.

2. Water Electrolysis Experimental Setup

Design of water electrolysis experimental Apparatus:

i.   An electrolyte - It is a substance containing free ions which are the carriers of electric current in the electrolyte. If the ions are not mobile, as in solid salt, then electrolysis can not occur. For example, an aqueous solution of common salt can act as an electrolyte because it contains free Na^+ and Cl^- ions, which are the carriers of electric current in solution but solid sodium chloride, can not act as an because it does not have free Na^+ and Cl^- ions. We use KOH as our electrolyte throughout our experiments as it has the highest conductivity.

ii.   A direct current (DC) supply - It provides the electrical energy necessary to create or discharge the ions in the electrolyte. Electrons in the external circuit carry electrical current. Electrolysis is the passage of a direct electric current through an ionic substance that is either molten or dissolved in a suitable solvent, resulting in chemical reactions at electrodes and separation of materials. BK Precision Model 9130 was used as DC power supply for this experiment. The specifications for this power supply are shown in Table 1.

Table 1: Specifications of BK precision DC power supply, model 9130

Output Voltage	0-30 V
Output Current	0-3 A
Load (Utilizing Remote Sensing)	≤0.01%+ 3mV
Ripple & Noise	≤0.5mVrms & 5mVp-p
Voltmeter Resolution	10 mV
Voltmeter Accuracy	≤0.05%+ 5mV
Current Meter Accuracy	≤0.15+ 5mA
Current Meter Resolution	1 mA

iii. Two electrodes - Electrode is an electrical conductor, which provides the physical interface between the electrical circuit providing the energy and the electrolyte. For example, graphite rods, platinum plates act as conductors /electrodes. We used Platinum wire for both anode and cathode electrode.

The following Figure 1 shows the electrolyte, battery (power supply) and electrodes (cathode and anode) required for electrolysis.
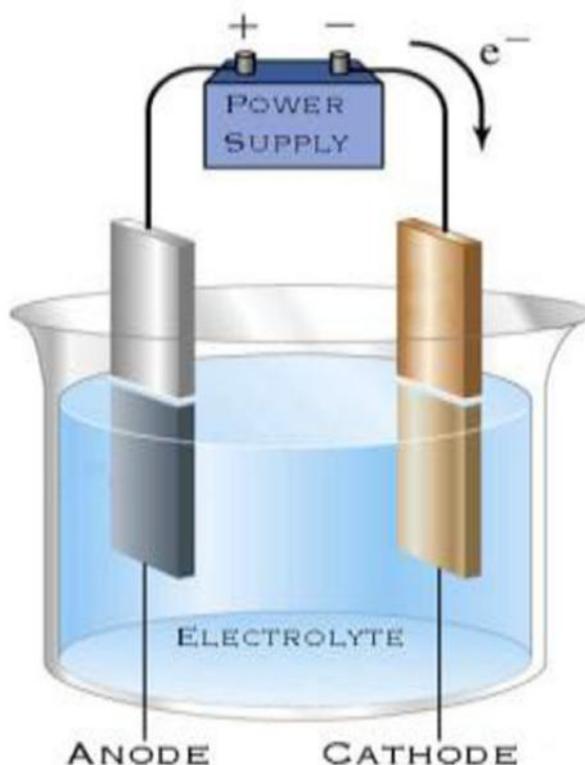
Figure 1: Apparatus required for electrolysis

Our experimental electrolyzer was constructed for baseline experiment with 200 ml, 0.4 M potassium hydroxide (KOH) electrolyte. Each electrode was made up of a 5 cm long, 0.5 mm diameter straight platinum wire, with a 2 cm length submerged in KOH solution. The two electrodes were kept 1 cm apart. The electrodes were connected to a DC power supply (BK Precision Model 9130). The effective surface area of electrode in electrolyte was calculated to be about 0.316 cm². A mercury thermometer was used to monitor the temperature of the electrolyte during testing. A hotplate stirrer is used in purpose of pushing the flow of reactant to the catalyst surface sites for faster reaction kinetics during experiments.
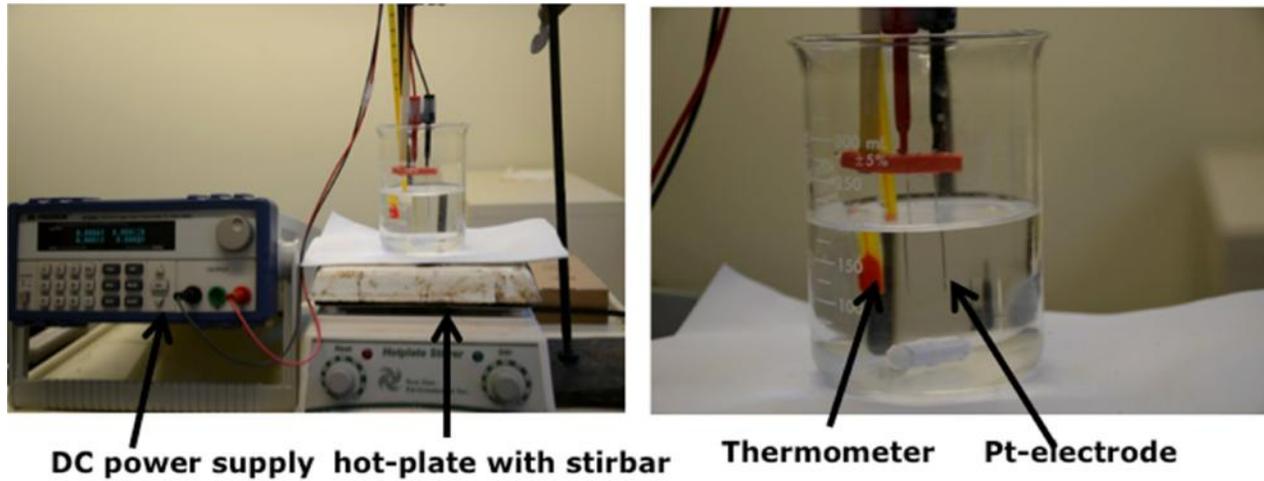
Figure 2: Design of experimental setup for baseline experiment and parametric study

3. Material and Method

This section aims to provide a concise review of the method used to evaluate the performance of water electrolysis.

3.1 Faraday's Law of Electrolysis

Faraday's 1st Law of Electrolysis states that the mass of a substance altered at an electrode during electrolysis is directly proportional to the quantity of electricity transferred at that electrode. In other words, hydrogen produced in water electrolysis is directly proportional to the current applied to the cell, so-called Current Efficiency.

Accordingly, hydrogen generation rate can be computed from the experimentally measured current density, I, by using the following conversion:

$$\text{Hydrogen Generation (sccm/cm}^2) = \frac{I\,(A/cm^2)}{0.1437}$$

in which *sccm* denotes cubic centimeter per minute at STP (standard temperature and pressure).

Figure 3 displays a relationship between hydrogen generation (sccm/cm^2) and input power density (W/cm^2) for a practical electrolysis process. The input power density is the product of current density (I) and cell voltage (V):

Power density

= Current Density x Cell Voltage   (4)
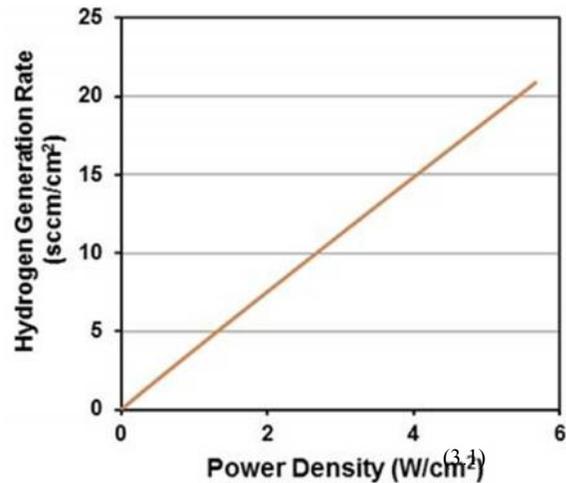
Figure 3: Hydrogen generation rate as a function of input power density for a practical water electrolyzer. The curve is plotted with arbitrary number showing the actual trend, not with any specific experimental data values.

3.2 Performance Curve

The performance of electrolysis cells are typically compared by plotting their polarization curves, which is obtained by plotting the cell voltage against the current density. The primary sources of increased voltage over reversible potential, which corresponds to a zero reaction rate, may include ohmic loss of electrolyte, overvoltage associated with oxygen and hydrogen reactions, and ohmic loss caused by electric resistance of electrodes and circuitry. Both overvoltage and ohmic loss increase with the increasing current density. Fig. 4 shows an example of the distribution of cell voltage [5].
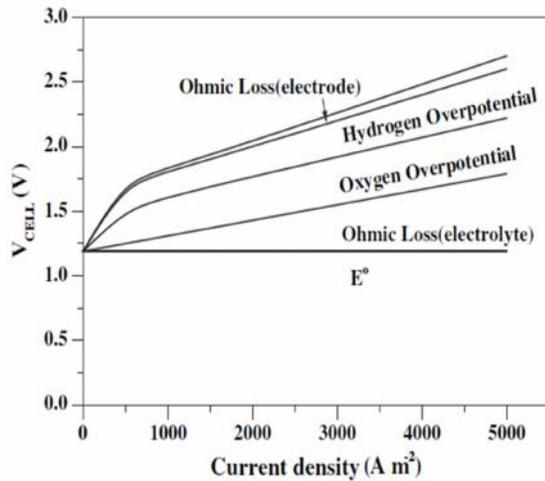
Figure 4: Polarization curves and distribution of cell voltage

In this research, the polarization curves would be made and presented at various operating parameters.

4. Results and Discussion

To optimize the parameters first experimental design approach was to study the parameters effect on water electrolysis performance. The experimental design for is shown in Table 2. The performance measurement can be defined by the eq. (5)

$$E_{cell} = E_{rev} + \eta_{HOR} + |\eta_{ORR}| + \eta_{OH^-} + \eta_{e^-} \tag{5}$$

Where,

E_{rev} = Reversible cell potential

η_{HOR} = Hydrogen overpotential

$|\eta_{ORR}|$ = Oxygen overpotential

η_{OH^-} = Ohmic overpotential due to OH$^-$ transport resistance

η_{e^-} = Ohmic overpotential due to electron transport resistance

The impact of various parameters on these different overpotentials is also denoted in column 3 of Table 2.

Table 2: Experimental design of parametric and reproducibility study

Exp #	Parameters	Overvoltage can be affected by parameters	Viability	No of levels	Baseline	Levels
1	Materials of electrode	$|\eta_{ORR}|, \eta_{HOR}, E_{rev}, \eta_{OH^-}$	✖	1	Pt	Pt
2	Operating pressure	E_{rev}	✖	1	P$_{atm}$	Atmospheric pressure
3	Thermometer location	$|\eta_{ORR}|, E_{rev}$,	✖	1	Close to biker wall	Close to biker wall
4	Type of electrolyte	η_{OH^-}	✖	1	KOH	KOH
5	Experiment time and steps		✖	1	Steady-state	60,80,100 then avg the data
6	Stir-bar rotation	$\eta_{OH^-}, |\eta_{ORR}|$	✔	3	3	0, 3, 6 (eq^p setting)
7	Electrolyte volume	η_{OH^-}	✔	3	200	150, 200, 250
8	Electrode location	η_{OH^-}	✔	3	Center	Center, halfway btw center & wall, close to wall
9	Electrode submerged length	$|\eta_{ORR}|$	✔	3	2 cm	1.5,2,2.5
10	Electrode distance	η_{OH^-}	✔	3	1 cm	0.5, 1, 1.5 (cm)
11	Electrolyte concentration	η_{OH^-}	✔	3	0.4 M	0.1, 0.2, 0.4(M)
12	Electrode design	$\eta_{OH^-}, |\eta_{ORR}|$	✔	1	Straight	Straight
13	Operating T	$\eta_{OH^-}, |\eta_{ORR}|, E_{rev}$,	✔	2	T$_{room}$	Room T, 61

We used only one material for electrode and it was platinum and it is considered to have the fastest kinetics for hydrogen evolution reaction rate [14]. For the simplicity of the experimental design only atmospheric condition was carried out throughout the all experiments. The thermometer was always put close to the biker wall. As KOH has the highest conductivity among the entire alkaline electrolyte exists, it was chosen for our experimental electrolyte. We used data at 60, 80 and 100 sec and average the data for any specific current density. Accordingly, based on these discussion, from experiment number 1-5, shown in Table 2, we didn't perform any experiments and we already chose the optimal condition and materials based on our limitation and fundamental simple experimental design. To compare the different parameters

effect on performance we established a baseline experimental design, which represented by column 6 in Table 2. The experimental condition for the baseline experiments is atmospheric pressure and room temperature. It consists with simple straight design two platinum as anode and cathode apart from each other precisely 1 cm and submerged approximately 2 cm in the center of the biker containing 0.4 M 200 ml KOH solution.

Based on experimental design the first experiment was done to find out the effect of stir-bar rotation, which is experiment number 6 in Table 2. We used magnetic stir plate and made the stir-bar rotation setting of 3, 6 and without any stir-bar rotation to measure the effect of stir-bar rotation on performance and the result is shown in Figure 5. It predicts that stirring is good to improve the performance of kinetic region but also increase mass transport resistance.
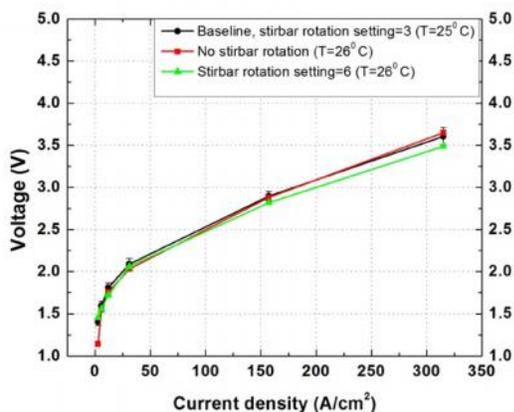
Figure 5: Effect of stirbar rotation on water electrolysis cell performance

One might think that the amount of electrolyte solution has impact on ohmic performance of the cell. So we design the experiment with three different amount of 150, 200, 250 ml of electrolyte volume, denoted by experiment number 7 in the Table 2 and compare the result with baseline. The Figure 6 represents the effect of electrolyte volume and confirms that it has minimal impact on performance as expected due to same length of electrode surface submerged into the electrolyte. The cell does not experience any ohmic loss for different amount of electrolyte solution as long as the distance between the electrode and electrolyte concentration are fixed.

Depending on the placement of the electrodes in different horizontal location inside the biker with the electrolyte solution may affect the performance. Considering this in mind, we designed the experiment as described by experiment number 8 in the Table 2 to place the electrode in center, close to biker wall and half distance between center and close to biker wall and investigated the impact of electrode location. Figure 7 describes the effect of electrode location submerged in the electrolyte solution. It proves that electrode location has minimal impact on performance.
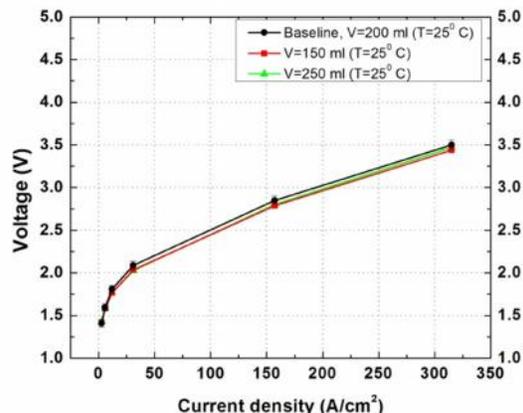
Figure 6: Impact of electrolyte volume in cell performance
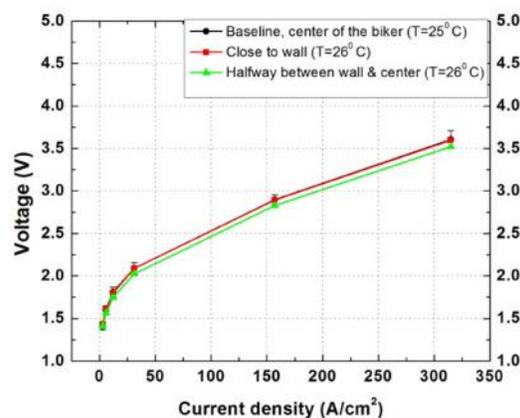
Figure 7: Effect of electrode location submerged in the electrolyte solution

The performance of any electrochemical cell depends on available reaction surface sites as in our case platinum surface area. The platinum surface area in our experimental design depends on the submerged length of the two straight-designed platinum into the electrolyte solution. The general way to express the performance is plot of voltage requirements versus current, in terms of current density, which normalized the current with surface area. So the overall performance would not be changed due to normalized surface area. The experiment number 9 in Table 2 has the purpose to compare these phenomena. 3 levels of experiment of submerged length of 1.5, 2, 2.5 cm were conducted and the result is shown in Figure 8. It confirms that electrode submerged length has no impact if the unit in x-axis is normalized to current density instead of current.
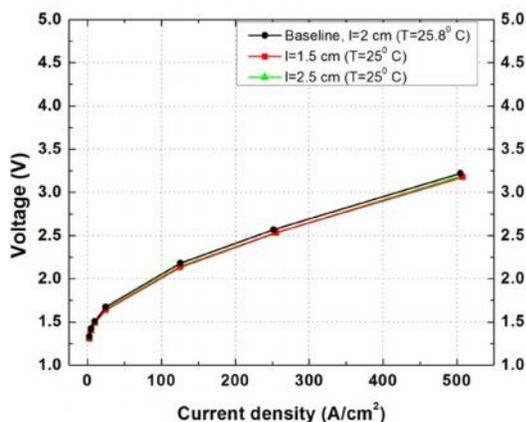
Figure 8: Effect of electrode submerged length into the electrolyte on cell performance

Figure 9: Impact of distance between the electrodes on cell performance

The resistance of electrolyte depends on various factors. One of them would be distance between anode and cathode electrode. The longer the distance between the electrode, the tougher the situation should be for OH⁻ ions to move from one electrode to another and releases its electron. When the space between the pair of electrodes decreases the performance of the cell increases due to the resulting decreases in electrical resistance between the electrodes that in turn leads to an increase in the electrical current [15]. To obtain the result how this distance may impact on cell performance, we construct the experiment number 10 in Table 2. Figure 9 shows that cell performance has almost linear relation with distance between electrodes.

The ohmic performance of water electrolysis should be strongly depends on concentration of the electrolyte solution. The higher concentration means that higher number of available reactant at the electrode surface area for reaction at same power input which leads to increase in hydrogen production efficiency. Figure 10 corresponding to experimental number 11 in Table 2 shows that electrolyte concentration has strong effect on cell performance. This behavior is attributed to the increase in the electrical conductivity of the solution due to the increase in the concentration of the potassium hydroxide. Increasing the electrical conductivity leads to an increase in the electrical current passing through the solution and consequently to a decrease of requirement of less voltage at same current density operation.

Figure 10: Effect of electrolyte concentration on water electrolysis cell

We do not need to conduct experiments for experiment number 12 in Table 2. For our limitation for further different design of the electrodes, we only did only one straight design electrode experiment.

A more popular way of improving electrolysis efficiency is increasing the process temperature, which lowers the voltage required to electrolyze the water. Heating the electrolyte provides the extra energy gain by the electrolyte and leads to lower the necessary Gibb's free energy, which makes the reaction to happen. Temperature effect was studied at room temp. (~26°C) and 61^0C and the comparison result is plotted in Figure 11. At observed from the data, cell performance increases with temperature due to reduced reversible potential, kinetic loss and ohmic loss.
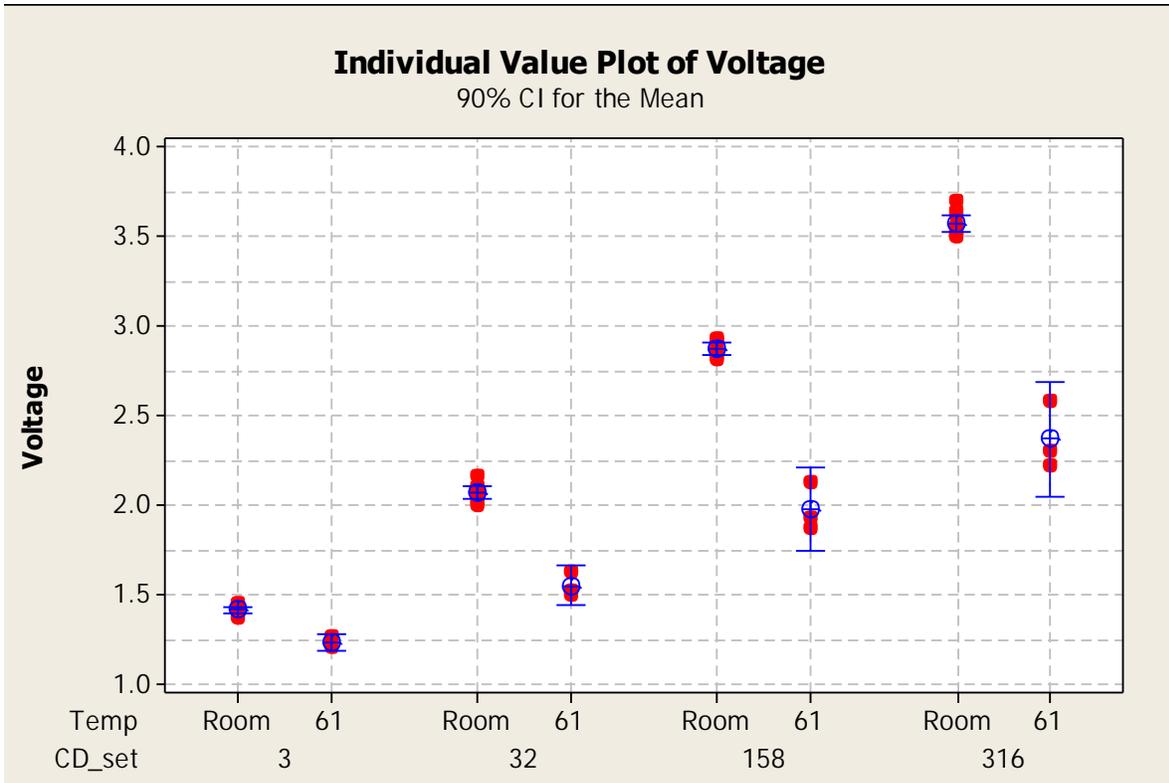
Figure 11: Effect of temperature on water electrolysis. (CD and CI inside the plots refer to current density and confidence interval respectively)

5. Conclusions

The current research efforts is to investigate the effects of operating parameters for the purpose of increase the hydrogen production efficiency through alkaline water electrolysis. The experimental design was based on fundamental theoretical understanding of water electrolysis and it covered the parameters like stir-bar rotation, electrolyte volume and concentration, electrodes location and submerged length and distrain between them and temperature. The results confirmed that reducing the space between electrodes, increasing the electrolyte concentration and operating temperature can improve the performance significantly.

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