
Elektrocatalysis

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1 Introduction

In this experiment we are testing and comparing the activity of the two electrode materials; Glassy Carbon, and NiO_x . After that we use a two-electrode setup with hydrogen evolution reaction and oxygen evolution reaction to compare the cell potential of the two materials. This investigation is mostly based on the work of Prof. Dr. Aliaksandr Bandarenka[1].

2 Theory

In electrocatalysis we always have two sides of the reaction: the reduction (RED) on the cathode and the oxidation (OX) on the anode.

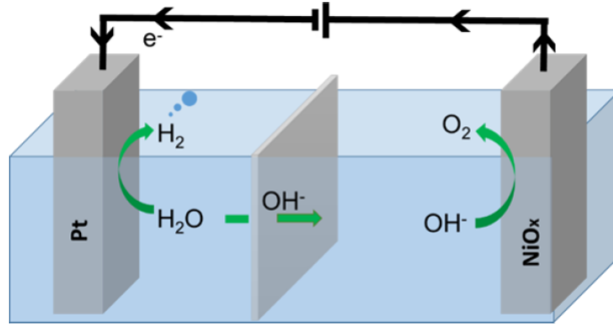


Figure 1: Schematic of alkaline water electrolysis. Taken from [1]

In Figure 1 we can see a general schematic of the process where we have the hydrogen evolution reaction (HER) on the left side and the oxygen evolution reaction (OER) on the right side. In reality the two reactions are splitted in a few more steps.

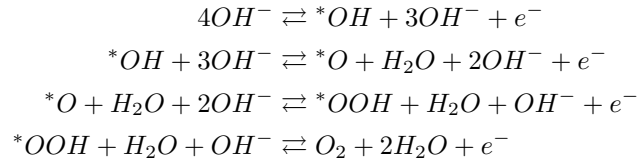


Figure 2: OER Reaction with intermediates

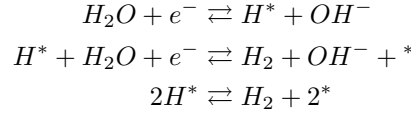


Figure 3: HER Reaction with intermediates

That is why we have to make sure that the binding energy between the intermediate product and the material on the electrode is neither too high nor too low so that every step of OX and RED is working most efficient.

Also in the following part we want to introduce shortly the concept of the overpotential. When the electrocatalytic cell is in a thermodynamical steady state we do not measure a current. In this state we have a minimal potential between the HER and OER of 1.23 V. If we lower for example the potential of the HER, which we had set to 0 V before, we measure a current because we now have a production of hydrogen. The aim is now to increase the current but also to keep the potential that differs from the start potential 1.23 V, the so called overpotential as low as possible. So the characteristics of a good OER catalysts are that it has minimal overpotential, that it interacts only with the desired substrate and that it is stable enough to withstand the potential. It is also important to mention that it takes a lot more overpotential for the OER to move away from the zero-current than for the HER. The whole concept is shown in Figure 4.

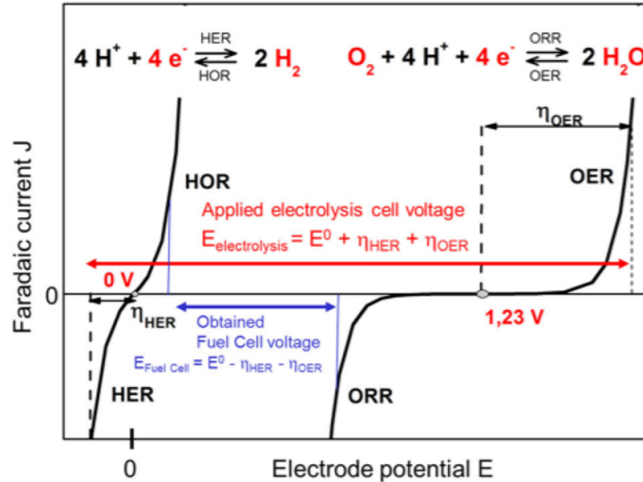


Figure 4: Schematic of the concept of the overpotential in an electrolysis cell. Taken from [2]

3 Experimental Setup

In general we have a three and a two-electrode-setup. To do the electrocatalysis in the second part of the experiment we use a simple two electrode setup like we see on the right side in Figure 5. To simply analyse the activity of one electrode and to measure the exact electrode potential we have to use the setup on the left.

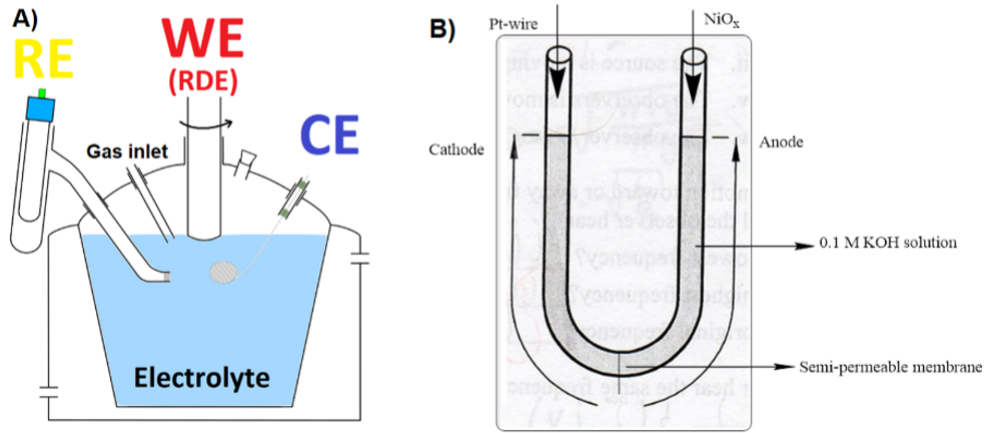


Figure 5: Schematic of a (A) three- and (B) two-electrode setup configuration. Taken from [1]

In the middle we see the working electrode (WE), on the right the counter electrode (CE) and on the left the reference electrode (RE) where another REDOX-reaction is happening which is really stable so we can consider the potential as constant. We use the RE to have an absolute potential with which we can compare our measurements of only one electrode material.

In this experiment we use Glassy Carbon and then NiO_x. Carbon is often used as a support material for electrocatalysis because its mechanical and chemical stability and it has a great conductivity. Furthermore, due to its abundance, carbon is a low-cost material. Also the electrochemical conductivity and high surface area of the carbon supports the catalytic activity. Moreover, carbon can be doped to further increase its catalytic properties, such as selectivity. These factors make carbon a good choice as a support material for electrocatalysts.

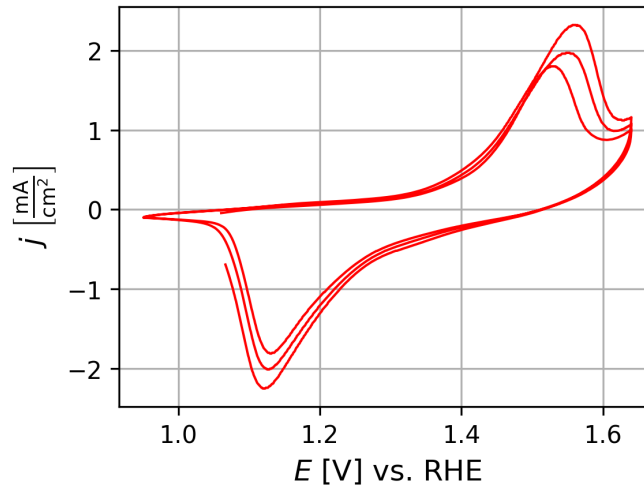


Figure 6: CV diagramm obtained during our electrochemical deposition of the NiO_x films. Growing peaks indicate the growth of the NiO_x films.

Finding the right catalyst has its challenges. One of these challenges arise from the very nature of the reactions involved in this experiment. The catalysis procedure is complicated by the OER. Because of the linear dependency of the 3 intermediates of the OER on each other, see Figure 2. This means it is difficult to find a suitable catalyst that has just the right binding energy for all intermediates in the OER, as stated by the Sabatier principle.

4 Procedure & Result

4.1 GC and NiO_x OER activities

Since we used a Ag/AgCl electrode in our three electrode setup, we have to convert our applied potentials from the Ag/AgCl scale to the RHE scale by using the Nernst equation,

$$E_{RHE} = E_{Ag/AgCl} + 0.197 \text{ V} + 0.059 \text{ V} \cdot pH,$$

where $pH = 13$ (pH is the solution of 0.1 M KOH).

We can then compare both activities in figure (7), where we see that NiO_x has a much lower overpotential for a given current than Glassy Carbon.

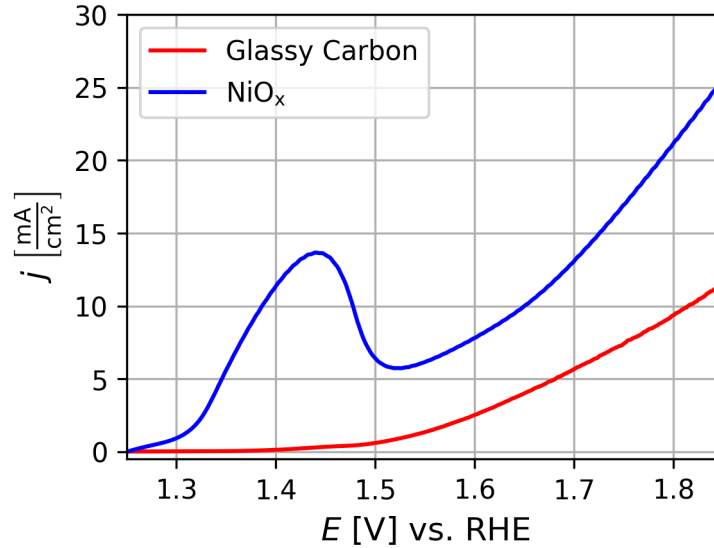


Figure 7: Comparison of the GC and NiO_x activities; the peak at ~ 1.45 eV is a Nickel peak

Compare for example the overpotential, η_{OER} , at $j = 10 \frac{\text{mA}}{\text{cm}^2}$:

$$\eta_{OER}^{GC} = 1.81498 \text{ V} \quad (1)$$

$$\eta_{OER}^{NiO_x} = 1.38567 \text{ V}. \quad (2)$$

The potential over the whole cell, should then be lower for NiO_x , according to the following equation given by the tutors

$$E_{electrolysis} = E^0 + \eta_{HER} + \eta_{OER}.$$

4.2 Electrolysis

To measure $E_{electrolysis}$ for both GC and NiO_x , we again have to convert our potential from $Ag/AgCl$ scale to RHE scale, just like in the activity measurement. This will give us the plot in Figure 8. We see that the potential is saturated after a short time for both GC and NiO_x , and that $E_{electrolysis}$ is indeed smaller for NiO_x than for GC :

$$E_{electrolysis}^{GC} \approx 4.99 \text{ V} \quad (3)$$

$$E_{electrolysis}^{NiO_x} \approx 4.09 \text{ V}. \quad (4)$$

This means NiO_x is more suitable for a fuel cell since less energy is getting lost in the current flow.

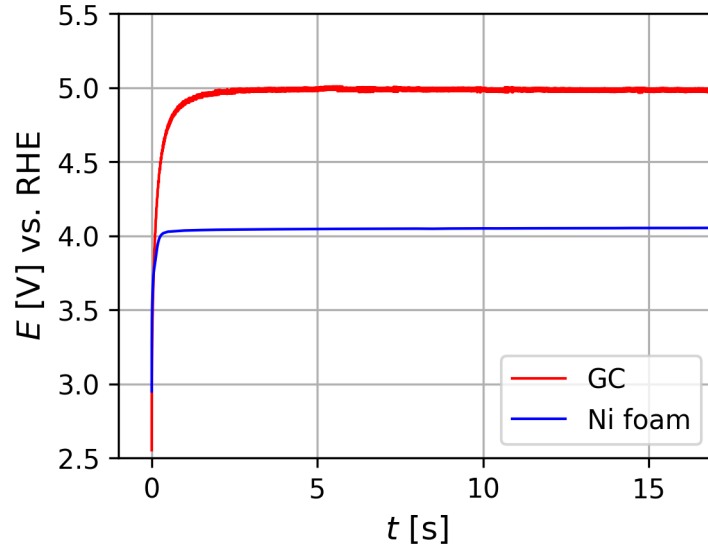


Figure 8: Measurement of the Electrolysis potential in U-shaped two electrode configuration; Current is constant at $\sim 5.0 \frac{\text{mA}}{\text{cm}^2}$

References

- [1] Prof. Dr. Aliaksandr Bandarenka, Physics department TUM, "Electrocatalysis: Alkaline Water Electrolysis", *URL:*
<https://www.ph.tum.de/academics/org/labs/fopra/docs/userguide-30.en.pdf>
- [2] Oxygen Electrocatalysis on Dealloyed Pt Nanocatalysts - Scientific Figure on ResearchGate. *URL:*
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