Electrocatalysis: Alkaline Water Electrolysis

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Physics of Energy Conversion and Storage

Things to do before the lab course

1. Please read the manual and safety instruction carefully.
2. For this lab course, EC-lab and Origin programs are required to analyze the obtained data.
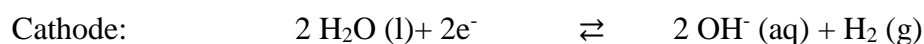
Things to do during the lab course

1. Take notes during the lab course, they will be important for your report.
2. Ask questions if you don't understand any part of the discussed topics and experiments

1. Introduction

1.1 Electrocatalysis

Electrocatalysis as a part of heterogeneous catalysis has a paramount role in sustainable energy conversion systems such as fuel cells, metal-air batteries, and electrolysers. The idea to use electrical current to control various chemical reactions has been very attractive since the time when humankind developed the very first electrical power sources. Initial experiments performed more than 200 years ago, for instance on water splitting to produce gaseous hydrogen and oxygen under ambient conditions, clearly demonstrated the power and promise of this approach. The latter has nowadays evolved into various large-scale industrial processes. Furthermore, it will play a key role in the future to secure sustainable energy production worldwide. In a simple case, in order to initiate a redox reaction using the above-mentioned approach, we need at least two electronically conducting electrodes and an ionically conducting electrolyte. By applying a certain potential, we can generate new compounds at the surface of the electrodes. However, in spite of the apparent simplicity, the efficiency of the overall process is often determined by the structure and composition of the electrode surface as well as by the nature of the electrolyte components.

For example, in order to minimize the energy losses during the water splitting and obtain hydrogen fuel for the future sustainable energy provision schemes, we need to develop two efficient electrocatalysts: for hydrogen and oxygen evolution, as illustrated in the **Figure 1**. The electrochemical water-splitting (Electrolysis) is a combination of HER (Hydrogen evolution reaction) and OER (Oxygen evolution reaction), which is highly energy efficient and pollution negligible. In alkaline media the two half-reactions are:

Cathode: $2 H_2O (l) + 2e^- \rightleftarrows 2 OH^- (aq) + H_2 (g)$

Anode: $2 OH^- (aq) \rightleftarrows H_2O (l) + \frac{1}{2} O_2 (g) + 2 e^-$

Overall reaction: $H_2O (l) \rightleftarrows H_2 (g) + \frac{1}{2} O_2 (g)$

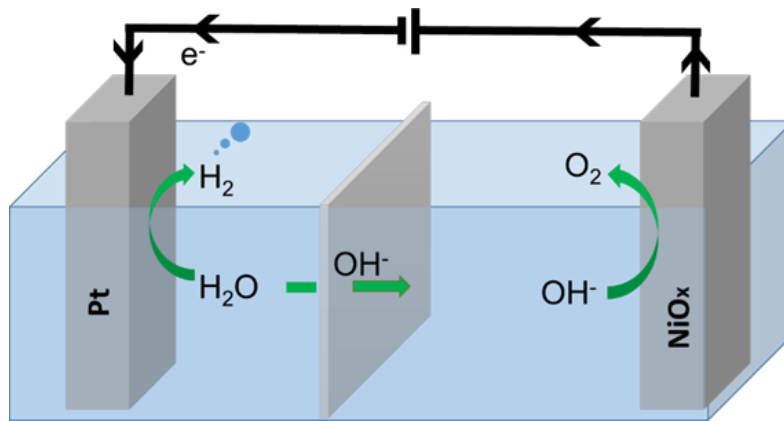In the following, these two chemical reactions in alkaline media are further discussed.

Figure 1. *Schematic of alkaline water electrolysis. For efficient electrolysis it is necessary to develop catalysts for the HER (e.g. Pt) and the OER (e.g. NiO$_x$).*

1.2 Hydrogen Evolution Reaction (HER)

Hydrogen gas is produced from the cathodic half-reaction of water splitting. This process is of great importance to a number of energy conversion devices, such as electrolysers. In alkaline media, the HER proceeds through the following reaction: **Fehler! Textmarke nicht definiert.**

$$2H_2O + 2e^- \rightarrow H_{2(g)} + 2OH_{(aq)}^-$$
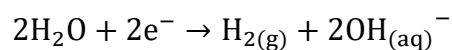
The thermodynamic equilibrium potential for the HER is given as $E^o_{H^+/H_2} = 0.00$ V vs so-called reversible hydrogen electrode (RHE). As mentioned above, electrode materials, electrode surface structure and electrolyte composition can influence the activity towards the HER.

1.3 Oxygen Evolution Reaction (OER)

The current bottleneck of the water-splitting is the large over-potential loss of OER compared to HER, therefore efficient and stable OER catalysts are required. In alkaline media, oxygen evolves through the following reaction:

$$2 \text{ OH}^- \text{ (aq)} \quad \rightleftharpoons \quad H_2O \text{ (l)} + \tfrac{1}{2} O_2 \text{ (g)} + 2 \text{ e}^-$$
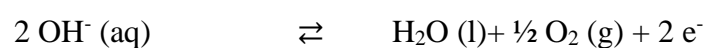
The thermodynamic equilibrium potential of this reaction is given as $E_{OER}^o = 1.23$ V vs RHE. However, due to the complicated reaction mechanism, a higher potential is needed in reality to drive the reaction. The difference between the potential that is needed to achieve a certain current density and the E_{OER}^o is called the over-potential. Hence, in order to maximize the efficiency of alkaline electrolysers, the aim is to minimize the over-potential. In order to do this, it is necessary to find highly active electrocatalytic materials for this reaction.

1.4 Sabatier Principle

For an optimal catalyst, the binding of the reaction intermediates is one of the defining characteristics. The Sabatier principle states that the best catalyst binds the intermediate "just right", neither too weakly, nor too strongly. If the interaction is too weak, the catalyst fails to bind and does not activate the reactant. However, if it is to strong, the surface can get blocked by intermediates or products, which fail to dissociate. Plotting the reaction rate or the over-potential against a so-called descriptor of the binding, *e.g.* the heat of adsorption of the intermediate to the catalyst, results in so-called "volcano plot". In general, the activity passes a maximum and the graph has triangle shape or resembles an inverted parabola, with the best performing catalysts close to its peak. Typical volcano plots for the HER and OER are shown in **Figure 2A** and **B**, respectively.
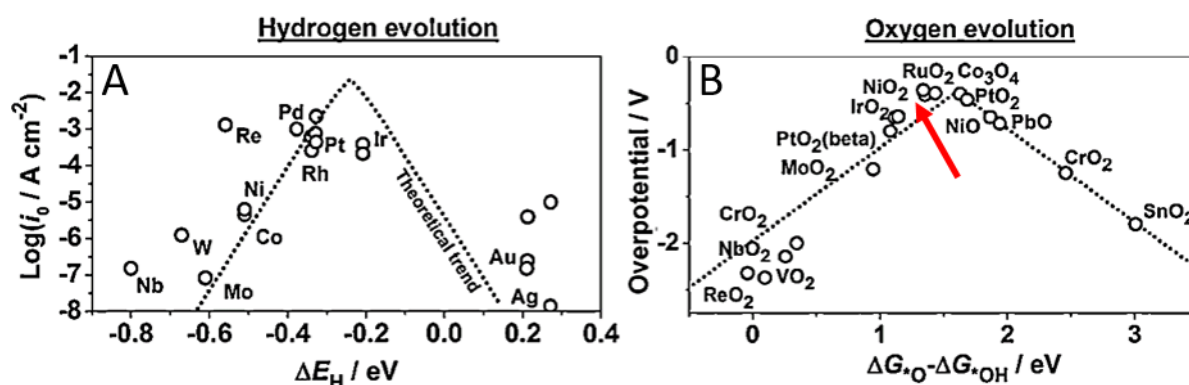

Figure 2*. Volcano plots for (A) HER and (B) OER. [1,2] Dotted lines represent the corresponding theoretical trends. For the OER, NiO₂ is among the best performing catalysts.*

In the case of HER (**Figure 2 (A)**) the choice of the descriptor, namely the binding energy of hydrogen, is quite simple, since there is only one intermediate. Platinum (111), for example is

quite close to the peak of the volcano, and binds hydrogen a few mV too strong. Due to its high electrocatalytic activity Pt is used in many commercial devices, enhancing the HER, despite of its high price.

As discussed before, the optimization for the OER is significantly more complex, because in principle, the binding energies of all three intermediates have to be considered, resulting in a multidimensional volcano plot. By choosing the difference of free enthalpy between *O and *OH as descriptor, **Figure 2 (B)** shows the volcano plot for the OER in reduced form. For the OER transition metal oxides like Fe, Ni, Co, Ru, Ir and also complexes are very promising candidates as catalysts. Due to the relative abundance of Ni, NiFe and Co oxides compared to complexes containing rare earth elements this course we will use NiO_x as a catalyst material.

2. Experimental set-up

2.1 Electrochemical cell

During this lab course we will use two- and three- electrode cell configurations for carrying out the experiments. A typical 3-electrode set-up consists of the working electrode (WE, the electrode under investigation), the reference electrode (RE) and the counter electrode (CE, to close the current circuit), as shown in **Figure 3A**. The electrolyte can be bubbled with desired gas (*e.g.* Argon to remove oxygen). The typical U-shaped 2-electrode set-up which will be used in this lab course is shown in the **Figure 3B**.
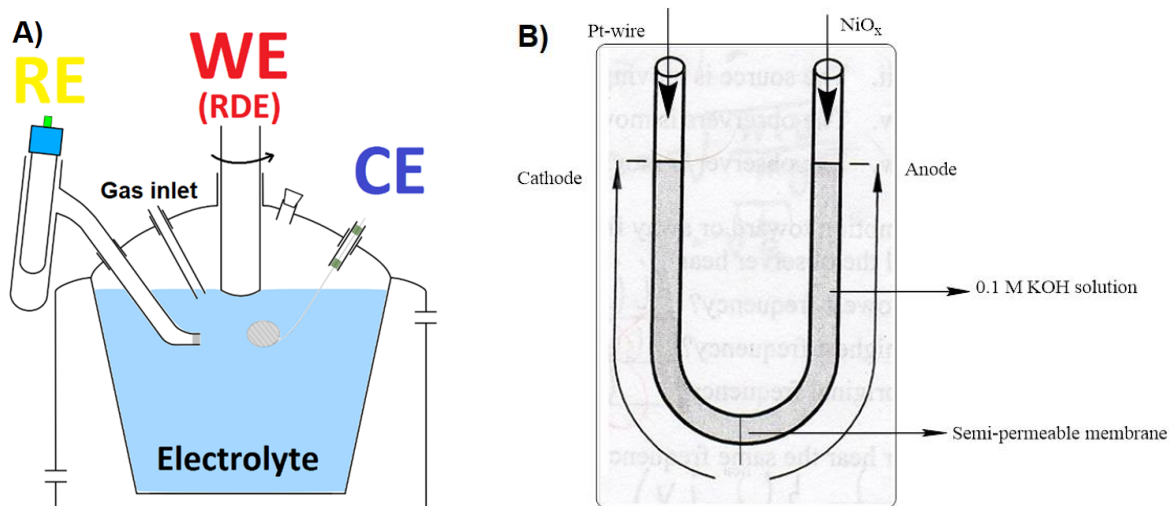
Figure 3. Schematics of (A) three- and (B) two-electrode setup configuration which will be used in this lab course.

2.2 Rotating disk electrode configuration

In order to investigate the kinetics of an electrocatalyst, prior to it being applied in an electrolyser, one can test it in a three-electrode hydrodynamic system known as the rotating disc electrode (RDE). **Figure 4 (A)** shows a picture of the RDE configuration.

The RDE consists of a disc (glassy carbon) engraved into a PTFE support, which acts as the working electrode (**Figure 4 (B)**). The support is attached to a rotator, which rotates about its vertical axis. The rotation is the key principle of the RDE. Around the vertical axis, the rotation creates a laminar flow along the working electrode which transports the reactant from the bulk solution to the electrode surface at a higher rate than in a stationary system.

In the RDE configuration, a polycrystalline glassy carbon electrode with diameter of 5 mm will be used as substrate for the Nickel oxide film. During the experiments the working electrodes will be rotated at 400 rpm. The RE is connected via an ion bridge, filled with 0.1 M KOH, to the electrochemical cell.
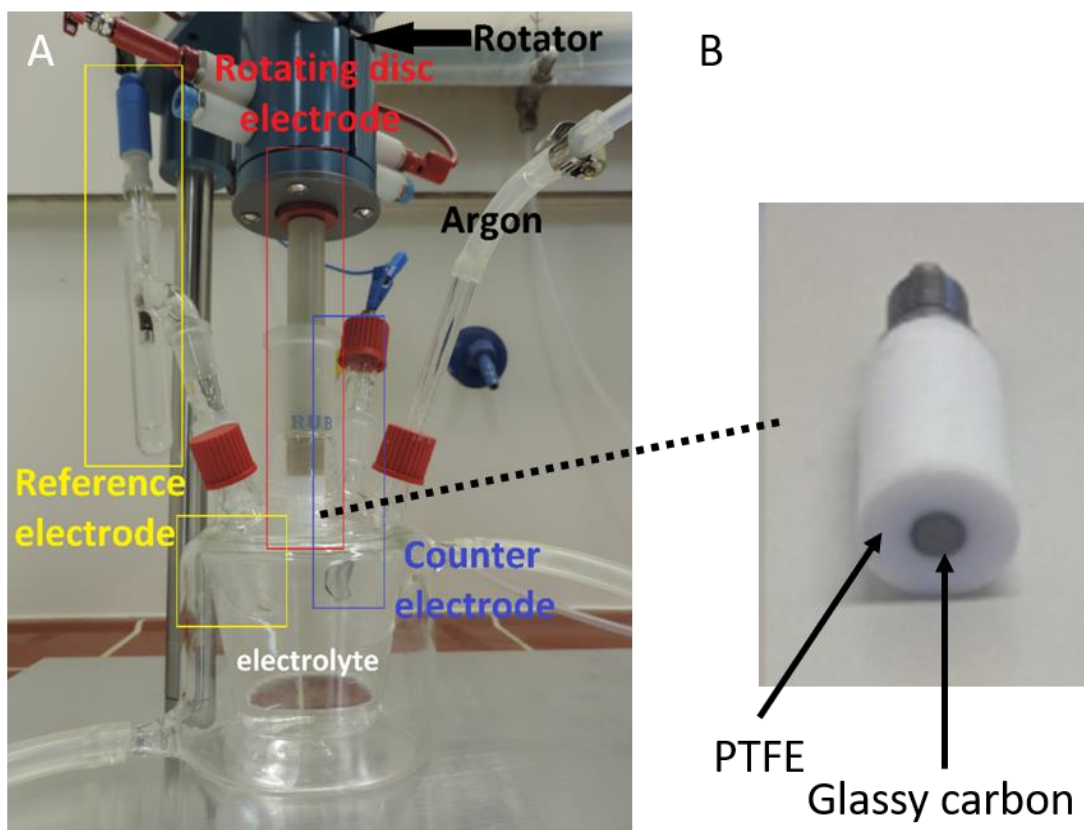
Figure 4. *(A) The RDE setup shown as a photo. The setup consists of the reference electrode, counter electrode and a working electrode which has a disc shape and can be rotated. The reference electrode is connected via a luggin capillary to the cell. (B) The glassy carbon electrode in the PTFE support.*

3. Experiments

In this lab course, you will first measure the OER activity of a glassy carbon electrode. Then, we will deposit NiO_x on the glassy carbon and again the OER activity will be measured. At the end, you will compare the activity of the two materials in two-electrode configuration, similar to real water electrolysers.

3.1 Preparation of the solution

For this lab course, you need to prepare a 0.1 M KOH solution. Please calculate the amount of KOH (solid) that needs to be diluted in water to obtain 200 ml of 0.1 M KOH before the experiment session and describe how to prepare it in your report.

Deposition solutions will be provided by your instructor during the lab course.

3.2 Testing the OER activity of the glassy carbon electrode

In the first step, you will measure the OER activity of the pure glassy carbon. This will be done in an RDE-setup. For this, the three-electrodes need to be connected to the potentiostat, which is controlled using the EC-Lab software (see **Figure 5** left image). In order to test the OER activity, the current over a potential range of 1.25 V – 1.85 V vs. RHE has to be recorded. The scan rate of the potentials should be $10\,mVs^{-1}$. Additionally, the instrument to control the rotator is will be connected. The rotation rate of the RDE should be set to 400 rpm (**Figure 5** right). We will need these results to compare the activity of the glassy carbon with that of the NiO_x.

3.3 NiO_x deposition

NiO_x thin films are electrochemically formed on the glassy carbon, while rotating at 400 RPM. The aim is to create a fully covered film, which exhibits the desired functional properties, especially the electro catalytic activity towards the OER without significant influence of the substrate material.

A typical cyclic voltammogram (CV) during the NiO_x deposition *[3,4]* is shown in **Figure 6**. The CV displays a rise and the growth of characteristic oxidation and reduction peaks, as commonly reported for NiO_x depositions *[5,6]*. The anodic peak corresponds to the oxidation
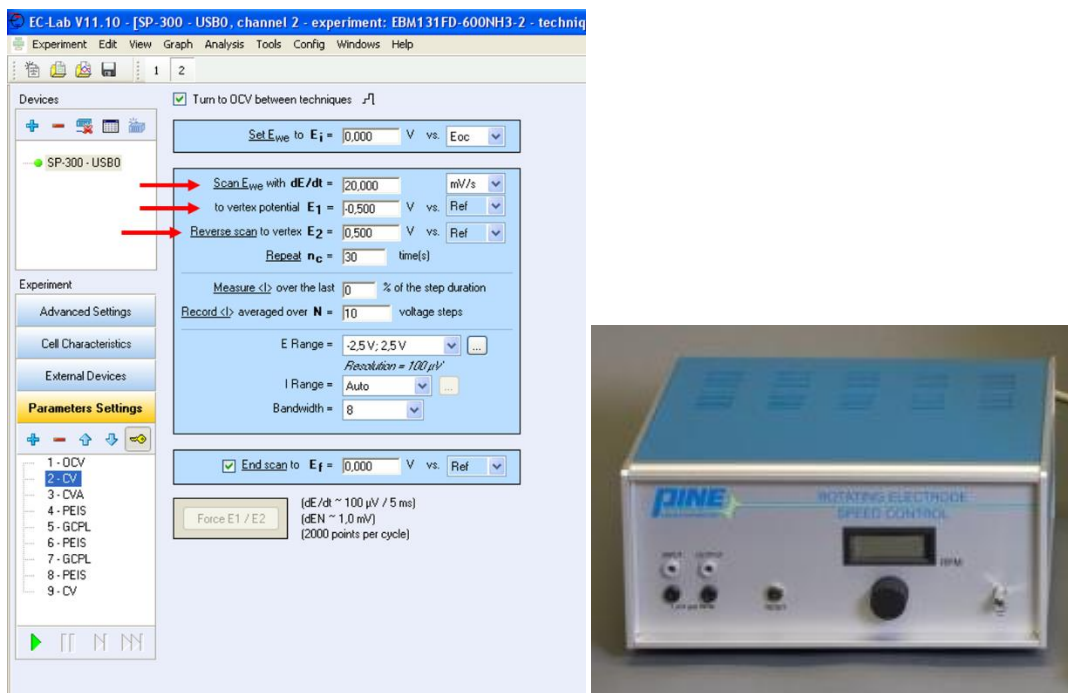
Figure 5. *On the left, the screenshot of the EC-Lab software, which is used to control the experiments. On the right, the photo of the device controlling the rotation speed.*

of $Ni(OH)_2$ to $NiO(OH)$ and the cathodic peak to the reverse reduction reaction. The OER which occurs close to the anodic limit of the CV, results in an additional anodic current. The growth of the redox peaks indicates a film growth, while the increase of anodic current near the anodic limit (1.9 V vs RHE) implies a rise in the catalytic activity towards the OER, at each cycle.

The solutions and electrode position conditions which are used for the creation of the NiO_x film are listed in Table 1.

Table 1. Deposition solution and conditions for the NiO_x catalyst.

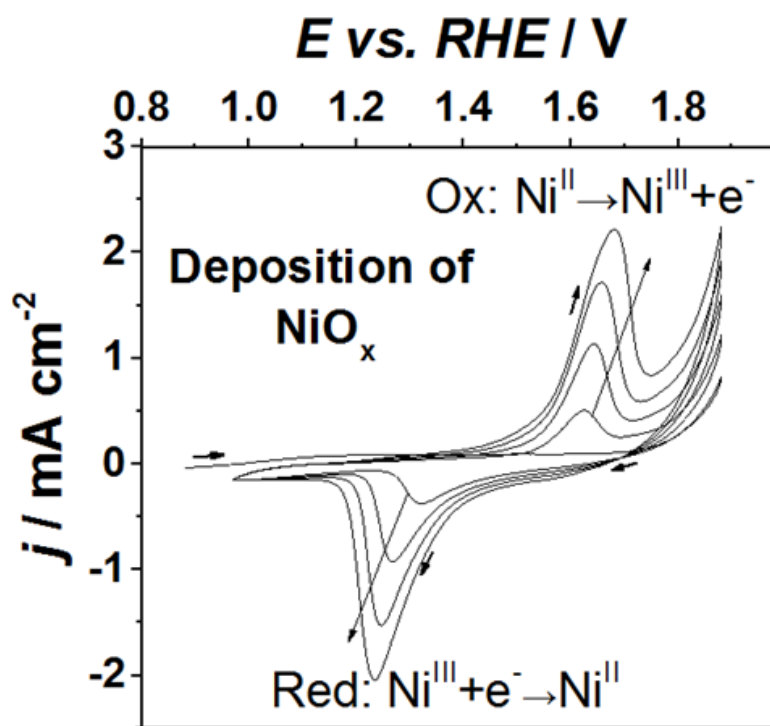| catalyst	solution composition	pH	electrodeposition conditions
NiO_x	0.13 M $NiSO_4 \cdot 6H_2O$ 0.13 M $NaOAc \cdot 6H_2O$ 0.10 M Na_2SO_4	7.0	Potential cycle between 0.95 and 1.86 V (vs RHE) at 50 mV s^{-1}; anodic deposition

Figure 6. Typical CVs obtained during the electrochemical deposition of the Ni oxide films. The growing peaks indicate the growth of the NiO_x film, as well as improving OER activity.

3.4 NiO_x Activity measurements

In order to investigate the OER activity of the deposited NiO_x film the potential range will again be set to 1.25 V – 1.85 V vs. RHE. The rotation rate should be set to 400 rpm and the scan rate of the potentials should be 10 mV s^{-1}.

3.5 Alkaline water electrolysis

The activity differences between glassy carbon and NiO_x as the OER catalyst, as well as between glassy carbon and platinum as the HER catalyst will be tested using the U-shaped two-electrode cell (shown in the **Figure 3B**).

4. Report

The report for this experiment should contain:

1) Short introduction of theoretical background.

2) A brief description of the performed experiments.

3) Explanation of the obtained measurements and comparison of the activities of glassy carbon and NiO_x.

4) A brief conclusion for your measurements.

Additional questions for your report:

1. What are the differences between three-electrode and 2-electrode cell configuration used in this lab course?

2. Convert the potentials applied during deposition of NiO_x from RHE scale to Ag/AgCl electrode scale using the Nernst equation (will be explained during the lab course).

3. Besides electrochemical activity, what are important characteristics of a good OER catalyst?

4. Why is carbon often used as a support material for electrocatalysts?

5. Why does the OER reaction mechanism complicate the catalysis? (hint: scaling relations)

5. References

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5. M. S. Wu, C. H. Yang, M. J. Wang, *Electrochimica Acta*, 54 (2008), 155-161.

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6. Safety Instruction

Upon direct contact with skin the KOH solution can cause severe skin damage. Therefore, please observe the following precautions:

a) Wear lab-coats at all times.

b) Wear protective eyewear at all times.

c) Wear protective gloves at all times

d) Wear closed shoes and long pants

e) Shorts and open shoes are not allowed.

f) Avoid touching your hair, face and cell phone with gloves during the experiments

Read these instructions carefully and ask the tutor if details are not clear.

I declare that I have taken note from the instructions above.

Date	Matriculation number	Signature