The effect of concentration of an electrolyte on the rate of production of Hydrogen in alkaline electrolysis.

**RATIONALE**

Eighty-ﬁve percent of the energy consumed globally is provided by fossil fuels, namely coal, oil, and natural gas [1]. Consuming fossil fuels at the rate needed to provide the world with energy produces so much greenhouse gas emissions as a by-product, that fossil fuels alone are consider the major contributor to climate change [2]. In this context, hydrogen has been proposed as a promising source of energy for over fifty years [3]. Hydrogen offers several advantages as an energy source: its combustion produces significant energy, water is the only by-product of combustion, and it can be produced from renewable and sustainable sources. In spite of these advantages, hydrogen has failed to be widely used in energy systems due to numerous barriers, including costs of production and storage and the availability of infrastructure [4].

Hydrogen can be produced by the electrolysis of water. Water electrolysis involves the decomposition of water molecules (H2O) into hydrogen gas (H2) and oxygen gas (O2) through the application of an electric current.

2 H2O(l) → 2 H2(g) + O2(g)

In terms of a commercial scale of Hydrogen production, the most well-established method is alkaline electrolysis [6]. This commonly uses aqueous potassium hydroxide as the electrolyte (and reactant) in the electrolytic cell with inert electrodes. In the alkaline electrolysis of water, the following reactions occur:

Reduction (at the cathode) 2 H2O(l) + 2 e- → 2 OH-(aq) + H2(g)

Oxidation (at the anode) 2 OH-(aq) → 2 e- + ½ O2(g) + H2O(l)  [6, p5]

As hydroxide ions are the species oxidised, the concentration of hydroxide ions is likely to have a significant influence on the rate of hydrogen production via the alkaline electrolysis method.

This investigation will examine the effect of varying the concentration of the alkaline electrolyte (KOH) on the production of hydrogen via the alkaline hydrolysis method. The effect of Hydroxide (OH-) concentration on the rate will be precisely determined by identifying the reaction order with respect to KOH concentration, using natural log analysis of the data.

**RESEARCH QUESTION**

To what extent does changing the concentration of potassium hydroxide electrolyte (0.2M to 1.0M) affect the rate of production of 25 mL of hydrogen gas via alkaline electrolysis?

**Original experiment**

The online simulation ‘Electrolysis Experiments’ (Crowley 2003) examined how changing an electrolyte’s chemical composition can affect the volume of hydrogen gas produced during electrolysis. The two electrolytes examined, acidified water and hydrochloric acid, offered different concentrations of H+(aq) available to undergo reduction. The higher concentrations of H+(aq) in the Hydrochloric acid did produce significantly higher amounts of hydrogen gas.

**Modifications to the methodology**

Table 1: The original experiment was modified by:

|  |  |
| --- | --- |
| Modification | Justification |
| Changing the independent variable from concentration of H+ (acidic electrolysis) to concentration of [OH-] (alkaline electrolysis) with silver electrodes. | This allowed the change in the independent variable - to concentration of OH- (not [H+]). This change enabled an investigation into the effect of hydroxide concentration on the rate of electrolysis |
| Timing the production of 25mL of Hydrogen gas. | This allowed the rate of production of Hydrogen (dependent variable) to be calculated. |
| Five concentrations of KOH (0.2 M, 0.4 M, 0.6 M, 0.8 M and 1.0 M) were used. | This should be sufficient variation in the independent variable to accurately identify a trend in the electrolyte effect. |
| Each concentration was trialled three times. | This should be sufficient to reduce and determine the random uncertainty for the dependent variable. |
| Reducing the total volume of hydrogen collected to a volume of 25 mL. | This reduced the time needed for the trials and made the investigation more efficient. |
| using a 25.00 ± 0.25 mL measuring cylinder rather than a test tube with a marker. | to more accurately quantify the volume of hydrogen gas produced (controlled variable) |

 **RISK MANAGEMENT**

Table 2: Assessment of risks

|  |  |  |  |
| --- | --- | --- | --- |
| **Source of Risk** | **Risk** | **Mitigation of risk** | **Response to occurance** |
| **Chemical**: Potassium hydroxide electrolyte exposure to eyes and skin (irritant, but not corrosive) | Medium | Appropriate PPE will be worn, including safety glasses and a lab coat. | If exposure to eyes occurs, the eye wash will be used to irrigate eyes. If skin exposure occurs, the area will be rinsed completely with water. Inform the teacher. |
| **Chemical**: Possible combustion of Hydrogen or Oxygen gas when collected | Slight | No flame sources will be used. Electrical contacts will not be manipulated until gas is released. Safety glasses worn. Laboratory will be ventilated using extraction fans | Assess for physical injury and treat appropriately. Assess equipment for damage and replace if necessary. Inform the teacher |
| **Environmental:** Disposal of Potassium Hydroxide electrolyte (avoiding local waterway contamination) [5, p4] | Slight | The electrolyte used in the investigation (and any excess) will be collected, returned to the prep room for storage and appropriate disposal.  | Nil |
| **Ethical:** No ethical concerns are associated with this investigation |

**Analysis**

**Raw data**

Table 3: Concentration of electrolyte and time for production of 25mL of hydrogen

|  |  |
| --- | --- |
| **Concentration of OH-** (mol/L) | **Time** (seconds) |
| **Trial 1** | **Trial 2** | **Trial 3** |
| 0.2 | 359.5 | 368.5 | 364.5 |
| 0.4 | 360.0 | 345.5 | 327.5 |
| 0.6 | 325.5 | 339.5 | 333.5 |
| 0.8 | 343.5 | 307.0 | 327.5 |
| 1.0 | 307.0 | 339.5 | 326.5 |

\*Operating temperature of the apparatus = 26.0 °C = 299.0 K

\*Pressure in the lab = 101 kPa

\*Uncertainty in time = ± 0.5 seconds

\*Uncertainty in 25 mL volume = ± 0.5 mL

**Processing of data**

Table 4: Calculations for secondary data – trials at 1.0M used

|  |  |  |
| --- | --- | --- |
| Explanation | Formula used to process data | Sample calculations for 1.0 M KOH |
| Calculation of average time for 25 mL of gas |  |  |
|  | \**\*Comparison of random and measurement uncertainty means random uncertainty will be used to represent uncertainty for time in the investigation.* |
| Calculation of moles of Hydrogen in 25 mL of gas |  | *mL* (sig fig continued) |
|  |  *moles* |
| *(note: all other values in n calculation are “known” values)* | *moles* *moles* |
| Rate of hydrogen production |  | *moles/s* *moles/s* |
|  |  |
| Natural log of rate and [KOH] |  |  |

Table 4: Concentration of KOH and the rate of electrolysis.

|  |  |  |
| --- | --- | --- |
| Concentration of OH-(aq) (mol/L) | Rate of H2 production (moles/s) | Uncertainty in rate of H2 production (%) |
| 0.2 | 2.46 x 10-6 | 3.24 |
| 0.4 | 2.60 x 10-6 | 6.72 |
| 0.6 | 2.69 x 10-6 | 4.10 |
| 0.8 | 2.74 x 10-6 | 7.60 |
| 1 | 2.76 x 10-6 | 7.01 |

Figure 1: Rate of Electrolysis

Figure 2: Natural log graph of OH- and Rate

**Identification of trends and relationships**

As the concentration of the Potassium hydroxide electrolyte in the alkaline electrolysis cell increased, the rate of production of Hydrogen gas increased. At the lowest concentration of 0.2 M the rate of production was 2.46 x 10-6 moles/L, and at the maximum concentration of 1.0 M, the rate was 2.76 x 10-6 moles/L. The relationship was non-linear, with smaller increases in the rate as concentration increased, and is best described by a power equation (with an R2 of 0.99):

Rate of H2 production = 3 x 10-6 x [OH-]**0.0748**

This relationship suggests that the change in concentration of KOH did not have a significant effect on the rate of production. An increase of five-fold in the concentration (0.2 to 1.0) resulted in an increase of 1.12 fold in the rate (2.46x10-6 to 2.76x10-6). The natural log graph indicates that the reaction order with respect to [OH-] is 0.075. Given that reaction orders are generally whole numbers, or multiples of 0.5; and an average uncertainty in the rate of 6%, the value of 0.075 can realistically be considered to be zero. A reaction order of zero with respect to [OH-] suggests that the concentration of KOH has no influence on the rate of Hydrogen production.

**Identification of Uncertainty**

There is significant uncertainty in the data. The rate of H2 production had an average uncertainty of under 6%, with higher uncertainty (~7%) at higher rates, and the highest uncertainty being 7.6%. These values are not high and should reflect a degree of certainty about the data. However, the rate values have only very small differences (12% range), and the values for rate do not differ by very much more than the uncertainty range (± 6%). This is most clearly shown in figure 1, where the rate values almost all lie within the uncertainty bars (error bars) of the other values. Given this, the rate values cannot be considered to be determined with any certainty.

There is also significant uncertainty in the trend. The trend line does initially appear to accurately depict the pattern in the data, and almost all the variation in the rate can be explained by the variation in the concentration (R2=0.99). However, given the similarity between the range in the rate values and the uncertainty, it is theoretically possible to draw a number of different trend lines which would all fit within the range of the uncertainties. Therefore, a trend line which does appear to accurately describe a trend in the data, the trend is not certain.

**identification of limitations**

The uncertainty (and reliability) of the data and trend was limited by using only three trials. The uncertainty was found to be reasonably low, but very significant. This indicates there should have been more than three trials for each concentration. This may have reduced the uncertainty to a point where the trend may have been conclusively identified.

The range of concentrations of KOH used has limited the application of these results to commercial situations. The concentrations of KOH used (0.2 to 1.0M) were not reflective of commercial operating concentration which are approximately five moles/Litre [6,p5]. This was a known limitation as concentrations of KOH within a commercial range are considered quite caustic, and significant additional safety procedures would have been needed. Therefore, the trend identified may be limited by not be representative of higher concentrations.

**Interpretation and Evaluation**

**conclusion**

The concentration of potassium hydroxide does not significantly affect the rate of hydrogen gas production in alkaline electrolysis. The relationship between concentration and rate was determined to be

Rate of H2 production = 3 x 10-6 x conc**0.0748**

This relationship showed that a 500% increase in the concentration resulted in only a 12% increase in the rate. The reaction order with respect to KOH was close to, and given the degree of uncertainty, likely to equal zero. It therefore appears that significantly increasing the concentration of potassium hydroxide in alkaline electrolysis should not be considered as an economical method for improving the production of hydrogen gas.

**evaluation of reliability**

The data recorded and thus the existing methodology would generally be considered reliable considering the relatively low relative uncertainty (average <6%) in the data, and a trend which appeared to accurately describe the pattern in the data.

However, the determined mathematical relationship between concentration and rate that was identified in the conclusion cannot be considered reliable. The variation in the measured rates was very small, and were determined to be well within the ranges of the uncertainties. Therefore, despite the relatively low uncertainty, these rate values cannot be considered reliable. It was further identified that the trend could vary significantly and still fit within the range of uncertainties. Given this, the precise mathematical description of the relationship would lack reliability.

Conversely, the conclusion that concentration of KOH does not significantly affect the rate of hydrogen gas production is considered highly reliable. The rate values varied so little when the concentration was changed very significantly, that no other general conclusion seems possible.

**evaluation of validity**

The main conclusion that concentration of the electrolyte does not significantly affect the rate of H2 production is likely to be valid. The very small variation in the rate vales contrasted greatly with the significant variations in the concentration, and very strongly suggests that for the concentrations used in this experiment, there was little to no variation in the rate of H2 production. However, the use of concentrations of the electrolyte in this investigation was well below commercial levels. This means this conclusion may not extrapolate with any validity to commercial electrolysis situations.

The specific mathematical relationship between concentration and rate which was identified in the conclusion cannot be considered valid. The use of only three trials meant that the uncertainty in the rate values was similar to the small variation in the rate values. This suggests that any precise mathematical relationship between concentration and rate could vary significantly, and cannot be considered valid.

**improvements and extensions**

The methodology of this investigation would be improved by doing more than three trials at each concentration. This would reduce the random uncertainty and improve the reliability of the data. It would also help a more valid identification of the mathematical relationship between rate and KOH concentration. Additionally, the concentration of the KOH electrolyte should be varied (with additional safety measures) beyond 1.0 M. This would increase the validity of the conclusion as it relates to commercial applications.

This investigation could be extended by investigating other factors which affect rate, specifically temperature of the electrolyte solution. This would enable a more comprehensive picture of the factors which affect the rate of hydrogen production in alkaline electrolysis. This investigation could also be extended by investigation the effect of hydroxide concentration in Anion Exchange Membrane (AEM) water hydrolysis to produce hydrogen gas. This would provide an indication if the interaction of the electrolyte is specific to hydroxide anion, or the methodology used for the electrolysis.

**REFERENCES**

1. Tverberg G. BP data suggests we are reaching peak energy demand. 2015. Available from: https://ourﬁniteworld.com/2015/06/23/bp-data-suggests-we-are-reaching-peak-energy-demand [Accessed: July 8th, 2023]
2. United Nations – Causes and Effects of Climate Change. https://www.un.org/en/climatechange/science/causes-effects-climate- change#:~:text=Fossil%20fuels%20%E2%80%93%20coal%2C%20oil%20and,of%20all% 20carbon%20dioxide%20emissions. [Accessed July 8th, 2023]
3. Winsche WE, Ho􀀁man KC, Salzano FJ. Hydrogen: Its Future Role in the Nation’s Energy Economy. Science. 1973; 180: 1325
4. Hanley ES, Deane J, Gallachóir BÓ. The role of hydrogen in low carbon energy futures—A review of existing perspectives. Renewable and Sustainable Energy Reviews. 2018; 82: 3027-3045
5. Industrial Chemicals (2021) *Potassium hydroxide: Human health tier II assessment*. Available at: <https://www.industrialchemicals.gov.au/sites/default/files/Potassium%20hydroxide_Human%20health%20tier%20II%20assessment.pdf> (Accessed: 20 November 2024).
6. Zhang, Y., Wang, Y., Zhang, Y., Liu, Y. and Wang, H. (2022) 'Hydrogen production via alkaline electrolysis: A review of recent advances and future perspectives', Energy Reports, 8, pp. 123-135. doi: 10.1016/j.egyr.2022.01.001.