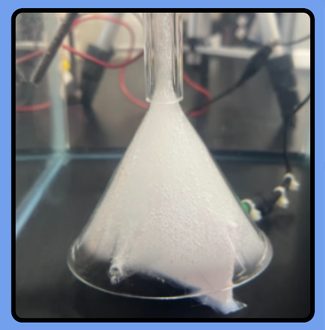
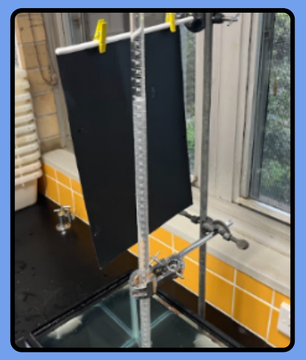


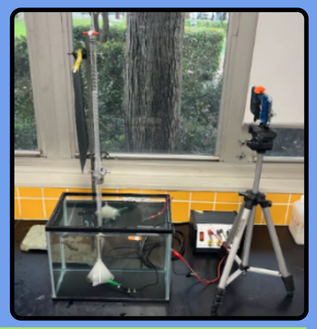
The potential for producing sustainable fuels: Non-precious metal oxide coated carbon electrocatalysts for hydrogen generation



Recently, the search for clean renewable energy has become a major priority in a hope to get closer to sustainable development and reducing climate change. Electrocatalysts are frequently used to increase the rate at which moles of hydrogen gas are produced by electrolysis, however, the expense and low availability of precious metals and rare earth metals as electrode materials has resulted in limited commercial interest in hydrogen production via the electrolysis method. In this study, non-precious metals oxides are claimed to have electrocatalytic activity comparable to that of precious metals.

Research Question:

To what extent do metal oxide surface coatings on carbon electrodes affect the rate of hydrogen gas production from the electrolysis of an alkaline solution?



Hypothesis:

H_0: There is no significant difference in the rate of hydrogen production when the carbon electrode is coated with a non-precious metal oxide.

H_A: There is a significant increase in the rate of hydrogen production when the carbon electrode coating is coated with a non-precious metal oxide.

Analysis

The highest rate of hydrogen production is shown for carbon cathode with the cobalt oxide coating (see Figure 1) at 2.36 μmol s^{-1}which is an 11-12% improvement over both the nickel oxide coated electrode and the carbon control. As shown in Table 1, the summary statistics of the regression analysis for cobalt oxide, nickel oxide coated carbon electrodes show a high degree of fit as indicated by all R square values above 0.97. Further, the P values are << 0.05 in all cases, leading to the working null hypothesis being rejected. Once again, this provides strong evidence that the quantity of hydrogen produced increases linearly for the 500 second duration of the experiment. The fitted slope for each regression line gives a measure of the rate at which mmol of hydrogen is produced at the cathode as the surface of the electrode is changed.

Results

Table 1: Regression analysis of Cobalt Oxide, Nickel Oxide and Carbon coating compared to rate of moles of hydrogen produced. Alpha = 0.05. Working hypothesis:
Ho - The slope of the regression line is equal to zero.
HA - The slope of the regression line is not equal to zero.

Statistic	Cobalt Oxide	Nickel Oxide	Carbon
Slope (mmol/s)	0.00236	0.00209	0.00212
Intercept (s)	0.00804	0.00592	0.00219
R Square	0.999	1.00	1.00
DF	26	24	25
F	1.92×10^{4}	2.22×10^{5}	1.85×10^{5}
Significance F	1.32×10^{-37}	2.40×10^{-47}	3.75×10^{-48}

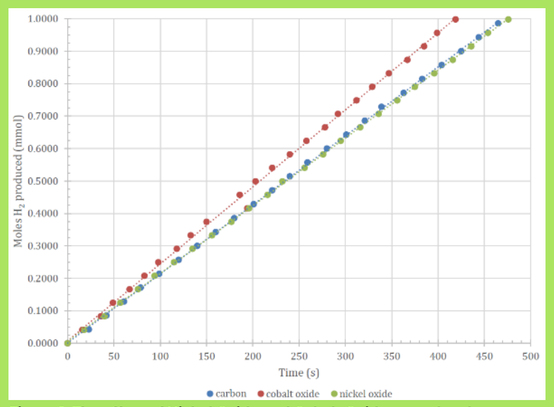


Figure 1: The effect of Nickel Oxide and Cobalt Oxide coated carbon electrodes on the millimoles of hydrogen gas produced as a function of time. Carbon electrode data was used as a control for comparison purposes.

Methodology

Electrode Preparation

Carbon electrodes were prepared by first washing graphite rods with distilled water before the rod was taped using electrical tape, leaving 10mm exposed at the tip of the electrode. 85mL of saturated copper sulfate solution was prepared and added to a 150 mL beaker. Two carbon electrodes were slotted into the two holes of a wooden jig (constructed from a 30 cm ruler) and suspended in the solution. Two wires with alligator clips were connected to the positive and negative terminals of a laboratory power supply and clipped onto each carbon electrode. The power supply was turned on to 12 volts and 10mm of the top of each electrode was plated with copper metal for 10 minutes. Afterward, the copper coating formed on the negative electrode allowed to air dry overnight. Wire strippers were used to strip electrical wires and then the uncovered copper wiring was wrapped around the copper plated area of the electrode. This was then physically secured using zip ties and heat shrink tubing was used to prevent contact with the solution during electrolysis

Metal oxide plating for electrocatalysts

Carbon electrodes were wiped with distilled water before the rod was taped using electrical tape exposing 50mm at the tip of the electrode. Cobalt chloride and nickel nitrate 0.5 mol L^{-1} solutions were prepared and added to separate 150 mL beakers. Two carbon electrodes were slotted into the wooden jig (constructed from a 30 cm ruler) and two electrical wires with alligator clips were connected to the terminals of a 9-volt battery and each carbon electrode. The electrodes were plated with either cobalt or nickel metal from each respective solution for 10 minutes. The cobalt or nickel metal coating formed on the negative electrode was allowed to dry and aged for at least one week to oxidise the surface.

Experimental Setup

A 10 mm hole was drilled into a 5x3 cm section of a plastic cutting board that was hot glued to the base of a 20L plastic fish tank to act at the mounting board for the working electrode of the electrolysis setup. The following surface area exposed are the following: Cathode: $9.71 \times 10^{-4} m^2$, Anode: $1.44 \times 10^{-3} m^2$. 15 litres of room temperature water was added to the tank. The carbon electrode (cathode) which was connected to the negative terminal of a laboratory power pack and inserted into the mounting board to secure it at the base of the tank. The other carbon electrode (anode) connected to the positive terminal was also submerged in the water. A glass funnel was inverted above the cathode to collect and feed hydrogen into a burette. After setting up the retort stand and boss head clamp, a burette filled with 0.1 mol L^{-1}NaOH was inverted and inserted into the neck of the funnel under water prior to being secured in place with the clamp. Then, 1.5 L of 1mol L^{1} NaOH was then poured into the container and allowed to stand for 3 minutes. A piece of black cardboard was hung on a plastic stirring stick with two pegs as a contrasting background behind the inverted burette.

Recording Data

Before turning the on the power pack to 8 volts an iPhone 13 Pro on a tripod was set to record, adjusting its frame to capture a vertical length of the burette that would allow for at least 15mL of hydrogen gas to be recorded. The data was extracted from the video replaying each of the trials on the built in video player of Google Drive and recording the volume of hydrogen produced at each timestamp.

Discussion

By investigating the effect of electrode voltage, surface area and coating, the experimental conditions to maximise the rate of hydrogen production, in the studied system was found to occur at the maximum voltage assessed (12V), maximum surface area assessed (0.00144 m^2) and with cobalt oxide electrode coating. The regression models utilised in this investigation are statistically significant shown by all P values << 0.05 and strong linear correlation between data points for each parameter examined. Thus, the investigation's null hypothesis stating that there is no significant difference in the rate of hydrogen production when the carbon electrode coating is changed can be rejected. Further, the findings of this investigation suggests that the optimum conditions for hydrogen production in alkaline solution industrially can potentially be found by maximising the applied voltage and surface area of cobalt oxide coated electrocatalysts.

Based on the literature review of this investigation, cobalt oxide and nickel oxide were identified as showing improved electrocatalytic properties in comparison to the carbon-carbon electrode systems (Sadiek, Mohammad, El-Shakre, & El-Deab, 2012; Zhang, Cui, & Liu, 2020). Nickel oxide, however, did not perform as well as cobalt oxide which may be due to the uneven patchiness of the oxide on the electrode. This may reveal a potential shortcoming in the methodology of the electrode preparation process in this investigation, namely the extent of the integrity of the metal oxide coating is unknown. With the very similar performance of the nickel oxide coated electrode to the carbon control suggesting that the surface properties of this electrode may be dominated by the underlying carbon surface below an incomplete nickel oxide coating. A simple improvement that could be addressed in future investigations would be to alter the electrode preparation process to increase the thickness of the nickel oxide layer at the carbon electrode surface by electroplating the electrodes for an extended period of time.

Conclusion

The rate of hydrogen production by electrolysis in alkaline solution was found in this study to increase with electrode applied voltage and surface area; cobalt oxide coated on the surface of the carbon cathode was also found to improve the rate of hydrogen production by 11-13%. Regression analysis found that the maximum rate of hydrogen production was dependent on applied electrode voltage, electrode surface area and electrode surface coating. This supports the rejection of the null hypothesis and suggests that preparation of the electrode surface is highly influential on the rate of hydrogen production. The extent of the cobalt oxide electrode coatings improved electrocatalytic performance warrants further research into the use of non-precious metal oxide coatings as novel electrocatalysts for hydrogen production.

References:

- Sadiek, I. M., Mohammad, A. M., El-Shakre, M. E., & El-Deab, M. S. (2012, January). Electrocatalytic activity of nickel oxide nanoparticles-modified electrodes: Optimization of the loading level and operating pH towards the oxygen evolution reaction. Retrieved from Science Direct: https://www.sciencedirect.com/science/article/abs/pii/S0360319911022105?via%3Dihub
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