Design and optimization of electrochemical cell potential for hydrogen gas production

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Abstract

This study deals with the optimization of best working conditions in molten melt for the production of H_2 gas. Limited research has been found that how electrochemical process occurs through the steam splitting via molten hydroxide. 54 combinations of cathode, anode, temperature and voltage have been tested for the optimization of best working conditions with molten hydroxide for hydrogen gas production. All this electrochemical investigation was carried out at 225 to 300 °C temperature and 1.5 to 2.5 V applied voltage values. The current efficiency of 90.5%, 80.0% and 68.6% had been achieved using stainless steel anodic cell with nickel, stainless steel and platinum working cathode respectively. For the nickel cathode, the increase in the current directly affected the hydrogen gas flow rate at the cathode. It can be hypothesized from the noted results that increase in current is directly proportional to operating temperature and applied voltage. Higher values were noted when the applied voltages increased from 1.5 to 2.5 V at 300

°C, the flow rate of hydrogen gas increased from 1.5 to 11.3 $cm^3\ min^{-1}$, 1.0 to 13 $cm^3\ min^{-1}$ in case of electrolysis @ stainless steel and @ graphite anode respectively. It is observed that the current efficiency of stainless steel anodic cell was higher than the graphite anodic cell. So, steam splitting with the help of molten salts was shown an encouraging alternate to current methodology for H_2 fuel production.

Keywords: Sustainable energy; Splitting steam; Electrolysis; Hydrogen gas production; Electrochemical cell and Variable cathodes.

1. Introduction

Hydrogen (H_2) has received focus among several alternative fuel sources because it provides the principal advantages and fulfils ideal fuel requirements. Hydrogen fuel is the same as electrochemical energy in terms of being a high-efficiency energy carrier and when it is used, it can lead to zero or near-zero emissions. For this reason, recently, many researchers and organizations have propagated H_2 fuel to minimise global warming hazards. The most studied technique for the production of H_2 gas from water is through the electrolysis of aqueous alkaline hydroxide solutions [1].

The published studies [2,3] clearly mention that 19 methods exist in for hydrogen gas production, including plasma arc decomposition, dark fermentation, coal gasification, biophotolysis, artificial photosynthesis, electrolysis and others. It was also concluded that among all electrical hydrogen production via electrolysis gives good energy efficiency as well as with the lowest cost rate. Electrolysis is the most common methodology to yield H_2 gas using water as a clean and renewable energy resource. Electrolysis has high product purity up to 99.9 vol%, this purity can be attained on both scales large and small. The only setback is that electrolysis can also be responsible for the emission of CO_2 gas if a non-renewable energy resource has been used to produce the required electrochemical energy [4,5]. The materials used to construct the electrolysis cell must also withstand certain tough operating conditions and need further development in order to commercialize this clean energy method for producing hydrogen gas as fuel. This clean fuel can be yielded directly from splitting water using different techniques. These techniques include photo electrochemical hydrogen production (photo electrolysis), thermochemical water splitting and water electrolysis [6]. This study focuses on using electrolysis to split water into its core constituents of H_2 and O_2 gas respectively [7].

Three main methods are currently under consideration for the production of hydrogen via water electrolysis: proton exchange membrane [8], solid oxide cell and alkaline melt. The electrochemical cell of alkaline electrolysis comprises of an alkaline aqueous electrolyte, two electrodes and a microporous separator for ion conduction. The hydroxyl ions generated at the cathode electrode are migrated to the anode and the remaining H^+ ions at the cathode electrode combine with electrons to form H_2 gas [9]. The two electrodes are cathode and anode, from which the cathode metal possesses a good catalytic activity and the anode electrode possesses an oxide coating layer. The molten melts of NaOH and KOH are applied as electrolyte solutions. The ion-conducting microporous separator permits the movement of hydroxyl ion and restricts the involvement of produced oxygen and hydrogen. The efficiency of alkaline electrolysis can reach 70% [10].

Electrochemical studies focused on molten hydroxides for the generation of hydrogen fuel via water splitting were demonstrated by Licht et al. and Al-Shara et al. [11,12]. These studies investigated various mixed and pure alkali hydroxides as electrolytes such as $Ba(OH)_2$, KOH, LiOH, NaOH at temperatures between 200 and 700 °C. The applied voltage range was maintained between 1.1 and 2.3 V using a nickel and platinum metal as an anode and a nickel plate as a cathode, respectively. It is also mentioned that molten hydroxides act as catalyst therefore there is no need for any additional heat [12]. A detailed study was performed by Nagai et al. [13], in which they focused on the H_2 production potentials and efficiency of the electrochemical cell with Ni-Cr-Fe alloy as the cathode material, under atmospheric pressure and using 10 wt% of KOH aqueous solution.

Licht et al. [14] reported an electrochemical study for the generation of ammonia from steam and air via an equimolar ratio of molten NaOH-KOH with suspended nano-Fe_2O_3 particles using nickel electrodes at a temperature of 200 °C and an applied voltage of 2 V. Ganley [15] studied the direct electrolysis by using the experimental conditions of 18 M of KOH, 400 °C temperature, 8.7 MPa partial pressure, fixed cathode of monel alloy and variable anodes of (cobalt-plated nickel, lithiated nickel, monel alloy, nickel). At temperatures as low as 80 °C, the study of Anani et al. [16] discovered a technique to produce high purity hydrogen gas at the cathode while maintaining high current efficiency during the electrolysis of hydrogen sulphide. The intermediary solution resulting in the generation of the latter contained an equimolar concentration of NaOH and NaHS at the experimental temperature. The two-electrode electrolysis process has been used in this study to apply a voltage to the cathode and anode to split steam through eutectic molten hydroxide. Subsequently, O_2 and H_2 gas were collected from the anode and cathode compartment respectively. Hydrogen gas was detected by using a hydrogen gas tube and hydrogen gas sensor where the actual rate of H_2 gas yield was measured using the pneumatic trough method.

There were limited studies that have been carried out how the electrochemical process occurs through the steam splitting with the help of molten salt’s solution for H_2 gas production. This study aims to record an escalation in the efficiency of H_2 gas production by optimizing several operating parameters such as temperature and applied voltage; or by changing the material used for cathode or anode construction in the electrochemical cell. The electrochemical analyses were performed by using graphite and stainless anodes and platinum, stainless steel and nickel cathodes. From literature it is analyzed that Ni, Pt and St.st metals were suitable for electrolysis because they are stable under highly alkaline solution, low cost, easily available [17,18]. 54 combinations of a cathode, anode along with different operating variables have been tested for the production of H_2 gas through the splitting of steam via molten hydroxide salt. This was a comparative study also, based on finding the most efficient electrochemical cell that increased the efficiency of steam splitting through electrolysis of eutectic molten hydroxide. All this electrochemical investigation was carried out at 225 to 300 °C temperature and 1.5 to 2.5 V applied voltage values.

2. Experimental

2.1. Two-electrode electrolysis

A mixture of 300 g of NaOH-KOH (49–51 mol%) was used as the electrolyte and placed inside the retort, before being heated to a temperature of 300 °C for 24 h. It must be noted here that the retort has already been placed inside the pore of the vertical tube furnace. A pure alumina crucible was used to hold the mixture of hydroxide salt. Stainless steel, platinum and nickel were used as the cathode; whereas stainless steel and graphite were used as the anode during the experiments, respectively. Prior to immersing the cathode and anode inside the eutectic molten hydroxide to begin electrolysis, each electrode was placed inside an alumina tube with 20 mm inside diameter.

The reason for covering the electrodes with an alumina tube was to prevent the mixing of H_2 gas with the O_2 gas formed as a result of the electrolysis process. This compartment should be tightly sealed to avoid any gas leakage. The diameter of the different electrodes used in this study and the calculated areas are listed in Table 1. The total duration of the steam electrolysis process was approximately 1800 s after which hydrogen gas was collected. Direct current (DC) source of power was used for voltage applications on both electrodes.

This applied voltage was altered between 1.5 V and 2.5 V. It is worth mentioning that although the voltage is listed as being positive, the negative terminal of the DC source was actually connected to the cathode. Therefore the polarity of this electrode, in reality, is negative.

2.2. Steam generation

Before the electrolysis process was performed, a combination of argon gas and steam was introduced to the eutectic molten hydroxide. Argon gas worked as a carrier for steam introduction into the bottle. In this study, steam was generated by placing a 500 mL dreschel bottle filled with 300 mL of distilling water, on a hot plate heater. The temperature of the hotplate can be varied from the insert temperature button. The argon gas inlet stream was connected to the inlet of the dreschel bottle head which was directly dipped into hot, distilled water. Then, the argon gas left the dreschel bottle from the outlet head. The stream of argon gas loaded with steam was connected to a ceramic tube which was then submerged in molten hydroxide [19].

Distilled water was heated up to 70 °C. The argon gas stream bubbled through the hot water and left the bottle loaded with water vapor. This was then introduced directly to the molten hydroxide. The humidity of the argon gas when it left the dreschel bottle at a temperature of 70 °C and an argon flow rate of 40 cm^3 min^{-1}, was about 50%. The steam flow rate was about 7.28 cm^3 min^{-1} and was calculated using Dalton’s law for gases. The residence time required to achieve saturation between the eutectic molten hydroxide and the humid mixture of argon gas was influenced by the salt volume in the crucible. The residence time needed to achieve the saturation between eutectic molten hydroxide and a humid argon gas flow rate was between 2–6 min.

2.3. Hydrogen gas production analysis

The start of the generation of H_2 gas at the cathode was detected by using a Gastec gas detector tube. This gas tube detector is capable of measuring up to 2 vol% of hydrogen gas. Thin glass tubes are usually available with outer calibration scales. These calibration marks help them to measure the concentrations directly [20]. Tubes undergo stringent quality control with each production percentage independently tested and calibrated.

A hydrogen gas sensor pro-gasbadge was also used to detect hydrogen gas produced up to 2000 ppm. This sensor has an interchangeable "smart" sensors monitor for hydrogen gas. There is a direct communication between the sensor and the Docking Station with the help of an infrared interface. As the gas produced at the cathode was confirmed as hydrogen gas, the production rate was measured using the water displacing method (Pneumatic Trough) and calculated as an actual gas rate using Dalton's law for gases. The hydrogen gas production rate due to steam splitting via the electrolysis of eutectic molten hydroxide was calculated using Eq. (1):

$$\text{Production rate}=\frac{\text{Mass of } H_2 \text{ produced}}{(\text{ Immersed area of cathode } \times \text{Duration of } H_2 \text{ production})}\times 100\% \quad (1)$$

The values that were inserted into this equation were determined as follows. The mass of H_2 gas production was found from the multiplication of the molecular weight and actual number of moles of the H_2 gas. The actual number of moles can be measured using the equation of state of gases at a temperature of 25 °C, partial pressure of hydrogen gas and the actual volume of hydrogen. The partial pressure of hydrogen was calculated using Dalton’s law for gases at 25 °C and 1 atm. The actual volume of hydrogen gas was calculated by multiplying the mole fraction of hydrogen gas by the total volume of the collected gas during the electrolysis process from the cathode compartment using water displacement method. As for the current efficiency of hydrogen gas production, this was calculated using Eq. (2):

$$\text{Current efficiency}=\frac{\text{Charge needed to produce } H_2 \text{ in theory}}{\text{Charge passed during electrolysis}}\times 100\% \qquad (2)$$

The values that were inserted into this equation were determined as follows. The amount of electric charge (Q) passing through the electrolytic mixture during hydrogen gas production can be obtained by integrating the current time plots. To calculate the charge needed to produce hydrogen gas, in theory, the number of electrons involved to split steam to hydrogen gas was multiplied by the Faraday constant (96485 C/mol) and the number of moles of hydrogen gas produced. Thus, higher electric charge flow will indicate more hydrogen gas produced at the cathode.

3. Results and discussion

The minimum amount of voltage and the overall amount of electrical energy needed for the generation of H_2 gas from water splitting at 25 °C temperature is 1.23 V [21]. The net reaction of water splitting can be represented as in Eq. (3):

$$H_2O + 2\,e^- \leftrightarrow H_2 + 1/2\ O_2 \qquad (3)$$

In practice, as because of the bubble formation, low reaction rate and the activation energy barrier of the reaction, the electrochemical cell voltage needs to be larger than the required cell voltage Therefore in this study, the cell voltages used were kept above the minimum cell voltage of 1.23

V even though it needs to be lower than this minimum value at high operating temperatures. The higher applied voltages between 1.5 and 2.5 V to split water were arranged in such an order to overcome any barrier for the electrolysis process and ensure continuous hydrogen gas production. The electrolysis process was operated in a temperature range between 225 and 300 °C.

3.1. Performance of stainless steel anodic cell

Stainless steel was employed as the anode material in the electrolysis process. Therefore it should be mentioned that when it was employed at high temperatures in the eutectic molten hydroxide, it had a passivate type behavior even though it was used in a corrosive environment [22]. The stainless steel anode undergoes passivation with the creation of an outer layer shield, and there is no influence on the response of the current-time plot which is directly reflected in the rate of hydrogen gas formation. These results were repeatedly obtained for four times over, and thus noises were not caused by experimental errors. The noise, as mentioned earlier, was due to steam splitting and the development of bubbles on the surface near the nickel cathode.

Ni, Pt and St.st electrodes were used individually as cathode in the designed electrochemical cell, to study the electrolysis and resultantly hydrogen production [23], against St.st anode. The other applied conditions were changing continuously to find the optimum ones, including temperature and voltage. Fig. 1 shows the current-time responses at operating temperature 300 °C. At this operating temperature, a different voltage was applied (1.5, 2.0 and 2.5 V respectively). These electrolysis processes were carried out as mentioned previously, under a steady argon gas flow rate 40 $cm^3\ min^{-1}$ and a fixed steam flow 7.23 $cm^3\ min^{-1}$. The reason for this comparison is to find out the most efficient cathode material during the electrochemical process for a higher rate of hydrogen gas production.

In addition to nickel, platinum metal was also selected as a cathode for the hydrogen evolution in the eutectic molten hydroxide [24]. The recorded current-time plots for all the tested combinations are shown in comparison against the St.st anode in Fig. 1 at different applied voltages. As mentioned previously, platinum is a precious metal and this prevents it from large scale industrial use, limiting its usage for laboratory scale investigations. In this study, a platinum wire of 0.5 mm diameter was used. Since the diameter of the used platinum is very small, it was necessary to increase the surface area that was exposed to the electrolyte to be approximately the same as the nickel electrode surface area. This was done to ensure a smooth comparison of current flow and production rate of hydrogen gas at the same operating conditions. Therefore, in order to achieve a surface area of 2.55 cm^2, it was simply rolled into a spiral shape with 15 cm of the wire length. This increase in the surface area significantly contributed to increasing the current flow value at different applied voltages.

It can be observed from the current-time plots @ St.st anode that current flow increases with an increase in the applied voltage at the applied operating temperatures. After electrolysis, no change can be observed on Pt electrode's surface. The reason for there being no change in the surface area of the electrode is because platinum is an inert metal and does not inhibit the reaction occurring at its surface. It simply acts as a means to transfer electric charge from the power supply to the electrolyte without undergoing any change. Platinum can also be classified as a corrosion resistance metal to specifically withstand sodium hydroxide melt under suitable conditions [25].

Stainless steel metal was also used as a cathode in the eutectic molten hydroxide to compare with other tested materials at the same operating conditions. It can be observed from Fig. 1 that the current increases with an increase in the applied voltage. It is observed that at 225 °C, the current response is stable and the current increases approximately with an increment of 0.2 A for every 0.5 V increase in the applied voltage. This observed phenomena of the current at 225 °C is not applicable when the temperature is increased to 300 °C. However, when the temperature increases, the current response curve begins to appear noisy, particularly at higher applied voltages. The escalation in the production of molecules of H_2 gas around the cathode is mainly liable for this noisy response of the current-time plot. Further surface morphology can be considered for this in future for more comprehensive analysis.

The important point that can be observed from the results of current time plot is that the overall recorded current is the highest when using the nickel as cathode material during electrolysis inside the eutectic molten hydroxide might because of its good catalytic potentials [26]. These observed results are consistent for the nickel electrode at different applied voltages and different operating temperatures. Furthermore, for the nickel electrode, when the applied voltage increases from 1.5 to 2.5 V, the current increased accordingly as confirmed from the mentioned plots and are in accordance with the literature [27].

In the testing, it was observed that at 225 °C the current increases from 0.2 A at an applied voltage of 1.5 to 1.4 A at an applied voltage of 2.5 V. For stainless steel and platinum electrodes, the recorded current-time plots show that their current responses are approximately the same at different applied voltages and different operating temperatures. While at 300 °C temperature, the current is recorded comparable, little bit higher for St.st than Ni at 1.5 and 2 V. It should be noted here that the steam and argon mixture was bubbled inside the eutectic molten hydroxide for an approximate duration of 600–900 s before the electrolysis process was started. From these plots obtained during electrolysis, the current flow observed was with some level of noise in most conditions. This noise observed is quite typical during electrolysis of steam via eutectic molten hydroxide and during the formation of hydrogen gas bubbles around the cathode.

When hydrogen molecules are formed, they migrate away from the cathode in order to allow other steam molecules to be split into forming new hydrogen molecules along with the oxygen. This transfer of the hydrogen and steam molecules to and from the nickel cathode surface during the electrolysis process can be listed as the reason for the noise noticed in the current-time plot. It is significant to mention here that the nickel cathode is highly stable for molten hydroxide water splitting as stated by literature [11], that corroborates with these research findings.

3.1.1. H_2 gas production potentials @ anodic stainless steel cell

The production of H_2 gas was analysed using three methods, including Gastec gas detector tube, hydrogen gas sensor (PRO-GASBADGE) and water displacement method. The gas sensor monitored the hydrogen gas produced up to 2000 PPM. The hydrogen gas sensor detected the hydrogen gas between 655 to 705 PPM at an applied voltage of 1.5 V to the electrolysis cell and at more than 2000 PPM at an applied voltage of 2 V. This confirmed that the only gas produced at the cathode is hydrogen. To quantify the amount of hydrogen gas produced at the cathode, the gas flow was collected in a measuring cylinder using the water displacement method. The hydrogen gas was collected and measured over a period of 10 minutes intervals.

The process was repeated four times and the production rate remained approximately constant. Fig. 2 shows the rate of hydrogen gas production at different cathodes (Ni, Pt, and St.st) at different operating temperatures and different applied voltages respectively. It is clear from this data that a steady increase in the hydrogen gas production rate at the cathode can be noticed when an increase in the operating temperature and applied voltage respectively, is enforced. This trend is valid for all examined cathode materials. Furthermore, the flow rate of hydrogen gas using a nickel electrode recorded the highest value in comparison to the other two used cathode materials i.e. stainless steel and platinum in this order respectively. For example, the hydrogen gas flow rate at 250 °C and applied voltage of 2 V using a nickel, stainless steel and platinum cathode were 5.0, 3.5, 3.0 $cm^3\ min^{-1}$ respectively. These results indicate that nickel has an enhanced level of catalytic activity in the current eutectic molten hydroxide, contributing towards splitting the steam with higher efficiency. Hydrogen gas production rates calculated with Eq. (1).

3.1.2. Current efficiency of the cell

The calculated current efficiency of the hydrogen gas using Eq. (2) is presented in Fig. 3 using different cathode materials and at different operating temperatures and applied voltages respectively. It is obvious from the above the results that the current efficiency of the hydrogen gas production rate using a nickel cathode reached up to 90.5% at 300 °C. This achieved value of efficiency shows that the value of the current in practical was approximately close to the value of the current in theory. Alternately, when platinum was used as a cathode, the current efficiency of the hydrogen gas production rate decreased with an increase in the temperature.

This implies that the platinum catalytic activity decreased to allow the reaction to occur with increasing temperature. The achieved current efficiency at 225 °C was about 107.5%. The reason for being the value of the current efficiency above 100% was due to the experimental error or other side reactions happened. When stainless steel was used as cathode against the same anode efficiency reached up to 90%. When interpreting the hydrogen gas production rate and current efficiencies, different factors that need to be taken into account are the ionic transfer and gas bubble behavior in the electrolyte. These factors, in turn, influence the current during electrolysis. The transfer of ions is measured from the flow field and viscosity of the electrolyte solution. With the development of the electrolysis process, viscosity increases as a result of electrolyte concentration. That’s why constant steam addition is carried out to preserve the constant viscosity and concentration of the electrolyte [28,29]. Yet, greater transport does not mean greater H_2 generation but it is right to say that it is associated with fast reaction rates. The more the reaction rate, the more will be the bubbles formed, and this can adversely obstruct interaction of electrolyte solution with electrode material [29]. For future work, to speed up the exit of the bubbles and eliminate them from the respective electrode compartment, the recirculation approach can be mechanically applied to electrolytes.

3.2. Performance of graphite anodic cell

Further electrochemical investigation undertaken in the eutectic molten hydroxide uses graphite as the material for the anode and alternates between nickel, platinum and stainless steel as the cathode. The reason for using graphite in place of stainless steel in this study is to compare the effect of changing the anode material on the electrolysis cell performance. Specifically, it must be investigated whether it has a direct effect on the hydrogen gas production rate and the current efficiency. This cell performance was also tested at different operating temperatures and different applied voltages. The current-time plot shown in Fig. 4 is noted at 300 °C respectively. These electrolysis processes were performed for 1800 s under an argon gas atmosphere. It is observed that the plots of current response using nickel and stainless steel electrodes is approximately similar at operating temperatures of 225 °C and 250 °C, the applied voltages of 1.5 and 2.0 respectively.

Alternately, when the operating temperature of the eutectic molten hydroxide is raised to 300 °C, the current response using a nickel cathode becomes higher than for the stainless steel cathode. This difference between the former and latter is approximately 0.2 A and 0.4 A at 2.0 V and 2.5 V respectively as shown in Fig. 4. On the other hand, the current response using a platinum cathode is recorded as the lowest among the three different materials at different operating temperatures and applied voltages respectively.

The electro-activity of the nickel cathode increased during electrolysis with increasing temperature. Platinum, however, showed no change in its electro activity even when the operating temperature of the eutectic molten hydroxide or the applied voltages was increased respectively. This finding can be considered as a promising finding for potentially novel, green technology aiming at producing hydrogen gas using cheap, untreated metal instead of precious platinum metal. The collection of the gas using water displacement method was carried out for 10 min and repeated twice to confirm the accuracy of the gas production rate.

3.2.1. H_2 gas production potentials @ anodic graphite cell

The hydrogen gas flow rate increases with an increase in the operating temperatures of the eutectic molten hydroxide and when the applied voltage increases during electrolysis, as seen in Fig. 5. For the nickel cathode, the hydrogen gas flow rate produced during electrolysis at 300 °C and an applied voltage of 2.5 V, records the highest flow rate followed by stainless steel and platinum under the same operating conditions. Alternately, the nickel electrode electro-activity for producing hydrogen gas reduces at a low temperature of 225 °C and at an applied voltage of 1.5 V to be lower than the stainless steel electrode gas flow rate at the same operating conditions, as seen in Fig. 5 [30]. When comparing the hydrogen gas flow rate for both the anodes made of stainless steel and graphite respectively; and using different cathode metals, no significant change can be observed in the gas flow rate as seen in Figs. 2 and 5.

It is still imperative in this regards to mention that when graphite is used as an anode, the reduction process can possibly be obstructed by carbon particles blocking the pores of the oxide. This can prevent electrolyte contact with the oxide and significantly hamper the overall electrolytic process as mentioned by [31]. Therefore, it is important to take care when using graphite repeatedly to avoid contaminating the electrolyte and contributing to unfavorable side reactions. The production rate for each electrode was calculated using equation (1). The production rate for hydrogen gas increases with an increase in the operating temperature of the eutectic molten hydroxide. The platinum cathode did not exhibit this behavior because its production rate decreases with increasing temperature. This behavior was seen even when stainless steel was used as an anode. The production rate of hydrogen gas decreases when the temperature increases to 300 °C. This result leads to the conclusion that electro-activity of platinum metal inside the eutectic molten hydroxide decreases with increasing operating temperature.

3.2.2. Current efficiency of the cell

Fig. 6, presents the range and the average calculated values of current efficiency for the electrochemical cell using different cathode materials and at different operating temperatures. The current efficiency of hydrogen gas production decreases with an increase in the operating temperature of the eutectic molten hydroxide. For example, as temperature increases from 225 to 300 °C, the current efficiency decreases from 101.6% to 68.0% using nickel metal as the cathode and graphite as the anode. The reason for being the current efficiency about 101.6% at 225 °C using nickel cathode can be explained as an experimental error. For use stainless steel and platinum cathodes, the current efficiencies were 115.3% and 102.3% respectively at 225 °C. The reason for being the current efficiency of them more than 100% is explained as an experimental error happened at this specific operating temperature. The reason for the decrease in current efficiency for hydrogen generation with an increased temperature of the eutectic molten hydroxide is because the formation of superoxide O^{2-} reduction increases and subsequently competes with the hydrogen formation reaction [11] as seen in Eqs. (4) and (5):

$$\text{Anode: } 4OH^{-} \rightarrow O_2^{-} + 2H_2O + 3e^{-} \quad (4)$$

$$\text{Cathode: } O_2^- + 2H_2O + 3e^- \rightarrow 4OH^- \qquad (5)$$

This finding relating to the decrease in current efficiency with increasing temperature and applied voltage respectively; and is not in agreement with the current efficiency findings for hydrogen gas production using stainless steel as an anode. The only exception to this rule was using platinum as the cathode. In conclusion, the current efficiency increases with an increase in the operating temperature of the eutectic molten hydroxide (for all cathode materials) and increasing the applied voltages in case of using either nickel or stainless steel as the cathode during electrolysis.

4. Conclusions

This study finds that steam splitting assisted the eutectic molten hydroxide electrolysis at high operating temperatures for hydrogen gas production, and is the way forward to reduce applied voltages. For the nickel cathode, the increase in the current directly affected the hydrogen gas flow rate at the cathode. Comparatively Ni cathode against stainless steel anode proved a good combination. The achieved current efficiency for Ni, increased from 63.2% to 90.5% with an increase in the operating temperature from 225 to 300 °C respectively. For the platinum cathode, the flow rate of hydrogen gas production increased from 1.6 to 4.5 $cm^3\ min^{-1}$ with an increase in the applied voltage from 1.5 to 2.5 V at 300 °C. For the stainless steel cathode and anode, the hydrogen gas flow rate also increased from 2 to 7 $cm^3\ min^{-1}$. However, when the graphite anode was used during electrolysis, the response of the current increased with an increase in the operating temperature. The subsequent production rate also increased, but the current efficiency decreased with an increase in the operating temperature for all three cathode materials. This behaviour can be attributed to the carbon particles that obstruct the reduction process by blocking the pore of the oxide and preventing the oxide from coming in contact with the electrolyte. Cost effective electrode material, with good stability and catalytic nature electrolyte will be a good option for the anodic electrode under these conditions for H_2 gas production.

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Table 1. Dimensions of the electrodes.

Electrode material	Diameter (cm)	Depth (cm)	Surface area (cm^2)
Nickel	0.5	1.5	2.55
Platinum wire	0.05	1.5 × 10.8	2.55
Stainless steel	0.5	1.5	2.55
Graphite	1.0	1.5	5.50

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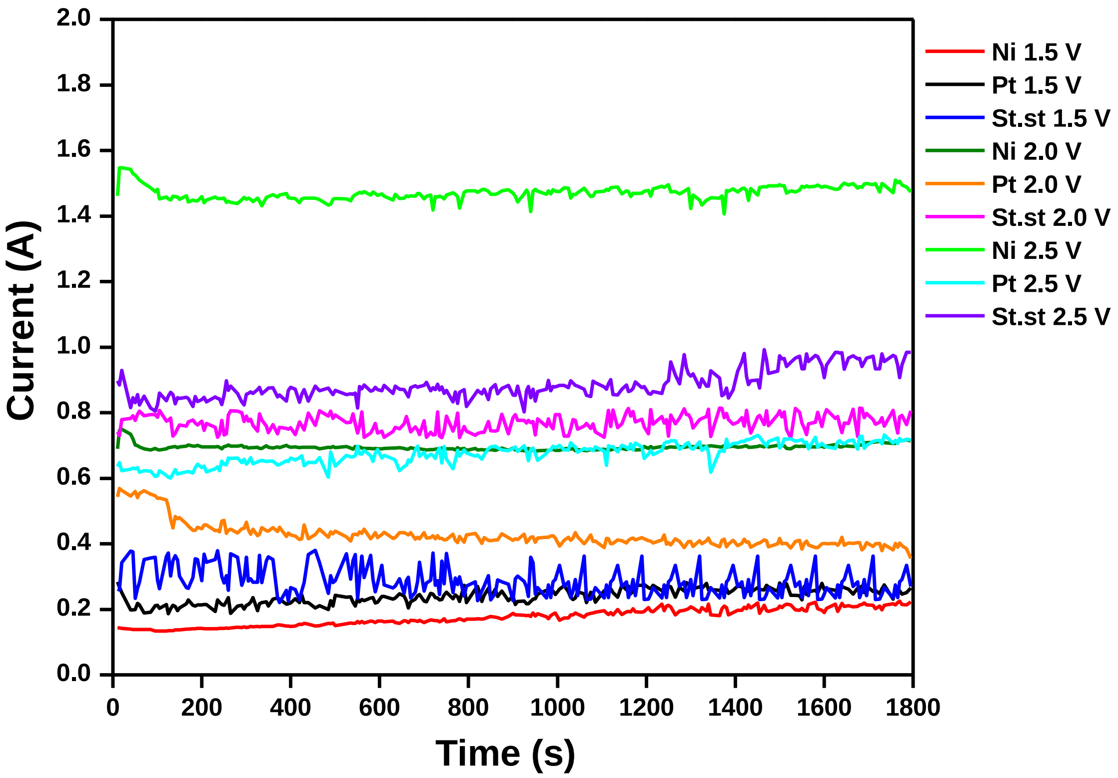

Fig. 1. Current-time plots @ stainless steel anode, vs Ni, Pt, and St.st cathodes recorded for 1800 s electrolysis at a temperature of 300 °C and applied voltages of 1.5 V, 2.0 V and 2.5 V.

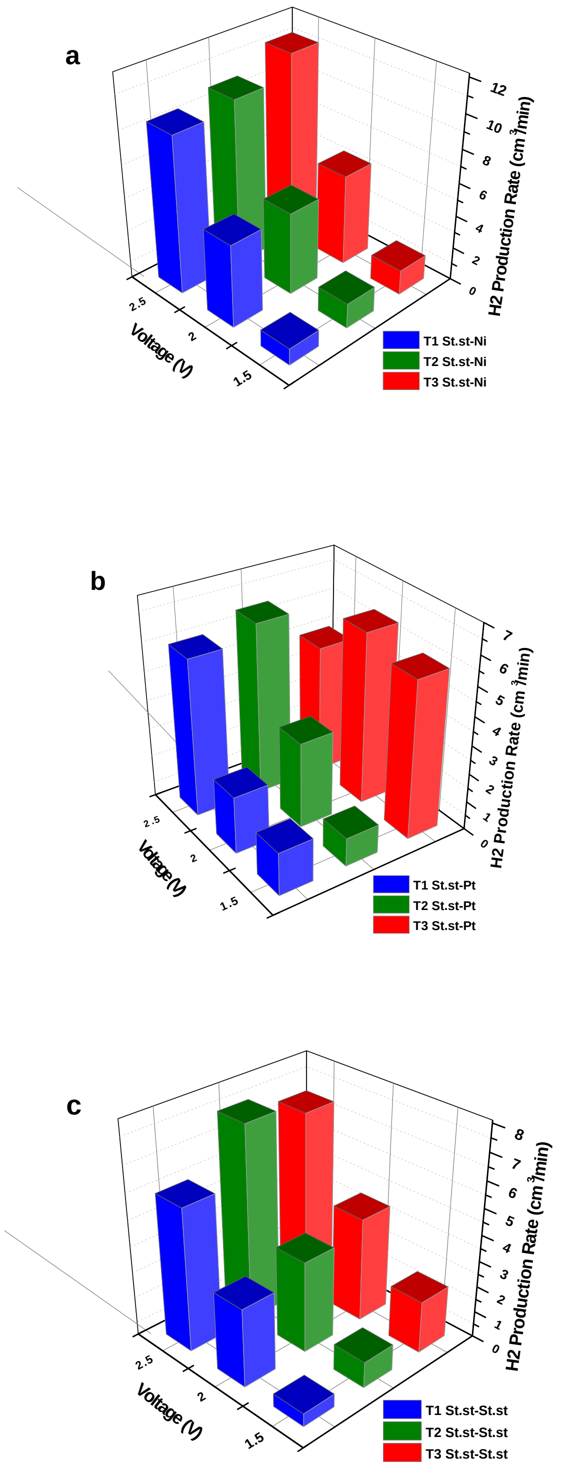

Fig. 2. Hydrogen gas production rate versus applied voltages at various operating temperatures; *T*1 (225 °C), *T*2 (250 °C) and *T*3 (300 °C) with St.st anode and different cathode materials; (a) Ni, (b) Pt and (c) St.st.

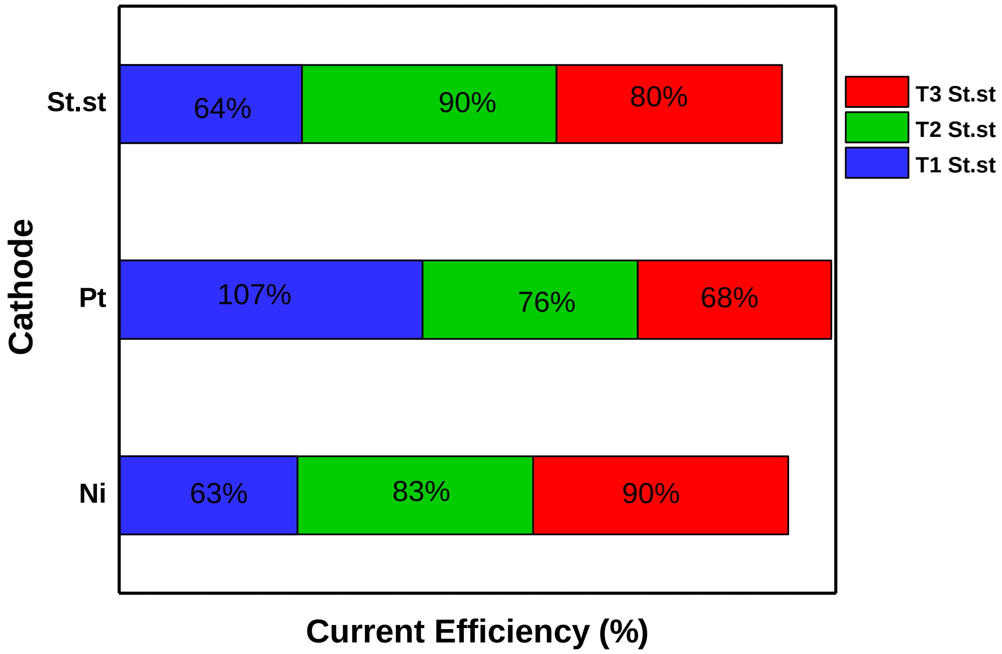

Fig. 3. Current efficiency of electrochemical cell for hydrogen gas production at different operating temperatures; *T*1 (225 °C), *T*2 (250 °C) and *T*3 (300 °C) with St.st anode.

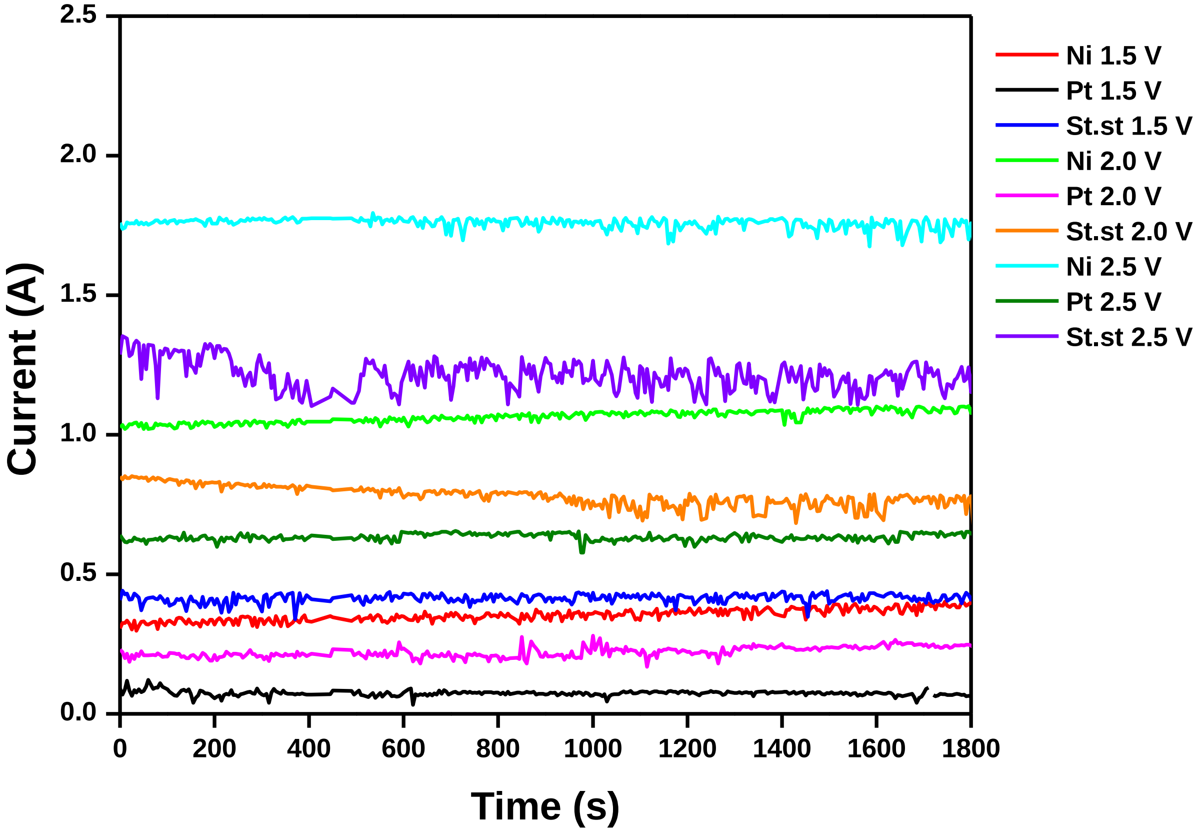

Fig. 4. Current-time plots @ graphite anode vs. Ni, Pt and St.st cathodes recorded for 1800 s electrolysis at 300 °C temperature with different applied voltages; 1.5 V, 2.0 V and 2.5 V.

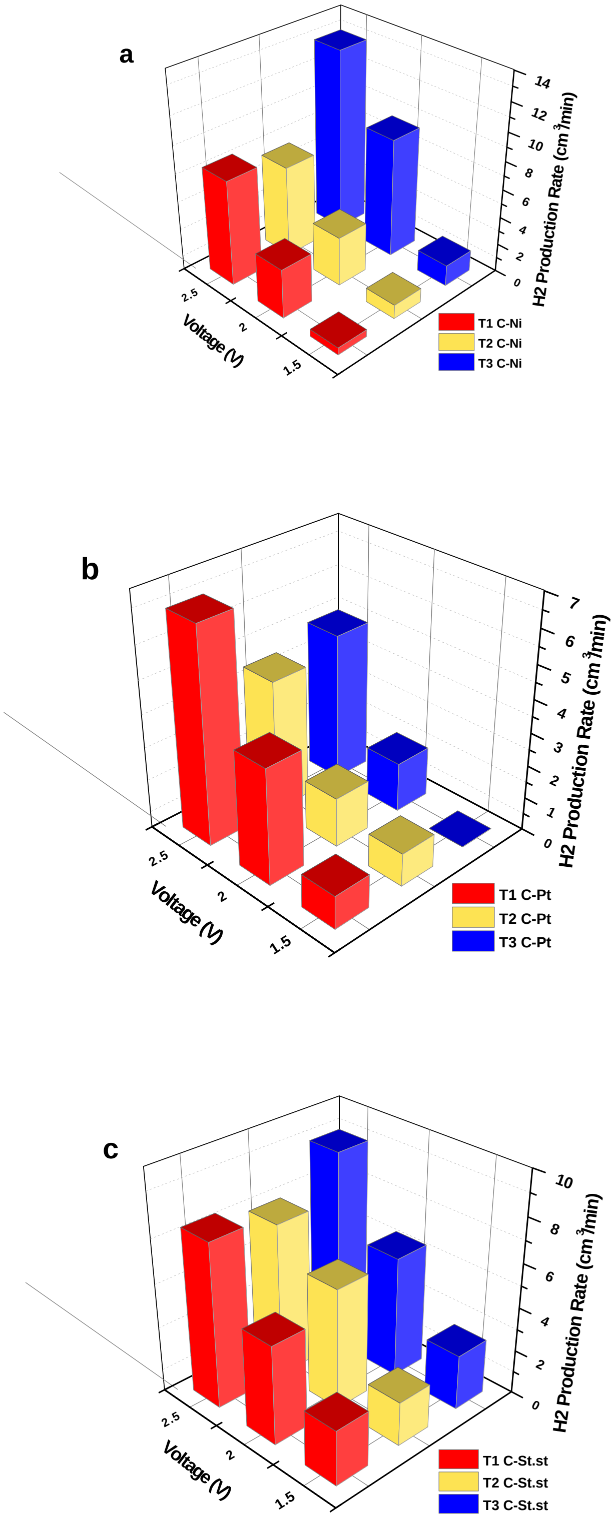

Fig. 5. Hydrogen gas production rate versus applied voltages at different operating temperatures; *T*1 (225 °C), *T*2 (250 °C) and *T*3 (300 °C) with graphite anode and various cathode materials; (a) Ni, (b) Pt and (c) St.st.

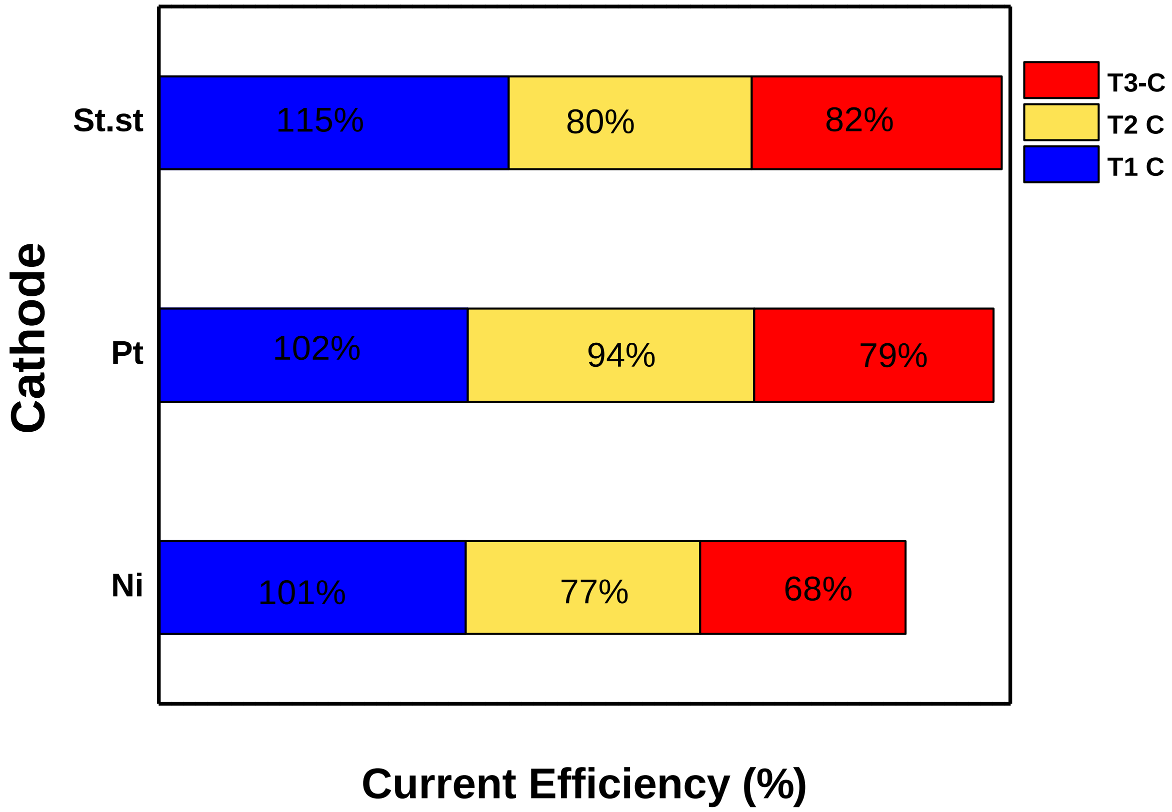

Fig. 6. Current efficiency of the electrochemical cell for hydrogen gas production at different operating temperatures; *T*1 (225 °C), *T*2 (250 °C) and *T*3 (300 °C) with graphite anode.

Graphical abstract

Various combinations of cathode, anode, temperature and voltage have been tested for optimization of best working conditions with molten hydroxide for H_2 gas production. Steam splitting is an encouraging alternate methodology for H_2 fuel production.