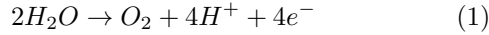


Electrolysis of Water

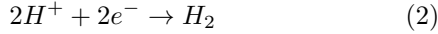
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I. INTRODUCTION

Water electrolysis is the process of separating the molecules of water H_2O into its constituents H_2 and O_2 gas. This is done in two separate chemical reactions. The oxidation of water,



and the reduction of Hydrogen ions.



The reaction described above does not happen all by itself. An electrical field needs to be applied over the water for the oxidation to be possible. The thermo-dynamical minimum (E_{\min}) voltage that needs to be applied is 1.23 V.

Water electrolysis by itself is a fairly slow process. Excess energy is used in order to increase the rate of the reaction as well as to overcome small hindrances in the liquid, the excess energy is called **Overpotential**. Beyond that, electrolyte in the combination with catalysts are other ways to optimize the process.

The usage of water electrolysis as a tool for hydrogen production has a lot of upsides. Water being the only ingredient and the single byproduct being oxygen makes the process comparably environmentally friendly to its alternatives [1].

As of today water electrolysis is responsible for about 4% [2] of the global Hydrogen production. The reason for the quite low market share in spite of all the previously mentioned upsides is that the process is simply too inefficient and its materials too expensive [3].

To find new materials that could make the process more effective is currently an active field of research.

The aim of the experiment is to find what catalysts correlate to the most effective form of hydrogen and oxygen production.

The Tafel equation describes the overpotential as a function of the rate of the electrochemical reaction. [4]

$$\eta = \pm A \times \log_{10} \left(\frac{i}{i_o} \right) \quad (3)$$

II. METHOD

A. Catalyst testing

Three electrodes are lowered down into water with the electrolyte mixed in with it. One Working Electrode (**WE**) from which all the measurements are made. One counter electrode (**CE**) that close the circuit and together with the **WE** establishes a homogeneous electric field. Lastly a final measuring electrode (ME) is inserted into the mixture in order to make reliable measurements of the working electrode. See 1 for a diagram of the setup.

On the end of the **WE** and the **CE** two metals are attached acting as catalysts for the chemical reaction.

Potential builds up potentiostat via the **WE** and later the **CE**. This potential cycles between ± 2 V in order to determine when if at all, current starts flowing through the circuit. This data is saved and processed inside a computer connected to the potentiostat.

See 2 for an example of what data the procedure described above might produce.

B. Gas collection

Empty tubes are lowered down into the water resting above the catalyst and subsequently have their air sucked out of them. Allowing the bubbles that inevitably form

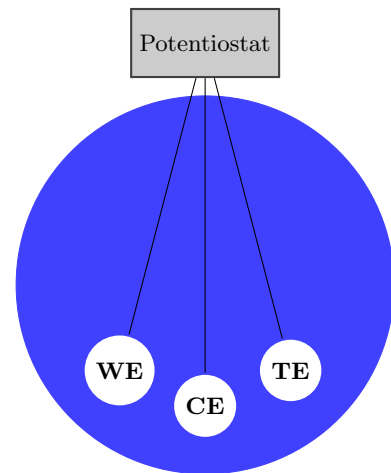


FIG. 1: Diagram of experimental setup.

CE: Counter electrode
WE: Working electrode
TE: Test electrode

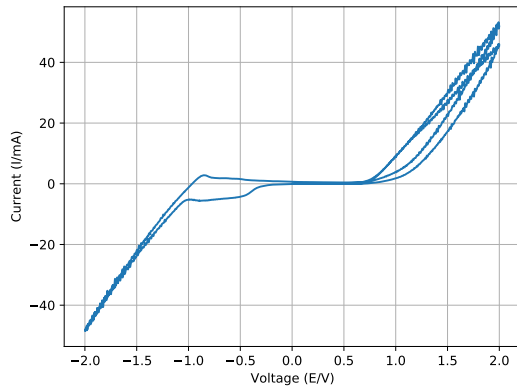


FIG. 2: Plot from the first Platinum measurement

on the catalyst to float up into the empty tubes.

All of the gas doesn't make it into the tubes but the amount that does are about equal for either reaction so the gases that gets trapped inside of the tubes is representative of the actual gas produced, proportionally to one another.

When placing down the tubes and sucking out all the air there is a need to get into physical contact with the electrolyte. Since 0.1 Mol KOH is highly corrosive we change it out for standard 1.0 Mol HCL (salt) which is safer.

The potentiostat is replaced with a more classical potential generator. Running a much stronger current through the circuit.

C. Analytical methods

The potentiostat goes through a set number of cycles for each measurement. This is done in order to make minimize any random errors that might occur. Unfortunately each cycle wasn't exactly the same length as the previous one, for reasons probably only known to the makers of the potentiostat, so in order to take sensible averages some points from the longer data cycles where cropped.

The removed sections of data comes from the middle of the data sets. Points that, wont be used for further analysis anyway.

In order to standardize the measurements we need to control for the differing sizes of the catalysts that where in the water. Therefore we divide each data point by the area of the corresponding catalyst in order to attain the current density.

We expect the relationship of the current density and the overpotential to be of exponential characteristic so we plot the $\log()$ of a part of the data that represents the overpotential. To plot the data for both the Oxygen evolution reaction (OER) and the hydrogen evolution

reaction **HER** we need to analyze different parts separately due to the nature of the logarithm as a function. See 4 for a graphical representation of this process.

We then use the Tafel equation to approximate a value for the Tafel slope (A). And then compare the theoretical value to the experimental one as a function of exchange current density.

III. RESULTS

All the data for all the experiments can be found at https://github.com/SixtenNordegren/Water_Electrolysis along with the code for of the data analysis. Due to the magnitude of data collected I won't be able to give each and every data set collected a fair showing. I will be presenting a selected few sets of data.

	Copper	Platinum	Nickel	Gold
Width (cm)	0.65 ± 0.1	0.80 ± 0.1	0.65 ± 0.1	0.65 ± 0.1
Length (cm)	0.60 ± 0.1	1.50 ± 0.1	1.30 ± 0.1	1.60 ± 0.1
Area (cm ²)	0.7 ± 0.2	1.2 ± 0.2	1.4 ± 0.2	0.9 ± 0.1

TABLE I: Table of measured length of catalyst submerged into water.

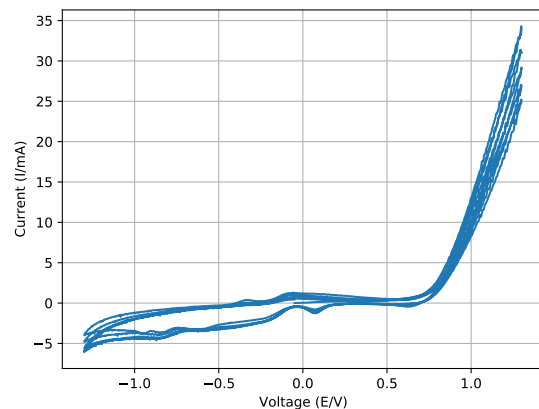


FIG. 3: Water electrolysis with gold as the **WE**, doing a particularly poor job (Pt is **CE**)

In table I we can see the measurements of what part of the metal catalysts that ended up in the water. This was done by extracting the catalyst after the experiment was performed and measuring the wet parts of the catalyst with a ruler. Since the catalysts where hanging from cables into the water, they couldn't be held perfectly perpendicular to the water surface, which often resulted in a slanted mark of water on the electrode. In those cases we simply averaged the length of the wet sides and calculated the area as if they were a perfect rectangles.

In table II and III we see the exchange current densities. These values where extracted by performing a linear

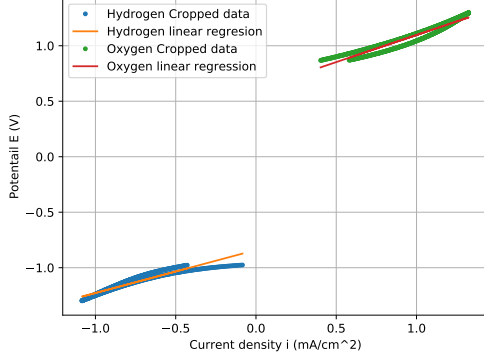


FIG. 4: Logarithm of the current exchange density. With linear regression for both the oxidation and the reduction.

regression on different parts of the logarithm of measured data and then solved for when $\eta = 0$. This is a good method a good chunk of the time, but some samples are bad enough catalyst as to barely have a reaction happen at all an example of this can be seen in figure 3. This in turn leads to some very inaccurate exchange current densities. So if a very perceptive reader find some of the values odd, compared to other literature values. That would be why.

Material	$i_{ecd} (A/cm^2)$
Platinum	2.92 ± 0.04
Copper	4.7 ± 0.5
Gold	0.032 ± 0.003
Nickel	10.2 ± 0.1
Iron	1.343 ± 0.007

TABLE II: Table of current exchange current density for the hydrogen reaction

Material	$i_{ecd} (A/cm^2)$
Platinum	0.32 ± 0.01
Copper	0.19 ± 0.01
Gold	0.64 ± 0.01
Nickel	0.57 ± 0.01
Iron	0.005 ± 0.007

TABLE III: Oxygen Exchange current densities

HER	V H_2 (mL)
Pt	2 ± 0.5
Au	2.6 ± 0.5

TABLE IV: Collected Hydrogen gas

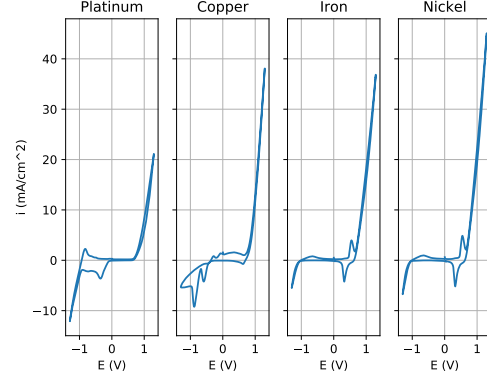


FIG. 5: Multiple data plots with average cycles.

The gas that was collected can be found in in table IV. Originally we were supposed to measure the oxygen production as well as the hydrogen production, but after the change of electrolyte the amount of O_2 gas produced was too small to measure.

In figure 6 we see the Tafel equation compared to some of the collected data. [5] The Tafel equation is calculated with the Tafel slope.

$$A = \mp \frac{\eta}{\log(i/i_o)} \quad (4)$$

$$A \approx 1.76 \pm 0.01V \quad (5)$$

Which is in turn generated by solving the Tafel equation 3 repeatedly for each data point in the current exchange density, and taking the average.

We can see the overpotential predicted by the Tafel equation in 6 compared to the collected data. The figure is in quite good agreement for the largest values, but diverges quite quickly for the smaller ones, this is due to the logarithmic nature of the Tafel equation.

IV. DISCUSSION

The question, what catalyst is best fitted to make either reaction as efficient as possible among those we tested is a rather intuitive experiment by itself. But what would make a catalyst effective? Since we are trying to create hydrogen we would want a catalyst that promotes lots of **HER** reactions to take place. Current in this case makes for a good variable to keep track of that will measure this.

The production of hydrogen moves electrons that is freed at the anode and recombine at the cathode. Closing the circuit and providing current. The more current is in

the circuit, the more reactions are taking place the higher the current [6] .

The graphs from the initial data is already a pretty good indicator weather the catalyst was an effective one or not. See the stark contrast between figure 2 and 3. We can already tell that when gold has a large negative potential over it, the total current is very low. At least when compared to the Platinum. In other words when Gold have a large negative charge acting as a catalyst for **HER** very few electrons seems to make it to the cathode and create hydrogen gas. Making it a bad catalyst.

To distinguish among the more effective catalysts however, we need to look a little closer. Since we risk letting the different sizes of the catalyst dictate the current.

The need for more detail seems to be unnecessary when it comes to the hydrogen production electrode, since **Pt** (Platinum) seems to outmatch all the other alternatives by mile. It's the only catalyst among those that we tested that at all managed to dip below a current density of $-10\text{mA}/\text{cm}^2$ and outclassed all the other alternatives. For oxygen production however there where plenty of viable alternatives, however it would seem that (**Ni**) Nickel would come out on top, reaching all the way up to the high $40(\text{mA}/\text{cm}^2)$'s. See figure 5 for a comparison between some of the current density measurements.

A. Error sources

The largest source of error for this experiment, or rather it's largest failure. Was the inability to measure the oxygen produced by the **OER**. This is strange since we did manage to measure a quite large current for plenty of different catalyst.

Moreover It seems that the gold managed to outproduce platinum in the **HER**.

1. New electrolyte

When measuring the gas intake we used a new electrolyte 1 Mol HCl instead of the 0.1 Mol KCl used in previous experiment. This seemed to have to a decrease in water oxidisation and an increase in oxidisation of whatever catalyst was used at the time. The precise reason for this is hard to place exactly. One reason might be that the PH value is different for each of the electrolytes PH 1Mol HCl mixture is around 7 and the 0.1Mol KCl is about 13. This might change the overpotential for either reaction slightly but due to the higher potential overall used in the experiment this seems minor.

2. Mixture of different elements

During the process different catalysts where tested sometimes in the same water-electrolyte bath. This might have had an adverse effect for either of the reactions. Particularly the gold reaction outproducing the platinum might be due to platinum ions floating around in that same experiment.

3. Irregular tube placement

It is also possible that, the capturing tubes. In-between measurements where moved between the hydrogen capture experiment and the gold capture measurement. Leading a high yield in gas from the gold.

The determination of effective catalysts where thankfully more reliable. However even this experiment isn't perfect. For most of the measurements there were a slight bump at the beginning of the **HER** this is due to Oxygen that's left on the catalyst from when it had a different charge which can react after the polarity switch and causing some current not pertaining to the experiment. To counteract this we pumped in some nitrogen but still didn't manage to entirely curb the occurrence.

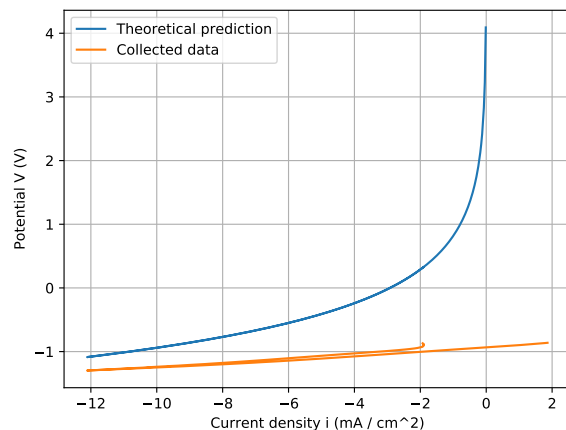


FIG. 6: Theoretical prediction using Tafel equation3 versus collected data. Collected from **HER**.

WE: Pt, **CE:** Pt.

V. CONCLUSION

Using an experimental setup to generate data for different catalysts and consequently analyzed that data. The best catalyst pair to maximise hydrogen production is found.

The overpotential is calculated 3 which unlocks the ability to compare the overpotential as a function of the current density then compare that theoretical prediction to the data that was gathered. 6. In an attempt to verify the predictions, tubes are set-up in order to collect the gas produced from the reactions but, ultimately fail and the results are found to be inconclusive.

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- [1] K. G. dos Santos, C. T. Eckert, E. De Rossi, R. A. Baricatti, E. P. Frigo, C. A. Lindino, and H. J. Alves, Hydrogen production in the electrolysis of water in brazil, a review, *Renewable and Sustainable Energy Reviews* **68**, 563 (2017).
- [2] K. Zeng and D. Zhang, Recent progress in alkaline water electrolysis for hydrogen production and applications, *Progress in Energy and Combustion Science* **36**, 307 (2010).
- [3] S. Shiva Kumar and V. Himabindu, Hydrogen production by pem water electrolysis – a review, *Materials Science for Energy Technologies* **2**, 442 (2019).
- [4] A. Bard, *Electrochemical methods : fundamentals and applications* (John Wiley & Sons, Inc, Hoboken, NJ, 2001).
- [5] The data for the current exchange density is inverted for the Tafel equation.
- [6] At least in principle, as we shall see later on in the discussion this isn't the whole story.