I-V Characteristic and Performance of Three Electrode Alkaline Electrolyzer

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Abstract
Hydrogen production by electrolysis of water is seen as a promising technique as it is environment friendly and it can use renewable energy source for the production of hydrogen gas. However, this technology has less than 4% contribution to the production of commercial hydrogen in the market. This is due to the high electricity consumption of the water splitting reaction. The main challenge to make this technology efficient and economically viable is to develop cost effective and highly efficient electrolyzer. Here we have developed a three electrode electrolyzer in which an extra electrode is inserted between conventional electrodes: cathode and anode. This novel electrolyzer utilizes an extra voltage source which reduces the overpotential and increases the anode current of the cell, which is responsible for the hydrogen production. Furthermore, we observed that, the operating resistance of the cell decreases under the application of the new voltage source. Our results demonstrate that the introduction of third electrode improves the performance of electrolysis by consuming less power as compared to the traditional or conventional two electrode electrolyzer system.

Introduction
The non-renewable energy sources are limited, but the global demand of the energy is increasing. So, the challenge to meet the demand is more prominent than ever. The optimum utilization of renewable power sources is unquestionably single way to address the exponentially growing demand [1]. Hydrogen fuel is considered as one of the potential answers to the ever-increasing demand of the sustainable energy. Hydrogen fuel has highest energy density value. It is highly efficient in energy conversion. When hydrogen is used in a fuel cell. It exhibits several advantages. Technologies related to hydrogen is looked upon by many. The hydrogen fuel employs various sustainable energy sources like solar and wind energy for the hydrogen production. This leads to uninterrupted supply of energy without the emission of carbon pollutants [2, 3]. But, the 90% of total hydrogen fuel is extracted from the fossil fuels. This extraction process involves the release of harmful carbon components as byproduct. So, in order to improve the popularity of hydrogen fuel, the production process should be sustainable and efficient [3–8]

Water electrolysis generally utilizes renewable energy sources to produce hydrogen fuel. So, it is taken as one of the ideal method for production of hydrogen [9, 10]. The required input for the electrolysis are: water and electricity.

Hydrogen production by splitting of water is one of the important technologies. This process enables to convert electrical energy to pure hydrogen fuel. Furthermore, no harmful carbon derivative pollutants are released. So, researchers all around the world are motivated to develop the advanced water splitting cells for sustainable production of hydrogen.

Hydrogen production by electrolysis is technologically very simple. Furthermore, the gas collected during this process is pure [11, 12]. So, the cost and effort needed for further purification is reduced. This process is also liked and recommended in the current situation because it is environment friendly and cost
effective. To make the system even more efficient, the energy loss should be reduced and the cost of the equipment should be cut down. So, the prospect of hydrogen production regarding the economy and improved technology is a matter of interest [13–20]. However, the contribution of electrolysis technology to the overall hydrogen in global market is not more than 4%. The main reason for this is: the cost associated with the electricity required to overcome the energy losses that occurs to achieve the splitting of water[21]. Hence, it is important to come up with a novel idea of electrolyzer which increases the efficiency of hydrogen production.

In the present work, we first time to our knowledge introduced three electrode system electrolyzer. We have modified the conventional two electrode electrolysis system to three electrodes by inserting a third electrode (grid) between cathode and anode. The introduction of this extra electrode was done so that the efficiency of the electrolyzer can be increased, thereby increasing the hydrogen production. Two voltage sources were given as input during the electrolysis process. This helped to overcome the ohmic loss of the reaction and thus decreased the overpotential, thereby increasing the hydrogen production.

Results

Three electrode electrolyzer design:

The schematic diagram of the used three electrode electrolyzer is shown in Figure 1.

The components used in assembling the electrolyzer is shown in Fig. 2.

The circuit diagram for our experiment is shown in Fig. 3. Here, V1 and V2 are two power supplies. V2 supplies non pulsating dc voltage whereas, V1 supplies Half Wave Rectified Pulsating DC (HWRPD) voltage. Since, negative terminal of V1 is connected to electrode 1, it acts as cathode. The potential difference between electrode 1 and grid due to V1 termed as Vcg. The positive terminal of V2 is connected to electrode2 and it acts as anode, and the potential difference across it is termed as Vag. Similarly, the current through cathode, anode and grid are called Ic, Ia and Ig respectively. Since, grid electrode is common to both power supplies V1 and V2, we call this connection as common grid configuration.

The whole system can be viewed as two electrolyzers: one at LHS powered by V1 and other at RHS powered by source V2. Therefore, when V1=0 (made by removing V2), it acts as two electrode system (RHS electrolyzer). Now when voltage V1 is applied, it acts as three electrode system and we study effect of V1 on I-V characteristics of electrolysis at RHS. Similarly, when V1= 0 it acts as two electrode electrolyzer at LHS, and we study the effect of voltage V2 on I-V characteristics of electrolysis at LHS.

I-V Characteristics for Different HWRPD Voltage Vcg

Fig. 4 shows the plot for anode current density (Ia) with applied voltage Vag at different fixed HWRPD voltage Vcg. Here, Vcg = 0 have been made by plugging out the power supply Vcg. In the figure, it is seen that when Vcg = 0V, Ia starts to appear from Vag =2.35V, which is the reaction starting voltage (Vs) of
water electrolysis. Above 2.35V, Ia increases linearly. As Vcg increases, Ia starts to appear at lower Vag values. Therefore, as Vcg increases Vs decreases and above Vs, Ia increases linearly as in Vcg = 0V case. Theoretically water starts to split at 1.23V, therefore, for Vcg = 0V case, the over potential is 1.12V. In similar ways, values for the reaction starting voltage and over potential are calculated for all other Vcg values and plotted in Figure 5.

In the figure it is seen that Vs decreases from 2.35V at Vcg=0V to 0.84V at Vcg=5V. similarly, the over potential is also observed to decrease with increase in Vcg. This shows that this external voltage source Vcg forces to reduce over potential of water electrolysis.

Fig. 6 shows the plot for operating resistance of the cell versus applied HWRPD voltage Vcg. The operating resistance of the cell is calculated from the slope of linear fit of Ia-Vag plot (Fig. 3). In the figure, it is seen that the operating resistance of the cell decreases with increase in Vcg. This shows that the application of external HWRPD voltage source Vcg results in reduction of operating resistance of the electrolyzer and hence improving its performance.

In Fig. 4, at fixed voltage Vag along the vertical line (say Vag = 4V), it can be seen that Ia increases with the increase in Vcg. This shows that Ia and hence performance of the cell can be improved by the application of external HWRPD voltage Vcg.

In order to see effect of external voltage source Vag on cathode current density (Ic), we applied fixed HWRPD voltage Vcg in left compartment of the cell (see Fig. 3) and measured Ic by varying Vag. Fig. 7 shows the variation of Ic with Vag at different HWRPD voltage Vcg. In the figure, it is seen that for Vcg < 0.5V, the cathode current density (Ic) is almost zero for all Vag voltage. When Vcg = 1V, 1.3V, 1.5V and 1.8V, cathode current density (Ic) starts to appear at Vag = 6.4V, 4.6V, 4V and 2.2V respectively. This infers that current density (Ic) appears even at Vcg < 2V (below Vs) when Vag is high. This shows that, the application of external voltage Vag forces the reaction to starts at lower Vcg value.

Fig. 8 shows the variation of Ic with cathode-grid HWRPD voltage Vcg at different fixed Vag = 0V, 1V, 2V, 3V and 4V. These data are derived by noting values of Ic at different voltage Vcg for fixed value of Vag by making vertical lines in X-axis. For Vag = 0V to 3V, Ic starts to appear from Vcg = 2V. But for Vag = 4V and 5V, Ic appears at Vcg = 1.5V and 1.3V which is far less than reaction starting voltage (Vs). This again shows that the application of high external voltage Vag forces to start splitting of water to its components at lower Vcg voltage reducing the over potential of reaction.

From the slope of best fit line of Ic Vs Vcg for different fixed Vag voltage curve, operating resistance of the cell is determined and plotted against Vcg and shown in Fig. 9. From the figure, it is seen that the operating resistance of cell decreases as Vag increases.

Fig. 10 shows the variation of grid current density Ig with Vag at different HWRPD voltage Vcg. In the figure it is observed that for the fixed voltages Vcg = 0V to 1.8V, on increase of Vag, the value of Ig decreases from the initial value zero (Ig = 0A) to negative value. At Vcg = 2V to 5V, Ig decreases from
positive value to zero and then to negative values. This implies that depending on $V_{cg}$ values the grid current ($I_g$) can be positive, zero and negative. The change in sign of grid current density ($I_g$) can be explained with the help of Fig. 3 above. In the figure, it is seen that due to voltage source $V_{cg}$, the current $I_g$ flows in the left compartment in clockwise direction as shown. Similarly, due to voltage source $V_{ag}$, current $I_g$ flows in right compartment of cell in clockwise direction. Thus, direction of current flow in grid electrode due to $V_{cg}$ is opposite to $V_{ag}$. When $V_{cg} > V_{ag}$, $I_c > I_a$, this results in positive grid current. Similarly, when $V_{cg} < V_{ag}$, $I_g$ becomes negative. When $V_{cg} = V_{ag}$, $I_g$ becomes zero. Therefore, depending on value of $V_{cg}$ and $V_{ag}$, $I_g$ can be positive, negative or zero.

In order to see the behavior of each current: $I_c$, $I_g$ and $I_a$ towards $V_{cg}$, all three currents are plotted with variation of $V_{cg}$ for two different $V_{ag}$ values ($V_{ag}=1V$ & $5V$). Figure 11 shows the variation of $I_c$, $I_g$ and $I_a$ with $V_{cg}$ at fixed $V_{ag}=1V$ and $5V$. From the figure and also, analysing the data profile, it is seen that these current $I_c$, $I_a$ and $I_g$ follow reaction $I_c=I_a+I_g$ where $I_c$ and $I_a$ always take positive value and $I_g$ can be positive or negative as discussed above.

In Fig. 11 (left), it is seen that when $V_{cg}$ is low ($V_{cg}=1V$), $I_g$ is always positive and current $I_c= I_g + I_a$. Therefore, when $V_{ag}$ is low flow of current in each compartment of cell is shown in the Fig. 12 (left). Similarly, when $V_{cg}$ is high (Fig. 11(right)), current $I_a$ is given as $I_a = I_c + I_g$. Current flow in each compartment in this case is shown in Fig. 12 (right).

**Variation of total current density ($I_a+I_c$) with Power Input (Pin)**

In Fig. 12, it can be seen that current $I_a$ flows in RHS compartment and current $I_c$ flows in LHS compartment of the cell. Therefore, current $I_c$ produces oxygen and hydrogen in LHS compartment of cell and current $I_a$ produces oxygen and hydrogen in RHS compartment of the cell because LHS side compartment of cell grid electrode acts as anode and in RHS side compartment of cell it acts as cathode. Therefore, due to voltage source $V_{cg}$, current $I_c$ flows in the LHS compartment of cell producing $H_2$ at cathode and $O_2$ at the LHS of grid electrode. Similarly, current $I_a$ flows in the RHS compartment of cell producing $O_2$ at anode and $H_2$ at the RHS of grid electrode (see Fig. 2). Thus $I_c+I_a$ represents the total $H_2$ or $O_2$ producing current. In order to see the performance of cell with the application of HWRPD voltage $V_{cg}$, total $H_2$ or $O_2$ producing current ($I_a+I_c$) is plotted against total electrical power input $Pin$ supplied to the cell for different fixed $V_{cg}$ values and shown in figure 12, $Pin$ is calculated using relation $Pin = V_{cg} \times I_c + V_{ag} \times I_a$. Here, it can be seen that for all $V_{cg}$, when $Pin$ is increased, the total oxygen or hydrogen gas producing current density ($I_c+I_a$) is also increased (non-linearly). In figure it can be seen that for the fixed $Pin$, say $Pin = 5W$, total current density ($I_c+I_a$) increases from 0.311A/cm$^2$ to 0.502A/cm$^2$ with the increase of $V_{cg}$. Increase in current density means increase in hydrogen and oxygen gas production. This shows that application of external supply $V_{cg}$ results in high improvement of $H_2$ and $O_2$ production indicating high improvement of the efficiency of electrolyzer. In the Figure 12, the lowermost curve, is $I_a + I_c$ vs $Pin$ curve for $V_{cg}=0$ case. When $V_{cg}=0$, $I_c=0$. So, this is basically plot for two electrode system (RHS compartment of the cell). In the figure, ($I_c+I_a$) is lowest for all $Pin$, when $V_{cg}=0V$ (i.e. for two electrode system). As $V_{cg}$ increases, curve shifts to higher ($I_c+I_a$) values. This implies that the total current density
for three electrode system is always high as compared to two electrode system. Therefore, for fixed Pin, Ic +Ia and hence, efficiency of the three electrode system electrolyzer increases with increase in external voltage source. However, this does not hold good for all Pin and Vcg values. For example, at Vcg=5V and Pin < 4.5W, the (Ic +Ia) curve (green filled) deviates downward below (Ic +Ia) case for Vcg=4V case.

In order to see the effect of type of voltage source used for Vcg, all experiments mentioned above case were repeated by replacing HWRPD source Vcg with using Full wave rectified dc as well as non pulsating dc source. The plot of all curve shows similar trend (not shown in the figure) in all cases and the best performance were seen with HWRPD source were used for Vcg.

Below we show only comparative study of (Ia + Ic) Vs Pin for HWRPD voltage replaced with DC voltage for Vcg is shown below. Fig. 13 shows the comparative plot of total current (Ic+Ia) with Pin for Vcg = 0V, 2V, 4V and 5V for DC and HWRPD voltage source. In the figure, it is seen that for fixed Pin (say 5W), the total current density (Ic+Ia) is high when HWRPD voltage source is used for Vcg. This means that hydrogen or oxygen gas production efficiency is slightly higher at high Pin when HWRPD voltage source (Vcg) is used in place of non-pulsating DC source. This shows that electrolyzer efficiency for half wave rectified voltage source is better than for non-pulsating DC voltage source.

We have also repeated all with grid (plate) electrode replaced b grid (steel mesh) electrode (to be published). We have also replicated whole experient in common cathode configuration (to be published), and in all cases, the performance of the cell was improved.

**Discussion**

In the Figure 4 and 5, it is observed that the reaction starting voltage and hence the overpotential of the reaction decreases with the increase in external voltage Vcg. It is due to the fact that the overpotential in water electrolysis is cumulative effect of concentration potentials due to transportation of reactant and product, the activation overpotential of both cathode and anode and ohmic overpotential caused by the resistance of the electrolyte. Since, the operating resistance of the cell decreases with increase in Vcg, this results in decrease in reaction starting voltage and overpotential of the reaction. Also as discussed earlier, when Vcg=0, the system acts as two electrode system cell & as usual the reaction starting voltage is 2.3 V. When Vcg is increased from 0 to 2.3V, (Vcg < Vs), water electrolysis reaction does not occur in left compartment of the cell. Therefore, no marked change in the current (Ic) can be observed. Since, Vcg is in series with Vag, the total voltage Vcg + Vag appears across anode and cathode electrode. Therefore, even for the values of Vcg< Vs, the total voltage Vcg + Vag across cathode and anode forces the water splitting reaction to start even at lower Vcg values.

In conclusion, this work shows that the introduction of the third electrode in the conventional electrolyzer boosts the electrolysis process. It does so by reducing the reaction starting voltage and decreasing the overpotential of the electrolyzer. Moreover, the introduction of third electrode with certain power supply connection induces the increment in both Ic and Ia. These currents are responsible for the production of hydrogen in the cell. Thus, the addition of an extra electrode increases the hydrogen production of the
system efficiently. Our work also shows the practical approach to enhance the performance of the electrolytic cell for the production of carbon neutral hydrogen fuel.

**Methods**

**Three electrode electrolyzer set up**

Our electrolyzer was constructed using two insulating polymer blocks and three steel plates. Three steel plates were used as electrodes. The insulating gasket were used in order to make the electrolyzer water tight (see Figure 2). The effective area of these electrodes is 1.5cm × 1.5cm. The polymer blocks were drilled at the top of the cell and gas pipes were fitted on this so that the hydrogen and oxygen gases produced during the electrolysis can be collected at the burette. A thin plastic film was adjusted at the upper part of the cell (not shown in the figure) between two gas pipes, to prevent the mixing of the gases.

**I-V characteristics measurement**

We have used power supplier (BAKU BK-1502DD) for dc power supply and an AC variate with half wave rectifier circuit for HWRPD source. The I-V characteristics for Ia, Ig and Ic versus Vag were taken by fixing the Vcg at 0V, 0.3V, 1V, 1.3V, 1.5V, 1.8V, 2V, 2.5V, 3V, 4V and 5V. In order to measure the current and voltage, two FLUKE 15B+, one FLUKE 17B+ and one DT 830 D multimeters were used. The DT 830 D was calibrated according to FLUKE 15B+.

**Chemicals used**

1 Molar NaOH solution was used as the electrolyte to carry out the experiment. The electrodes were cleaned with Ethyl Alcohol (C₂H₅OH) before carrying out the electrolysis.

**Declaration:**

All these datas are authentic and can be shown upon request.

**Declarations**

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We thank University Grant Commission of Nepal for providing the fund for the experiment.

**Author's contribution:**

*Diwakar Prasad Kafle*: Methodology Implication, Experimental Setup, Data recording, Data analysis, Writing: Original manuscript; *Sushil Dumre*: Methodology Implication, Data recording, Data analysis, draft preparation *Saroj Tripathi*: Project Management; *Shankar Prasad Shrestha*: Supervision, Project Administration, Idea development and circuit design and editing
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**Figures**

![Figure 1](image)

Figure 1

The schematic diagram of the three electrode electrolyzer
Figure 2

Picture of homemade three electrode electrolyzer using locally available materials
Figure 3

Power supply connection for three electrode electrolysis in common grid configuration.

Figure 4

Graph showing the relationship between current density ($J_a$) and applied voltage ($V_{ag}$) for different values of $V_{cg}$.
Variation of anode current density ($I_a$) with $V_{ag}$ at different fixed HWRP DC voltage $V_{cg}$ for three electrode electrolyzer system.

![Graph](image)

**Figure 5**

Variation of over potential voltage ($V_o$) and reaction starting voltage $V_s$ with HWRPD voltage $V_{cg}$
Figure 6

Variation of the operating resistance (R) of the electrolyzer with external variable HWRPD voltage Vcg (The resistance R is derived from Ia-Vag characteristic curve)
Figure 7

Variation of cathode current ($I_c$) with $V_{ag}$ at different fixed half wave rectified voltage $V_{cg}$
Figure 8

Variation of cathode current (Ic) with HWRPD Vcg at different voltage fixed Vag
Figure 9

Variation of operating resistance (R) of the electrolyzer (The resistance R is derived from Ic-Vag characteristic curve)
Figure 10

Variation of grid current ($I_g$) with variable $V_{ag}$ at different fixed HWRPD voltage $V_{cg}$.

Figure 11
The variation of $I_c$, $I_g$ and $I_a$ with $V_{cg}$ at fixed $V_{ag}=1\text{V}$ (left) and $5\text{V}$(right)

**Figure 12**

Direction of flow of currents when grid current is positive (right) and negative (left)
Figure 13

Variation of total current density (Ia + Ic) Vs Pin for HWRPD Vcg.
Figure 14

Comparison of total current density ($I_{c+I_a}$) Vs Pin for DC (unfilled) symbol and pulsating DC (filled) symbol