Hydrogen Evolution Research with non-Noble Metal Catalysts and Methanol Electrolysis

Sami Tuomi
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Aalto University
School of Chemical Engineering
Department of Chemistry and Materials Science
Electrochemical Energy Conversion and Storage
Supervising professor
Tanja Kallio, Aalto University

Preliminary examiners
Peter Vesborg, Technical University of Denmark
Elisabet Ahlberg, University of Gothenburg

Opponent
Carina Lagergren, KTH Royal Institute of Technology
Abstract
Transformation towards increased energy productions by renewable sources requires advanced methods for energy storage due to intermittent nature of solar and wind power. Hydrogen is considered as a potential energy carrier and storage in a chemical form. Hydrogen can be produced by splitting water using excess electrical energy and then later used in a hydrogen powered vehicle, consumed in industry or turned back to electricity by a fuel cell.

Hydrogen evolution reaction (HER) requires efficient catalyst to enable the reaction. Platinum is widely exploited catalyst for HER but due to rarity and price, non-noble metal catalysts are widely researched. In this thesis, two catalysts based on abundantly available elements and simple preparations are presented and their catalytic behavior researched in depth.

Molybdenum carbide nanoparticles supported on carbon catalysts was prepared by a modified carbothermal reduction method. The catalytic activity for the hydrogen evolution reaction was analyzed both in an electrochemical cell at various pH and in a laboratory-scale electrolyzer. These nanoparticles were found to be very active in catalyzing hydrogen evolution reaction in acidic media and appeared to promote kinetics leaning toward the Volmer-Heyrovsky mechanism at low pH. The catalyst was shown to be suitable for hydrogen production in a laboratory-scale electrolysis cell, retaining its performance during a four-week durability experiment.

HER mechanism on nitrogen functionalized few-walled carbon nanotubes (N-FWCNT) was analyzed in acidic media with a pH series and by Tafel slope analysis. The results suggest that the HER proceeds via the Volmer-Heyrovský mechanism. Overall hydrogen surface coverage on N-FWCNT is also suggested to affect the HER rate. Furthermore, durability of N-FWCNTs was demonstrated by operating a full electrolyzer cell for five weeks.

The basic concept of methanol–water solution electrolysis with an alkaline membrane was developed and the functionality validated with experimental studies. The measurements were performed with a membrane electrode assembly consisting of an anion exchange membrane, Pt cathode and either PtRu or Pt anode. Hydrogen production efficiency was measured and the effects of temperature and methanol concentration on the electrolysis performance were investigated. PtRu was found to be a better catalyst at low potentials. Proof-of-concept for alkaline methanol electrolysis was successful.

Keywords hydrogen evolution, electrolysis, catalysis
Tekijä
Sami Tuomi

Väitöskirjan nimi
Vedynekehitys epäjalometallikatalyteillä sekä metanolielektrolysillä

Julkaisija
Kemian teknisen korkeakoulun

Yksikkö
Kemian ja materiaalitieteeneen laitos

Tiivistelmä


Avainsanat vedynekehitys, elektrolyysi, katalyytimet
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Sami Tuomi - Helsinki, November 2018
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List of Publications

This thesis consists of a summary of the following publications which are referred to in the text by their numerals.


Author’s Contribution

**Publication 1:** Hydrogen Production by Methanol-Water Solution Electrolysis with an Alkaline Membrane Cell

The author prepared the research plan and planned the experimental procedures. The author assembled the alkaline membrane methanol electrolyzer and carried out the electrolyzer tests. The results were analyzed jointly with Dr. Santasalo-Aarnio and Dr. Kanninen. The author wrote the manuscript of the article in supervision of Prof. Kallio.

**Publication 2:** Molybdenum carbide nanoparticles as a catalyst for the hydrogen evolution reaction and the effect of pH

The author prepared the electrochemical researches and planned the experimental procedures. The author carried out electrochemical measurements, electrolyzer tests and analysis of the results. Dr. Guil-Lopez prepared and characterized the catalysts. The author wrote the manuscript of the article in supervision of Prof. Kallio.

**Publication 3:** Experimental and Computational Investigation of Hydrogen Evolution Reaction Mechanism on Nitrogen Functionalized Carbon Nanotubes

The author prepared the electrochemical researches and planned the experimental procedures. The author carried out electrochemical measurements, electrolyzer tests and analysis of the results. Mr. Kronberg assisted in the experimental research. Dr. Borghei prepared the catalysts in supervision of Prof. Nasibulin and carried out characterization with Dr. Sainio, in supervision of Prof. Kauppinen. Mr. Pakkanen executed computational section of the research in supervision of Prof. Laasonen. The author wrote the manuscript of the article, excluding computational experiments and analysis, in supervision of Prof. Kallio.
# List of Abbreviations and Symbols

<table>
<thead>
<tr>
<th>Abbreviation</th>
<th>Description</th>
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<tbody>
<tr>
<td>CNT</td>
<td>carbon nanotubes</td>
</tr>
<tr>
<td>FWCNT</td>
<td>few-walled carbon nanotubes</td>
</tr>
<tr>
<td>GC</td>
<td>glassy carbon</td>
</tr>
<tr>
<td>HER</td>
<td>hydrogen evolution reaction</td>
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<tr>
<td>ICP-AES</td>
<td>Inductively coupled plasma atomic emission spectroscopy</td>
</tr>
<tr>
<td>MEA</td>
<td>membrane electrode assembly</td>
</tr>
<tr>
<td>N-FWCNT</td>
<td>nitrogen functionalized few-walled carbon nanotubes</td>
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<tr>
<td>PEM</td>
<td>proton exchange membrane</td>
</tr>
<tr>
<td>RDE</td>
<td>rotating disc electrode</td>
</tr>
<tr>
<td>RDS</td>
<td>rate-determining step</td>
</tr>
<tr>
<td>RHE</td>
<td>reversible hydrogen electrode</td>
</tr>
<tr>
<td>TEM</td>
<td>transmission electron microscopy</td>
</tr>
<tr>
<td>TGA</td>
<td>thermogravimetric analysis</td>
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<tr>
<td>XPS</td>
<td>X-ray photoelectron spectroscopy</td>
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<tr>
<td>XRD</td>
<td>X-ray diffraction</td>
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<table>
<thead>
<tr>
<th>Symbol</th>
<th>Description</th>
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<tbody>
<tr>
<td>$E$</td>
<td>electrode potential</td>
</tr>
<tr>
<td>$E^0$</td>
<td>standard potential</td>
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<tr>
<td>$f$</td>
<td>$nF/RT$</td>
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<tr>
<td>$F$</td>
<td>Faraday’s constant</td>
</tr>
<tr>
<td>$j$</td>
<td>current density</td>
</tr>
<tr>
<td>$j_0$</td>
<td>exchange current density</td>
</tr>
<tr>
<td>$k$</td>
<td>reaction rate constant</td>
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</tbody>
</table>
\( n \) number of electrons transferred in the reaction
\( \eta \) overpotential
\( \eta_{10} \) overpotential to reach 10 mA cm\(^{-2}\) current
\( R \) universal gas constant
\( T \) temperature
\( \Theta \) hydrogen surface coverage
1. Introduction

Energy production is transferring towards renewable sources, which is seen by significant increase in installed solar and wind based energy supply [1]. However, due to intermittent nature of these renewable energy sources, large-scale energy storage is becoming the limiting factor towards sustainable energy production. Storing energy in chemical bonds is a promising approach as chemical energy can be transformed to back to electric, kinetic and heat energy when needed or used in chemical industry sector. Water electrolysis is considered as one of the key technologies for intermittent renewable energy conversion and storage. Hydrogen evolution reaction (HER) is the cathode reaction in this process and thus, effective electrocatalyst are required to overcome the reaction barriers enabling the reaction to proceed with meaningful rate.

The conventional method to produce hydrogen with electrical current is water electrolysis, where water molecule is split to form hydrogen and oxygen. However, the energy consumption for the reaction is high, which has led to research of electrolyzing methanol due to many advantages compared to water electrolysis [2-6]. Methanol electrolysis has standard potential 0.02 V, which is significantly lower than 1.23 V required for conventional water electrolysis. In practical applications the used voltage for methanol electrolysis is above 0.4 V [2,4,6] and for water electrolysis above 1.4 V [7-9]. Considering the lifetime expenditure of a proton exchange membrane (PEM) electrolyzer unit, the cost of electricity account for approximately 65 % of the total costs [10]. Methanol electrolysis have been estimated to save up to 70 % of required energy consumption, resulting to 50 % cost savings when the price of methanol is also taken into account [11].

Price of the electrolyzer components are important for small-scale electrolyzer units, e.g. portable application or intermittent use. PEM electrolyzers use mostly Nafion
membranes that are expensive due to complicated manufacturing process, which have led to research of anion exchange membranes to be used in electrical cells. Another advantage with alkaline membrane is enhanced kinetics of methanol oxidation in alkaline environment [12,13] enabling use of smaller amount of prestigious catalysts or even utilizing non-precious metal catalysts [14-16]. In addition, methanol crossover from anode to cathode is well-known problem with Nafion membranes resulting in increased fuel consumption and generating impurities to the hydrogen stream [17-19]. Hydrocarbon based anion exchange membranes have shown lower permeation rates for methanol and for example, Fumapem FAA-2 membrane has only 16 % methanol cross-over rate compared to Nafion 115 [20].

The concept of methanol-water solution electrolysis using an alkaline membrane is introduced and verified in Pub. I. The performance of the electrolysis method was analyzed with different temperatures and methanol concentrations as well as the efficiency of the cell was proved.

On the other hand, electrolyzers utilizing PEM are promising alternatives for current commercial electrolyzers utilizing alkaline liquid electrolyte because of superior HER kinetics in acidic environment. Thus the former has raised interest researching new materials and methods to increase the performance and to decrease the cost of the electrolysis cell. [21-31]

Platinum is widely used catalyst for the HER because of the high activity but its scarcity renders the possibilities to utilize it in mass produced devices. In the search for more cost-efficient options, different sizes and shapes of molybdenum sulfide particles and films have raised interest during past decades [32-38]. Molybdenum sulfide are active from its edge sites where sulfur atoms are able to mediate HER in similar manner as platinum and hydrogenase enzymes that are found in nature systems [39,40]. However, the activity of molybdenum sulfide is limited by the number of edge sites on the catalyst surface [39]. For the reason, molybdenum carbides (Mo2C) have got growing attention in the HER catalyst research as a non-noble metal alternative. The advantage of molybdenum carbide is that the catalytic activity is dependent on the surface orientation rather than the number of edge sites [41]. This enable a lot more flexibility and opportunities for catalyst synthesis to develop more active catalysts. Different Mo2C structures have
been synthesized showing that by varying the preparation conditions it is possible to produce structures from nanoparticle to nanorods [42-56].

The underlying HER mechanism of the HER on molybdenum carbides has not been investigated in detail despite of the research on catalytic activity. In Pub. II Mo$_2$C/C nanoparticles catalytic activity for the HER was analyzed in an electrochemical cell at various pHs to understand better the reaction mechanism. The reaction mechanism analysis was complemented by Tafel slope analysis.

In search for Pt-replacing catalysts for HER, various carbon nanomaterials have shown promising results [53,57-60]. Pristine carbon nanotubes form an excellent backbone for electrocatalyst development due to appealing electrical properties and structure. While the catalyst itself is not by itself efficient electrocatalyst, modifications that increase catalytically active sites yields interesting materials.

Nitrogen doped carbon nanotubes have been found to be active in oxygen reduction and evolution reactions in alkaline media [61-64]. In addition, nitrogen functionalized carbon nanotubes have recently shown activity towards HER in alkaline and acidic conditions [65,66]. As the catalysts consists of elements that are abundantly available, price and supply security of the materials will not be an issue. Due to the above-mentioned reasons, nitrogen doped carbon nanotubes are considered as potential replacer for platinum. Preparation of nitrogen functionalized few-walled carbon nanotubes (N-FWCNT) catalysts and investigation of the HER activity and mechanism by electrochemical methods was carried out and verified by computational analysis in Pub. III.

In the field of catalyst research, the focus should not be entirely on scanning through different catalysts with interesting properties and finding the best activity for a given reaction. It is important also to understand the underlying phenomenon causing the activity. There are multiple external factors affecting the reaction, e.g. temperature, pH, voltage, electrolyte species. Pub. II and III unveil the importance of these parameters at HER. This result is important not only to find the best circumstances for the reaction to take place but also to underline the significance of the research conditions when comparing experimental results from different catalysts.
Long-term stability and activity are crucial factors in real application electrolyzers. No matter how good the performance of the electrolyzer is, it is worthless if the catalysts cannot withstand the conditions inside the electrolyzer cell. For that reason, Pub. II and III demonstrates the long-term stability over multiweek experiments. Stability measurements are constantly undervalued in catalyst research and consist only of single electrode measurements in an electrochemical cell for short period of time.
2. Theoretical Background

To be able to understand and analyze the HER it is essential to know possible reactions and phenomena involved in the process. This provides several tools to quantify experimentally which reactions are occurring at the given conditions.

2.1 Electrochemical catalysis

Electrochemical reaction involves electric charges moving between an electrode and a reacting specie in an electrolyte. This process can be described with a reactant O that is reduced to R by receiving an electron from the electrode.

\[ \text{O} + e^- \rightarrow \text{R} \]  \hspace{1cm} (1)

When a chemical reaction is forced to occur by an external electrical energy, it is called electrolysis. Each chemical reaction has its own standard potential, which describes how high potential at minimum is needed to drive the reaction.

Even though adequate potential is applied over the electrochemical system, it is possible that the reaction does not occur. This is due to the reaction barrier that needs to be overcome to enable the reaction. Nevertheless, we can use materials that are able to lower the reaction barrier of the electron transfer. They are called electrochemical catalysts and they are crucial to facilitate various types of electrochemical reactions both in nature and in artificial devices.
2.2 Hydrogen evolution reaction mechanism

Hydrogen evolution under acidic conditions follows st:

1. Proton adsorption to surface with electron transfer (the Volmer reaction):

   \[ \text{H}_3\text{O}^+ + \text{e}^- + * \rightarrow *\text{H}_{\text{ads}} + \text{H}_2\text{O}. \]  

2. Hydrogen evolution by a reaction of a surface hydrogen atom and a solvated proton (the Heyrovský reaction):

   \[ *\text{H}_{\text{ads}} + \text{H}_3\text{O}^+ + \text{e}^- \rightarrow * + \text{H}_2 + \text{H}_2\text{O}. \]

3. Hydrogen evolution by a reaction of surface hydrogen atoms (the Tafel reaction):

   \[ *\text{H}_{\text{ads}} + *\text{H}_{\text{ads}} \rightarrow 2* + \text{H}_2. \]

Here * denotes the active free surface site of the catalyst and *\text{H}_{\text{ads}} adsorbed hydrogen atom on the catalyst site. The HER starts with Volmer reaction, where proton is adsorbed electrochemically to active catalyst site. The reaction is then continued either by the Heyrovský reaction, the combination of an adsorbed hydrogen atom, and a solvated proton or with the Tafel reaction, the combination of two adsorbed hydrogen atoms. The reaction mechanism varies based on the kinetics of the reaction with the chosen catalyst material. However, the rate-determining step (RDS) can be dependent also of the applied overpotential as more of the active sites are covered with hydrogen atoms when overpotential is increased.

2.2.1 Tafel analysis

If an electron transfer occurs straight between an electrode and a reactant molecule, it is called a redox reaction. A simple electrochemical redox reaction can be described by
the Butler-Volmer equation, which describes how the electrical current on an electrode depends on the electrode potential, considering that both cathodic and anodic reaction occur on the same electrode.

\[
j = j_0 \left[ e^{\alpha_f \eta} - e^{(\alpha-1)f \eta} \right]
\]  

(5)

where \( j \) is the kinetic current density of the electrode, \( j_0 \) is the exchange current density, \( \alpha \) is the charge transfer coefficient, \( f \) equals to \( nF/RT \) where \( n \) is the number of electrons transferred in the electrode reaction, \( F \) is the Faraday’s constant, \( R \) is the universal gas constant and \( T \) is temperature. \( \eta \) is the overpotential defined as \( \eta = E - E^0 \), where \( E \) is the electrode potential and \( E^0 \) is the standard potential.

At low overpotentials the Butler-Volmer equation can be linearized to

\[
\eta = \frac{RT}{nFj_0} j
\]  

(6)

With high overpotentials either the anodic or cathodic term of the Butler-Volmer equal becomes negligible. With high negative overpotential only the cathodic reaction is significant, and the equations can be written as

\[
\eta = \frac{RT}{(1-\alpha)nF} \ln j_0 + \frac{RT}{(\alpha-1)nF} \ln |j|
\]  

(7)

\(|j|\) as a function of \( \eta \) forms a linear line that is called Tafel slope and it can be used to analyze the reaction mechanism and the RDS of an electrochemical reaction.
Kinetics of hydrogen evolution reaction have been modelled in detail [67]. If the reaction proceeds via Volmer-Heyrovský mechanism and the Heyrovský reaction is the RDS, the Tafel slope is 40 or 120 mV dec⁻¹ at low or high overpotentials, respectively. If the reaction proceeds via Volmer-Tafel mechanism and the Tafel reaction is the RDS, the Tafel slope is 30 mV dec⁻¹ at low overpotentials. At high potentials the reaction is kinetically limited and independent of overpotential. If the Volmer reaction is the RDS, the Tafel slope is 120 mV dec⁻¹.

### 2.2.2 pH analysis

The electrolysis current is dependent of pH and in addition, with different reaction mechanism the the current behavior with changes in pH are different. This enables to study the reaction mechanism by altering the electrolyte pH.

The reaction rates for the Volmer-Heyrovský reaction are:

\[ v_1 = k_1 [H^+] (1 - \theta) e^{(\alpha - 1) f \eta} \]  
\[ v_{-1} = k_{-1} \theta e^{\alpha f \eta} \]  
\[ v_2 = k_2 [H^+] \theta e^{(\alpha - 1) f \eta} \]

where \( v_1, v_{-1} \) and \( v_2 \) are the reaction rates of the forward Volmer reaction, backward Volmer reaction and forward Heyrovský reactions, respectively; \( k_1, k_{-1} \) and \( k_2 \) are the respective reaction rate constants; \( \theta \) is the hydrogen surface coverage; \( f = RT/F \) and \( \eta \) is the overpotential.

Assuming steady state of reactions at certain overpotential, and thus that the proton coverage is constant:
\[
\frac{d\theta}{dt} = v_1 - v_{-1} - v_2 = 0 \quad (11)
\]

\[
k_1[H^+](1 - \theta)e^{(a-1)f\eta} - k_{-1}\theta e^{a_f\eta} - k_2[H^+]\theta e^{(a-1)f\eta} = 0 \quad (12)
\]

When \( \theta \) is solved from the equation:

\[
\theta = \frac{k_1[H^+]}{(k_1 + k_2)[H^+] + k_{-1}e^{f\eta}} \quad (13)
\]

Considering limiting case \( \theta \approx 0 \), it is achieved at low overpotentials when \( k_{-1} \gg k_1, k_2 \). Then surface coverage can be expressed as:

\[
\theta \approx \frac{k_1[H^+]}{k_{-1}} e^{-f\eta} \quad (14)
\]

As we are examining a steady state system, the net rate of the Volmer reaction must equal to the rate of the Heyrovský reaction. This results to:

\[
\frac{i}{F} = 2v_2 = 2 \frac{k_2 k_1[H^+]^2}{k_{-1}} e^{(a-2)f\eta} \quad (15)
\]

And can be derived to:

\[
\frac{\partial \log i}{\partial \log[H^+]} = 2 \quad (16)
\]

Decreasing the pH by one unit will result in a hundredfold increase in the current.
With same principles the current behavior can be calculated for the case $\theta \approx 1$ which is achieved when $k_1 \gg k_{-1}, k_2$, at high overpotentials:

$$\frac{i}{F} = 2k_2[H^+]e^{(\alpha-1)f\eta} \quad (17)$$

$$\frac{\partial \log i}{\partial \log [H^+]} = 1 \quad (18)$$

Decreasing pH by one unit will lead to current increase tenfold.

With the Volmer-Tafel mechanism the preceding hydrogen adsorption step is identical as previously and for the Tafel reaction:

$$v_3 = k_3\theta^2 \quad (19)$$

Taking the steady state assumption:

$$\frac{d\theta}{dt} = v_1 - v_{-1} - 2v_3 = 0 \quad (20)$$

$$k_1[H^+](1 - \theta)e^{(\alpha-1)f\eta} - k_{-1}\theta e^{\alpha f\eta} - 2k_3\theta^2 = 0 \quad (21)$$

For the case $\theta \approx 0$, obtained as $k_{-1} \gg k_1$, achieved at low overpotentials, the surface coverage is:

$$\theta \approx \frac{k_3[H^+]}{k_{-1}}e^{-f\eta} \quad (22)$$
This results in current behavior:

\[
\frac{I}{F} = k_3 \frac{k_1}{k_{-1}} [H^+]^2 e^{-2f\eta}
\]  

(23)

\[
\frac{\partial \log I}{\partial \log [H^+]} = 2
\]

(24)

As previously with zero surface coverage, the current increases hundredfold, when pH is decreased by one unit.

considering \( \theta \approx 1 \) which is obtained \( k_1 \gg k_{-1}, k_2 \), requiring high overpotentials:

\[
\frac{I}{F} = k_3 = \text{constant}
\]

(25)

This means that the current is kinetically limited and is independent of pH or overpotential.

This analysis assumes the surface coverage to be constant. The condition is met when the latter reaction is the RDS.

### 2.3 Methanol electrolysis

Water electrolysis is the conventional method to produce hydrogen by splitting the water molecule into hydrogen and oxygen. This is achieved by applying a voltage over two electrodes that are submerged into water. However, it is possible to split methanol instead of water resulting in the formation of carbon dioxide on one of the electrodes and hydrogen on the other.
There are two requirements for the electrolysis system to be functional: The two electrode compartments must be separated in the liquid to avoid short-circuit, and the electrodes must be connected by electrolyte that conducts ions from one electrode to another. These features are usually obtained by one of these three methods: liquid electrolyte with a diaphragm, electrolyte membrane or solid electrolyte. This thesis concentrates solely on the electrolyte membrane applications.

### 2.3.1 Alkaline methanol electrolysis

Alkaline membrane methanol electrolysis system components are shown in Fig. 1a. Anion exchange membrane with anode and cathode electrocatalysts is placed in the middle of the cell. The electrode layers on both side of the membrane are connected through and external electric circuit including a DC power source. Methanol-water solution is fed to the anode compartment and methanol is oxidized with hydroxide ions forming carbon dioxide, water and electrons. The electrons move to cathode through the external electric circuit.

\[ \text{CH}_3\text{OH} + 6\text{OH}^- \rightarrow \text{CO}_2 + 5\text{H}_2\text{O} + 6e^- \]  

\( E^\circ_2 = 0.81 \text{ V vs. SHE} \)  

Water transport through the membrane to the cathode side, where it is reduced producing hydrogen and hydroxide ions. Hydroxide ions move through the anion exchange membrane to the anode side.

\[ 2\text{H}_2\text{O} + 2e^- \rightarrow 2\text{OH}^- + \text{H}_2 \]  

\( E^\circ_2 = -0.83 \text{ V vs. SHE} \)
The resulting cell reactions for complete methanol-water solution electrolysis yields carbon dioxide and hydrogen as the products.

\[
\text{CH}_3\text{OH} + \text{H}_2\text{O} \rightarrow \text{CO}_2 + 3\text{H}_2 \quad (30)
\]

\[
E^0 = -0.02 \text{ V vs. SHE} \quad (31)
\]

To endure hydrogen production at the cathode it is essential to keep the electrode free of oxygen. Otherwise more advantageous fuel cell type reaction will replace hydrogen formation.

Figure 1. Schematic of alkaline (a) and acidic (b) membrane electrolyzers. (Unpublished)

2.3.2 Acidic methanol electrolysis

The overall reaction in acidic methanol electrolysis is the same as in the alkaline reaction. Nevertheless, the electrode reactions and transported species are different. In acidic electrolyzer (Fig. 1b) at the anode methanol reacts with water to produce carbon dioxide, protons and electrons. Protons transfer through the membrane and electrons via external power supply to the anode.
Anode: \( \text{CH}_3\text{OH} + \text{H}_2\text{O} \rightarrow \text{CO}_2 + 6 \text{H}^+ + 6 \text{e}^- \)  

\[ E_\text{a}^0 = -0.02 \text{ V vs. SHE} \]  

At the cathode the protons and electrons react producing hydrogen gas.

Cathode: \( 6 \text{H}^+ + 6 \text{e}^- \rightarrow 3 \text{H}_2 \)  

\[ E_\text{c}^0 = 0 \text{ V vs. SHE} \]

Total reaction: \( \text{CH}_3\text{OH} + \text{H}_2\text{O} \rightarrow 3 \text{H}_2 + \text{CO}_2 \)  

\[ E^0 = -0.02 \text{ V vs. SHE} \]

Because cation exchange membranes are not totally impermeable to other species, traces of water and methanol pass through along with the protons. However, the water and methanol can be removed from the hydrogen stream by use of a molecular sieve [68-76].
3. Experimental approaches

Electrochemical reaction thermodynamics and kinetics can be analyzed by various methods which all yields different information of the reaction. In addition to just analyze the reaction occurring at the surface of the catalyst, it is also possible to analyze short and long-term effects on the catalyst itself.

3.1 Catalyst preparations and properties

Two different type of experimental catalyst, Mo$_2$C nanoparticles and N-FWCNT, were used in the HER measurements. In this chapter the preparations and most important properties of the catalysts are briefly described.

3.1.1 Molybdenum carbide nanoparticles

The catalysts were prepared using a modification of the carbothermal reduction carbonization method [77]. The preparation process provided Mo$_2$C nanoparticles supported on carbon carrier (Mo$_2$C/C). The controlled preparation conditions allow the synthesis of molybdenum carbide nanoparticles with an average diameter of 12, 15 and 29 nm for the 10, 20 and 50 wt% Mo loadings, respectively. The synthesized Mo$_2$C/C catalysts were investigated and analyzed using ICP-AES chemical analysis, TGA, XRD, XPS and TEM. Mo loadings received by both ICP-AES and TGA were similar and close to the nominal values. This verifies that no significant losses of Mo occurred during synthesis. The catalysts nomenclature and their main characteristics are summarized in Table 1. Preparation process and characterization are presented in detail in Pub. II.
Table 1. Main properties and characteristic of the Mo$_2$C/C catalysts.

<table>
<thead>
<tr>
<th>Samples</th>
<th>Experimental Mo-loading (wt% Mo)</th>
<th>XRD Results</th>
<th>t$_{Mo_2C}$ (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>10 Mo$_2$C /C</td>
<td>9</td>
<td>C</td>
<td>12</td>
</tr>
<tr>
<td>20 Mo$_2$C /C</td>
<td>21</td>
<td>Mo$_2$C</td>
<td>15</td>
</tr>
<tr>
<td>50 Mo$_2$C /C</td>
<td>52</td>
<td>Mo$_2$C</td>
<td>29</td>
</tr>
</tbody>
</table>

*Mo$_2$C (JCPDF: 01-079-0744; C-graphite (JCPDF: 00-023-0064).

3.1.2 Nitrogen functionalized carbon nanotubes

FWCNTs were synthesized via chemical vapor deposition and underwent acid treatment to yield oxygen functional groups on the nanotube walls. Then, polyaniline was deposited on the functionalized FWCNTs and finally the nanotubes were subjected to pyrolysis to obtain N-FWCNTs. The samples are denoted as N-FWCNT-4, N-FWCNT-6, N-FWCNT-8, for the samples with 4, 6 and 8 h of acid functionalization, respectively.

XPS measurements were carried out to reveal the surface composition of the N-FWCNTs. The results (Table 2) show that the surface concentration of oxygen increases from 0.7 to 1.3 at% with increased acid treatment time from 4 h to 8 h. Similarly, nitrogen concentration increases from 0.59 to 0.74 at%. Increased acid treatment time enables more functional oxygen groups to attach to the nanotubes and thus increase anchoring of polyaniline on the surface of FWCNTs. Despite different acid treatment conditions, the relative distribution of N-functional configurations is similar for all the samples. Detailed preparation procedure and characterization is available in Pub. III.
Table 2. The atomic concentrations of N-FWCNTs according to XPS and the percentages of different nitrogen species of all nitrogen as derived from the peak deconvolutions. The error associated with each value is roughly ± 10% of the value.

<table>
<thead>
<tr>
<th>Atomic concentration (%)</th>
<th>Percentages of N species of all nitrogen</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>C</td>
</tr>
<tr>
<td>N-FWCNT-4</td>
<td>98.7</td>
</tr>
<tr>
<td>N-FWCNT-6</td>
<td>98.3</td>
</tr>
<tr>
<td>N-FWCNT-8</td>
<td>98.0</td>
</tr>
</tbody>
</table>

3.2 Electrochemical measurements

The electrocatalytic HER activities of the catalysts were investigated with rotating disc electrode (RDE) experiments using glassy carbon (GC) electrodes with a radius of 5 mm. The catalyst was mixed with 5 wt% Nafion solution and a solvent to form an ink which was deposited on the electrode.

A platinum mesh and nickel foam were used as the counter electrodes for the Mo₂C and N-FWCNT measurements, respectively, and a reversible hydrogen electrode (RHE) as a reference electrode. Currents are normalized against the geometrical area of the GC electrode.

The electrolyte solutions for pH series were prepared by mixing appropriate amount of 1 M sulfuric acid with 1 M sodium sulfate to obtain the desired pH while maintaining electrical conductivity.
3.3 Electrolyzer cell measurements

The electrolysis cell used in the experiments was assembled by sandwiching membrane electrode assembly (MEA) between gas diffusion layers and Teflon gaskets backed up by graphite blocks with serpentine flow field channels and finally clamped together.

With alkaline MEA commercial carbon supported Pt catalyst (60 wt% Pt/C) was used as the cathode catalyst and either carbon supported PtRu alloy (40 wt% Pt – 20 wt% Ru /C) or the Pt/C as the anode catalyst. The membrane used was Fumapem FAA-2 anion exchange membrane by FuMa-Tech. The MEA was prepared by spraying catalyst ink onto both sides of the membrane. After painting, the MEA was dried in vacuum and hot pressed. The MEA was ion exchanged to hydroxide form before use. For more detailed formula, see Pub. I.

For the acidic measurements the MEA was made by spraying catalyst ink onto both the sides of Nafion 115. The experimental catalysts were used for the cathode and commercial 60 wt% PtRu on carbon support for the anode. After painting, the MEA was dried in a vacuum oven and hot pressed. Detailed descriptions are presented in Pub. II and III.
4. Electrochemical measurement results

4.1 Molybdenum carbide nanoparticles

Due to the unique surface and electronic properties of molybdenum carbide it has risen a lot of interest as a hydrogen evolution catalyst. To be able to improve the performance of the catalyst it is crucial to understand the reaction mechanism of the HER on the catalyst surface. Moreover, reaction conditions strongly influence the catalytic properties, which is important to be taken into account when developing full-cell electrolysis systems.

4.1.1 HER activity

The lowest overpotential to achieve 1 mA cm$^{-2}$ electrolysis current (background corrected) was with the Mo$_2$C/C catalyst with 50 wt% Mo loading, which required 109 mV. The 20 and 10 wt% catalysts required 170 mV and 149 mV overpotential, respectively (Fig 2). It is assumed that smaller particles size of 10 wt% resulted in lower required overpotential for 1 mA cm$^{-2}$ current than with 20 wt% catalyst. Similar behavior have been reported with wide range on reactions [78-87]. Shape of the polarization curve of 10 wt% catalyst is different than the other two suggesting a different mechanistic behavior. The lower current to obtain 1 mA cm$^{-2}$ current with 50 wt% catalyst is assumed to result from higher amount of molybdenum resulting in higher amount active surface sites for HER and thus, higher currents at low overpotentials. Required overpotentials to reach 10 mA·cm$^{-2}$ current were 183, 246 and 253 mV for the 50, 20 and 10 wt% catalysts, respectively. When overpotential is further increased, the current density for 20 wt% catalyst increases more rapidly than for the 10 wt%. This trend implies that at high overpotentials the higher Mo loading with 20 wt% catalyst trumps the activity benefit 10 wt% catalyst got at low overpotentials from the smaller particle size. The obtained currents with these catalysts are significantly higher than the obtained current Mo$_2$C bulk catalyst, which required 190 mV to reach 1 mA·cm$^{-2}$ current and was raised only to 3 mA·cm$^{-2}$ at 400 mV overpotential. This trend shows clearly the benefit of nanosizing catalysts and thus, increasing the amount of catalytically active surface sites.
Fig. 2. The polarization curves for the Mo$_2$C/C catalysts with 10, 20 and 50 wt% Mo loadings, bulk Mo$_2$C and the commercial Pt catalyst (a) and Tafel slopes for the Mo$_2$C/C catalysts (b). (Unpublished)

The obtained Tafel slopes (Table 3) of 74, 74 and 92 mV dec$^{-1}$ for the 50, 20 and 10 wt% catalysts, respectively. The values are not representative for any single reaction mechanism with low or high surface proton coverage. The values are significantly higher than expected for both mechanisms at low overpotentials when the proton coverage is close to zero but not as high as expected for the Volmer-Heyroshky mechanism at high high overpotentials when the proton coverage is close to 1.

Table 3. Tafel slope values and regions for Mo$_2$C/C catalysts.

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>Tafel region (mV)</th>
<th>Slope (mV dec$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>50 wt% Mo$_2$C</td>
<td>110-160</td>
<td>74</td>
</tr>
<tr>
<td>20 wt% Mo$_2$C</td>
<td>170-240</td>
<td>74</td>
</tr>
<tr>
<td>10 wt% Mo$_2$C</td>
<td>140-200</td>
<td>92</td>
</tr>
</tbody>
</table>

4.1.2 Reaction mechanism analysis

For detailed analysis of the electrochemical properties the 50 wt% molybdenum carbide catalyst was chosen for further studies. In addition to Tafel slope analysis the reaction mechanism of the HER was investigated by analyzing the rate of the reaction at various pHs (Fig. 3a).
At low pH there is a clear change in the behavior already at low overpotentials, below 100 mV (Fig. 3b). Then there is a second change in the Tafel slopes around 150 mV overpotential. The obtained slope values at lower overpotential region are in the range of 59-78 mV dec\(^{-1}\) with pH 0.39 - 1.84 and 111 and 117 mV dec\(^{-1}\) for pH 0.11 and 0.23, respectively. The values close to 120 mV at low pH’s suggest that either the reaction is limited by the Volmer reaction or by the Heyrovský reaction with high surface coverage. At the high overpotential region Tafel slopes of 60 - 71 mV dec\(^{-1}\) were observed with pH 0.39 - 1.84 and 86 mV dec\(^{-1}\) for pH 0.11 and 0.23. These values are indicating that there is no single dominant reaction mechanism but the reaction proceeds with either mixed mechanism or intermediate surface coverages. The observed increase in the Tafel slopes at low pH, both with low and high overpotentials, is assumed to results from increased surface proton coverage when the electrolyte proton concentration is increased, which is normal behavior for adsorbing species. This means that the Tafel slope values changes when the pH of the electrolyte is adjusted.

Fig. 3. Polarization curves for 50 wt% Mo\(_2\)C/C catalyst in H\(_2\)SO\(_4\) pH series (a) and respective Tafel slopes with low pH solutions (b) measured at \( v = 10 \text{mV s}^{-1} \), rotation 3000 rpm. (Unpublished)
Table 4. The Tafel slope values for the HER on the 50 wt% Mo₂C/C catalyst.

<table>
<thead>
<tr>
<th>pH</th>
<th>Low overpotential</th>
<th>High overpotential</th>
<th>Tafel region (mV)</th>
<th>Slope (mV dec⁻¹)</th>
<th>Tafel region (mV)</th>
<th>Slope (mV dec⁻¹)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.87</td>
<td>80-120</td>
<td>59</td>
<td>130-150</td>
<td>60</td>
<td></td>
<td></td>
</tr>
<tr>
<td>1.44</td>
<td>80-120</td>
<td>61</td>
<td>130-150</td>
<td>60</td>
<td></td>
<td></td>
</tr>
<tr>
<td>1.01</td>
<td>80-120</td>
<td>68</td>
<td>130-150</td>
<td>60</td>
<td></td>
<td></td>
</tr>
<tr>
<td>0.66</td>
<td>80-120</td>
<td>66</td>
<td>130-150</td>
<td>62</td>
<td></td>
<td></td>
</tr>
<tr>
<td>0.39</td>
<td>80-120</td>
<td>78</td>
<td>130-150</td>
<td>71</td>
<td></td>
<td></td>
</tr>
<tr>
<td>0.23</td>
<td>80-120</td>
<td>117</td>
<td>150-170</td>
<td>86</td>
<td></td>
<td></td>
</tr>
<tr>
<td>0.11</td>
<td>80-120</td>
<td>111</td>
<td>150-170</td>
<td>86</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

According to the derivation of the reaction rates (Chapter 2.2.2) the slope of log $i$ vs. pH is around 2 for both the mechanisms at low overpotentials but at high overpotentials the slope is 1 or 0 for the Volmer-Heyrovský or Volmer-Tafel mechanism, respectively. When the background corrected logarithm of the electrolysis current is plotted as a function of pH, linear dependency is observed in the pH range 0.11 to 0.66 (Fig. 4a). The results show slope of 2 with overpotentials up to 50 mV in the pH range 0.11 - 0.66 (Fig. 4b). There was no linear relation at pHs above 0.66. Increasing overpotential resulted in decrease in the slope value, which is expected for both the mechanism. The change in the slope value between 50 and 200 mV is assumed to origin from the transition from zero surface coverage to full coverage. The slope lowers to 0.67 at 200 mV before starting to slowly raise with increasing overpotential. As the slope value is between 0 and 1, which are the defining values for the Volmer-Tafel and Volmer-Heyrovský mechanisms, it is expected the reaction proceeds with mixed reaction mechanism. The values of the slopes rise closer to 1 which implies leaning towards the Volmer-Heyrovský mechanism when the overpotential is increased. These results support the findings from Tafel slope analysis that there is no single dominant reaction mechanism at the chosen pH and overpotential conditions.
Fig. 4. The linear slopes of the log \( i \) vs. pH at chosen overpotentials (a) and the log \( i / \text{pH} \) slopes vs. chosen overpotentials for the 50 wt% Mo\(_2\)C/C catalyst at the low pH sulfuric acid buffer solutions. (Unpublished)

4.1.3 Reliability considerations

It is evident that there is a possibility that a platinum based counter electrode may dissolve in H\(_2\)SO\(_4\) electrolyte and deposit to the measured working electrode [88-90]. Even though platinum dissolves well to H\(_2\)SO\(_4\) it is not evident that the platinum deposits at the working electrode, rather it is case sensitive. It is also a time and potential dependent process meaning that longer times at high overpotentials results in more dissolved and deposited platinum. If the deposition happens, the catalytic activity on the working electrode increases due to superior activity of Pt towards the HER reaction. This would been seen in the results as decreases overpotential to obtain certain currents, or other way around as an increased current with the same overpotential. It also would affect the Tafel slope by lowering it closer to 30 mV dec\(^{-1}\) which is typical for Pt catalyst in the HER [91].

Platinum mesh was used as a counter electrode in the electrochemical measurements with Mo\(_2\)C catalysts in Pub. II. Therefore, it is necessary to analyze the measurements results and consider if the results are reliable.

The required overpotentials to obtain 10 mA·cm\(^{-2}\) current were 183 mV, 246 mV and 253 mV for the 50, 20 and 10 wt% catalysts, respectively. These are similar as
previously measured with Mo-based catalysts as shown in Pub II. The same is true for the Tafel slopes of 74, 74 and 92 mV dec\(^{-1}\) for the 50, 20 and 10 wt% catalysts, respectively. All of the results are far from the results obtained with platinum-based catalysts where the required HER overpotential is some tens of mV and the Tafel slope is around 30 mV dec\(^{-1}\). The pH series with 50 % Mo\(_2\)C was measured starting from the highest pH and progressing towards the lowest pH. If platinum would be deposited on the working electrode in significant quantities, this would be seen in as abnormal high currents at low pH. The obtained currents at low pH follows the theoretical prediction that the log \(i\) is linear with the decreasing pH (Fig. 4). If deposited platinum increased the activity of the catalyst this would be seen as an anomaly in the data set. While the results seem not to be affected by the use of platinum counter electrode that possibility cannot be ruled out totally.

4.2  Nitrogen functionalized carbon nanotubes

Previously fairly low activity for nitrogen functionalized nanotubes have been reported without any explanation for the reaction mechanism or the catalytic site. Since the catalyst is interesting option because of the electrochemical properties and production possibilities, it is desired to understand in depth the origin of the HER activity on the catalyst surface.

4.2.1  HER activity

All of the three different N-FWCNTs (see Table 2) show similar catalytical activity for the HER (Fig. 5). The required overpotential to reach 10 mA cm\(^{-2}\) current are around 250 mV for each catalyst and the maximum current at 400 mV overpotential range from 55 to 62 mA cm\(^{-2}\). There is small fluctuation in the currents with N-FWCNT-4 due to bubble formation and removal on the electrode surface during hydrogen evolution. This might occur because of the shorter acid treatment time resulting in more hydrophobic CNTs [92]. Currents with N-FWCNT-6 and N-FWCNT-8 show smooth curves that is typical for continuous hydrogen removal from the electrode surface.
The observed activity of the N-FWCNTs towards HER is significantly higher than earlier reported for N-doped carbon catalyst with similar loading and conditions\[65\]. They have reported 5.5 mA cm\(^{-2}\) current at 300 mV overpotential where as our catalyst show current of 19 mA cm\(^{-2}\). Current state-of-the-art non-noble metal HER catalyst, e.g. Ni\(_2\)P, MoS\(_2\) and Mo\(_2\)C, requires 120-220 mV overpotentials to reach 10 mA cm\(^{-2}\) current density \[36,93-96\]. The obtained 250 mV with the researched N-FWCNT catalysts is only slightly higher than with the aforementioned catalysts.

HER activity on pristine and acid treated FWCNTs and in addition on a commercial 60 wt% Pt/C are presented in Fig. 5a. This clearly shows that both pristine and acid treated FWCNTs show very low activity for the HER. Comparing the results to N-functionalized samples it is evident that the functionalization has a critical role in creating electrochemical activity towards the HER.

The Tafel slopes of 116, 114 and 128 mV dec\(^{-1}\) for N-FWCNT-4, N-FWCNT-6 and N-FWCNT-8, respectively, were obtained from potential range 160 to 200 mV with background corrected currents. The results are close to 120 mV dec\(^{-1}\) which suggest either Volmer-Heyrovský mechanism with a fast proton adsorption followed by a slow electrochemical desorption step or Volmer reaction being the RDS. As the catalytic active sites are in vicinity of N-functional spots and the hydrogen are adsorbed exactly on top of carbon atom (detailed discussion in Pub. III) it is anticipated that the reaction does not proceed with Volmer-Tafel mechanism, which requires two close by adsorbed hydrogen atoms. This means that the reaction can proceed only by combination of surface hydrogen atom and a solvated proton.
4.2.2 Reaction mechanism analysis

Due to all the three N-FWCNT-4, N-FWCNT-6 and N-FWCNT-8 showing similar activity towards HER, measurements were continued only with N-FWCNT-8. The HER currents in H$_2$SO$_4$ pH series (Fig. 6a) show constant enhancement as the pH is decreased from 1.5 to 0.3. Tafel slopes of 187, 136, 125 and 120 mV dec$^{-1}$ for pH 1.5, 1, 0.6 and 0.3, respectively, were observed from the potential range 160 to 200 mV with background corrected currents. The Tafel slope values are approaching 120 mV dec$^{-1}$, which is the theoretical value for the Volmer-Heyrovský reaction if the reaction is limited by the Volmer reaction or by the Heyrovský reaction at high surface coverages. This is strong indication that proton concentration affects the reaction mechanism of the HER on N-FWCNT. As the availability of protons in the electrolyte increases, this can support both the adsorption of protons to the catalyst surface (the Volmer reaction) as well as reaction of surface hydrogen atom with solvated proton (the Heyrovský reaction).
Figure 6. Polarization curves for the hydrogen evolution on N-FWCNT-8 in H_2SO_4 pH series (a) and respective Tafel slopes (b) measured at \( v = 10 \text{mV s}^{-1} \), rotation 3000 rpm. (Pub. III)

The slope of the log \( i \) vs. pH (Fig. 7a) rises from 0.2 close to 1 when overpotential is increased (Fig. 7b). This implies that there is no evident dominant reaction mechanism at low overpotentials but as overpotential is increased the slope value approach 1, which is characteristic for the Volmer-Heyrovský reaction. The same phenomenon was observed with the Tafel slopes (Fig. 6b) as increased hydrogen coverage resulted in typical values for the Volmer-Heyrovský mechanism.

Figure 7. The linear slopes of the log \( i \) vs. pH at chosen overpotentials (a) and the log \( i \) / pH slopes vs. chosen overpotentials for the N-FWCNT-8 catalyst in the low-pH sulfuric acid electrolytes (b). (Pub. III)

The reaction mechanism has been analyzed by computational methods in Pub. III. The results confirm that proton surface coverage has strong influence on the hydrogen
adsorption energies, which explains the low current densities at low overpotentials. These calculations also show that the Heyrovský reaction is the rate-determining reaction in the HER, which is in agreement with the experimental studies carried out at low pH.

Comparing experimental results, the N-FWCNT is clearly more active than pristine CNT, and this is in good agreement with the calculations: the calculated reaction barrier (ca. 1 eV) of pristine CNT is much higher than the barriers for N-doped CNT (ca. 0.6 eV).

4.3 Effect of iR compensation

The electrochemical measurements with Mo2C and N-FWCNT catalysts in chapters 4.1 and 4.2 are presented without iR compensation. Considering electrochemical analysis of reaction kinetics, it is relevant to compensate the part of overpotential occurring from the resistance of the electrolyte to get more precise results. In this chapter the electrochemical results are presented with estimated iR compensation and the effect to the results are analyzed.

The electrolyte resistance can be determined with impedance spectroscopy and this have been done in Pub. II and III at 0,5 M H2SO4. The resistance is dependent of the used electrolyte, and thus the same values can not be used for all the used electrolytes. The resistance is also dependent on the distance between working electrode and reference electrode, which means that it is not possible to calculate the resistance from known conductivity values for H2SO4 solutions. However, the relative conductivities of used electrolytes compared to 0,5 M H2SO4 can be estimated from previously measured values for conductivity of H2SO4 and Na2SO4 solutions [97]. This enables good estimation of the resistance with different pH electrolytes and thus, allow implementing iR compensation.
4.3.1 Effect of iR compensation on Mo$_2$C catalyst results

With Mo$_2$C catalyst the overpotentials to achieve 1 mA cm$^{-2}$ current decrease by approximately 1 mV to 108, 169 and 149 mV for 50 wt%, 20 wt% and 10 wt%, respectively (Fig. 8a). In similar fashion the overpotentials to reach achieve 10 mA cm$^{-2}$ current decreases by approximately 10 mV to 173, 236 and 243 mV. The obtained Tafel slopes (Fig. 8b) 64, 66 and 88 mV dec$^{-1}$ are slightly lower than the values without iR compensation; 77, 77 and 92 mV dec$^{-1}$. In both cases, the slopes are not characteristic for any reaction mechanism at low or high potentials but rather suggest mixed reaction mechanism or partial proton surface coverage.

![Fig. 8. The iR compensated polarization curves for the Mo$_2$C/C catalysts with 10, 20 and 50 wt% Mo loadings, and bulk Mo$_2$C (a) and Tafel slopes for the Mo$_2$C/C catalysts (b). (Unpublished)](image_url)

In the pH series measurements (Fig. 9a), the 50 wt% Mo$_2$C catalyst shows two different areas in the Tafel slopes (Fig. 9b). The obtained Tafel slopes (Table 5) are 0 to 2 mV dec$^{-1}$ lower than without iR compensation, except for pH 0.11 and 0.23 at higher potential region, where those had 4 mV dec$^{-1}$ lower slope. These changes do not cause meaningful effect on the reaction mechanism analysis. The values at low overpotential region with pH 0.11 and 0.23 are close to 120 mV dec$^{-1}$, which implies that the reaction is limited by the Volmer reaction or by the Heyrovský reaction with high surface coverage. At all other cases the Tafel slopes are between the determining values and thus, indicates that the reactions proceed with mixed reactions mechanism or intermediate surface coverages.
Fig. 9. The iR compensated polarization curves for 50 wt% Mo$_2$C/C catalyst in H$_2$SO$_4$ pH series (a) and respective Tafel slopes with low pH solutions (b) measured at $v = 10$ mV s$^{-1}$, rotation 3000 rpm. (Unpublished)

Table 5. The Tafel slope values for the iR compensated HER on the 50 wt% Mo$_2$C/C catalyst.

<table>
<thead>
<tr>
<th>pH</th>
<th>Low overpotential</th>
<th>High overpotential</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Tafel region (mV)</td>
<td>Slope (mV per decade)</td>
</tr>
<tr>
<td>1.87</td>
<td>80-120</td>
<td>59</td>
</tr>
<tr>
<td>1.44</td>
<td>80-120</td>
<td>60</td>
</tr>
<tr>
<td>1.01</td>
<td>80-120</td>
<td>68</td>
</tr>
<tr>
<td>0.66</td>
<td>80-120</td>
<td>66</td>
</tr>
<tr>
<td>0.39</td>
<td>80-120</td>
<td>78</td>
</tr>
<tr>
<td>0.23</td>
<td>80-120</td>
<td>116</td>
</tr>
<tr>
<td>0.11</td>
<td>80-120</td>
<td>109</td>
</tr>
</tbody>
</table>

The changes to the effective overpotential from iR compensation slightly change the log $i$ vs. pH slopes (Fig. 10). At low overpotential there is no significant changes but at high overpotentials the slope reaches value of 0.97 at 300 mV overpotential, which is very close to the theoretical value of 1 for the Volmer Heyrovský mechanisms at high surface coverages.
4.3.2 Effect of iR compensation on N-FWCNT catalyst results

As the three different catalysts (N-FWCNT-4, N-FWCNT-6, N-FWCNT-8) were measured in same electrolyte and provided similar results, the effect of iR compensation is similar to all of them. The required overpotential to reach 10 mA cm\(^{-2}\) current lowered to approximately 240 mV (Fig. 11a). The Tafel slopes are 126, 116 and 127 mV dec\(^{-1}\) for N-FWCNT-4, N-FWCNT-6 and N-FWCNT-8, respectively, taken from potential range 160 to 240 mV (Fig. 11b). The results are close 120 mV which is representative value for Volmer reaction being the RDS or Heyrovský reaction at high surface coverages. The biggest impact of iR compensation is that the Tafel slopes are linear for a longer potential range.
Figure 11. The iR compensated HER polarization curves (a) and Tafel plots (b) for the N-FWCNT-4, N-FWCNT-6, N-FWCNT-8 catalysts in 0.5 M H$_2$SO$_4$, 3000 rpm rotation, 10 mV s$^{-1}$ scan rate. Acid treated FWCNT and pristine FWCNT are shown in (a). (Unpublished)

The pH series with N-FWCNT-8 gives Tafel slopes of 186, 131, 119 and 116 mV dec$^{-1}$ for pH 1.5, 1, 0.6 and 0.3, respectively, taken from potential range 160 to 200 mV (Fig. 12). As with non-iR compensated results the Tafel slope values gets close to 120 mV dec$^{-1}$ with decreasing pH showing the effect of proton concentration to the HER.

Figure 12. Polarization curves for the hydrogen evolution on N-FWCNT-8 in H$_2$SO$_4$ pH series (a) and respective Tafel slopes (b) measured at $v = 10$ mV s$^{-1}$, rotation 3000 rpm. (Unpublished)

The iR compensation slightly increases the log $i$ vs. pH slope values at high overpotentials (Fig. 13). The highest measured value is 1.03 at 350 mV overpotential. Slope value of 1 is characteristic for the Volmer-Heyrovský reaction at high surface coverages,
implying that the reaction does proceed with this mechanism at high overpotentials, where proton surface coverage is increased.

Figure 13. The linear slopes of the log \( i \) vs. pH at chosen overpotentials with iR compensation (a) and the log \( i / \text{pH} \) slopes vs. chosen overpotentials for the N-FWCNT-8 catalyst in the low-pH sulfuric acid electrolytes (b). (Unpublished)

4.4 Comparison to state-of-the-art non-metal catalysts

Table 6 summarizes comparison of the researched catalyst materials against some of the most promising non-noble metal catalysts. The potential where the HER current reaches 10 mA cm\(^{-2}\) (\(\eta_{10}\)) is often taken as a comparison point for the catalysts. It is far more useful than using so called onset potential where the HER reaction starts as there are no unambiguous practice to determine it. Tafel slope describes how well the reaction is accelerated when the overpotential is increased. As shown in Pub. II the HER is strongly dependent on the reaction conditions and thus, great care should be taken when comparing different studies. This is also acknowledged in a recent review article of Mo-based HER catalysts [98]. 0.5 M H\(_2\)SO\(_4\) is the current standard for acidic HER measurements but nevertheless, still some of the experiments have been carried out with different electrolytes. The loading of the catalyst on the electrode naturally affects the obtained HER currents.
Another issue comparing different catalysts is the subjective aspect of the electrochemical measurements and the obtained numerical results. While in theory Tafel slope is formed when log $i$ is compared against applied voltage, in many cases there are no straight slope or it is limited to a narrow potential window. While Tafel slope might seem auspicious at glance but in reality, the current might rise sluggishly with increased overvoltage. Thus, a catalyst with higher $\eta_{10}$ and Tafel slope values might outperform the catalysts with lower values when the performance is analyzed at higher currents. For example, comparing Ni$_2$P nanoparticles [99] and FeP nanoparticles [100] which have similar $\eta_{10}$ values (120 mV & 123 mV) but the FeP catalyst has lower Tafel slope of 50 mV dec$^{-1}$ compared to 81 mV dec$^{-1}$ of the Ni$_2$P catalyst, it looks evident that the FeP would be favorable catalyst. However, this is not the case as at overpotential of 230 mV FeP reach current value of 40 mA cm$^{-2}$, which is significantly lower than 100 mA cm$^{-2}$ obtained with Ni$_2$P. This example underlines that the performance of the catalysts should not be measured only at low overpotentials because the performance for HER in realistic conditions for applications might be really different.

Another consideration is the reliability of the presented results. Mo$_2$C nanosheets has shown a $\eta_{10}$ value of a mere 19 mV and a Tafel slope of 29 mV dec$^{-1}$ [101]. In the article they are stating that the catalyst shows similar activity as the widely used platinum and much higher than ever reported for Mo-based catalyst. They used platinum wire as the counter electrode for their measurement, which have been proven to dissolve while the working electrode is at the HER potentials in 0.5 M H$_2$SO$_4$ and potentially deposit to the working electrode surface. It would be advisable to conduct a post-mortem analysis of the working electrode and show that there are no traces of platinum present before further research with the catalyst.

The $\eta_{10}$ value and Tafel slopes are higher for the researched Mo$_2$C and N-FWCNT catalysts than for most of the state-of-the-art non-noble metal catalysts. This would imply that the required power to produce hydrogen would be higher with the researched catalysts. Nevertheless, easiness of preparations, suitability for electrolyzer cells and long-term stability are crucial features for a real-application catalyst in addition to electrochemical performance. The latter two features are evaluated in Chapter 5.
Table 6. Comparison of state-of-the-art non-noble metal catalysts.

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>Ref.</th>
<th>Electrolyte</th>
<th>Loading (mg cm$^{-2}$)</th>
<th>$\eta_{10}$ (mV)</th>
<th>Tafel slope (mV dec$^{-1}$)</th>
<th>Tafel range (mV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mo$_2$C Nanoparticles/C</td>
<td>Pub. II</td>
<td>0.5 M H$_2$SO$_4$</td>
<td>0.6</td>
<td>173</td>
<td>81</td>
<td>150-170</td>
</tr>
<tr>
<td>N-FWCNT</td>
<td>Pub. III</td>
<td>0.5 M H$_2$SO$_4$</td>
<td>0.6</td>
<td>240</td>
<td>127</td>
<td>160-200</td>
</tr>
<tr>
<td>Mo$_2$C/CNT-graphene</td>
<td>[53]</td>
<td>0.5 M H$_2$SO$_4$</td>
<td>0.7</td>
<td>130</td>
<td>58</td>
<td>80-130</td>
</tr>
<tr>
<td>MoC–Mo$_2$C heteronanowires</td>
<td>[102]</td>
<td>0.5 M H$_2$SO$_4$</td>
<td>0.1</td>
<td>126</td>
<td>43</td>
<td>50-130</td>
</tr>
<tr>
<td>MoP nanoparticle network</td>
<td>[103]</td>
<td>0.5 M H$_2$SO$_4$</td>
<td>0.4</td>
<td>125</td>
<td>54</td>
<td>40-100</td>
</tr>
<tr>
<td>Ni$_2$P nanoparticles</td>
<td>[99]</td>
<td>0.5 M H$_2$SO$_4$</td>
<td>1.0</td>
<td>120</td>
<td>81</td>
<td>150–200</td>
</tr>
<tr>
<td>FeP nanoparticles/GS</td>
<td>[100]</td>
<td>0.5 M H$_2$SO$_4$</td>
<td>0.3</td>
<td>123</td>
<td>50</td>
<td>0-60</td>
</tr>
<tr>
<td>CoP Nanowires/CC</td>
<td>[104]</td>
<td>0.5 M H$_2$SO$_4$</td>
<td>0.9</td>
<td>67</td>
<td>51</td>
<td>5-60</td>
</tr>
<tr>
<td>CoP nanocrystals/CNT</td>
<td>[59]</td>
<td>0.5 M H$_2$SO$_4$</td>
<td>0.3</td>
<td>122</td>
<td>54</td>
<td>10-70</td>
</tr>
<tr>
<td>CoS$_2$ nanowires</td>
<td>[93]</td>
<td>0.5 M H$_2$SO$_4$</td>
<td>1.7</td>
<td>145</td>
<td>52</td>
<td>100-150</td>
</tr>
<tr>
<td>Mo$_2$C nanosheets/NC</td>
<td>[101]</td>
<td>0.5 M H$_2$SO$_4$</td>
<td>0.6</td>
<td>19</td>
<td>29</td>
<td>0-30</td>
</tr>
<tr>
<td>Ni$_3$P microparticles</td>
<td>[105]</td>
<td>0.5 M H$_2$SO$_4$</td>
<td>177</td>
<td>66</td>
<td>41</td>
<td>20-70</td>
</tr>
<tr>
<td>WS$_2$-WO$_3$-rGO</td>
<td>[106]</td>
<td>0.5 M H$_2$SO$_4$</td>
<td>0.7</td>
<td>113</td>
<td>37</td>
<td>70-120</td>
</tr>
<tr>
<td>MoS$_2$-Fe film</td>
<td>[94]</td>
<td>1.0 M H$_2$SO$_4$</td>
<td>-</td>
<td>170</td>
<td>39</td>
<td>150-190</td>
</tr>
<tr>
<td>Ni$_2$P nanoparticles</td>
<td>[95]</td>
<td>1.0 M H$_2$SO$_4$</td>
<td>0.4</td>
<td>135</td>
<td>87</td>
<td>60-140</td>
</tr>
<tr>
<td>Mo$_2$C/CNT</td>
<td>[55]</td>
<td>0.1 M HClO$_4$</td>
<td>2.0</td>
<td>152</td>
<td>58</td>
<td>0-200</td>
</tr>
</tbody>
</table>
5. Electrolyzer cell measurements results

Previous chapter concentrated on the catalyst activity and reactions mechanism in the HER. Nevertheless, real hydrogen production systems require much more than just efficient catalysts. The electrolyte membranes ability to transfer ions from one side to another is crucial to the overall reaction rate of the hydrogen production. Methanol crossover through the membrane may cause poisoning of the cathode catalyst or interferes the HER.

Conditions in the electrolyzer cell are different from the electrochemical cell and the measurements provides valuable information of behavior of catalysts in realistic conditions. Often long-term durability is underrepresented in catalysis research, but it is one of the most important features for commercial applications. For this reason the investigated catalysts performances have been analyzed also in long-term tests.

5.1 Alkaline membrane methanol electrolysis

Alkaline membrane electrolyzer was assembled (Pub. I) and its performance was verified with two commercial HER catalysts, Pt and PtRu (Fig. 14a). PtRu catalyst provided better performance than Pt at low voltage region, below 1.2 V. The catalyst active sites can be poisoned by CO, which is produced in partial methanol oxidation process. With PtRu catalyst the CO is oxidized from the surface at lower voltages than with Pt [107], which explains the higher activity with PtRu at low voltages. At voltages over 1.2 V the electrolysis currents with Pt reaches the current obtained with PtRu. At the cathode, when the potential is increased, CO is oxidized from the surface and is not hindering anymore the hydrogen production. As pure Pt catalyst has more active sites than PtRu it is expected to be more active at high voltages. However, the low voltage region is interesting for interesting for applications and thus PtRu was chosen for more detailed studies.

The current efficiency of hydrogen production was verified by comparing the electrolysis current to the hydrogen production rate (Fig. 14b). The hydrogen production rate is very close to the theoretical values and the production rate increases as expected with
elevated currents. Hydrogen production efficiency is over 90 % of the theoretical value at all measurement points.

Figure 14. Comparison of Pt and PtRu anode catalysts at 30 °C with 1 mol dm$^{-3}$ methanol (a), hydrogen production rate dependency of the current density (b), the effect of fuel concentration at 30 °C (c) and the effect of temperature with 1 mol dm$^{-3}$ methanol (d). (Pub. 1)

Methanol electrolyzer is preferred to operate with concentrated methanol solution to minimize the required fuel storage space. For the reason the performance of the electrolyzer cell was researched with 1, 2, 5 and 10 M methanol solutions (Fig. 14c). The 1 and 2 M solutions resulted in a similar electrolysis currents but with 5 and 10 M solutions the currents started to decrease. This behavior is assumed to result from the morphological changes in the membrane which affect its properties. It has been shown that the membrane swells and ion conductivity decreases with increasing methanol concentration [108]. In addition, water transport slower through the membrane with higher concentrations as the self-diffusion coefficient is lower. The above-mentioned reasons explain, why lower currents are obtained with concentrated methanol solutions. Moreover, high concentration fuel enhances methanol crossover from anode to cathode resulting in impurities in the produced hydrogen.
The concentration effect was also studied at higher temperatures, 50 °C and 70 °C, and provided similar results. The gap between 5 and 10 M solutions compared to low concentrations solutions increased and became evident. The elevated temperature is expected to affect the morphology of the membrane and thus affecting the transportation properties.

The performance of the alkaline methanol electrolyzer was studied at 30 °C, 50 °C and 70 °C temperatures with 1 M methanol as a fuel (Fig. 14d). As expected, the currents rise with increasing temperature at all voltages. The currents at 1 V voltage reach values of 10.1, 24.0 and 48.9 mA cm\(^{-2}\) at 30 °C, 50 °C and 70 °C, respectively. Mass transport and reaction kinetics are enhanced resulting in lower concentration and activation over-potentials [109]. The obtained current with alkaline membrane is lower than electrolyzers with acidic membranes [2,5]. There are two obvious reason for the lower currents. First, ion conductivity of the FAA-2 membrane is significantly lower than with Nafion 115 [109] which increases the required overpotential as electrolyte resistance is increased. Second, the catalyst loadings (0.5 mg cm\(^{-2}\)) are much lower than used with the acidic electrolyzers (3 mg cm\(^{-2}\) [2], anode 2.5 mg cm\(^{-2}\) and cathode 1.5 mg cm\(^{-2}\) [5]). In addition, the onset potential to see significant electrolysis currents are approximately 0.72, 0.70 and 0.65 V at temperatures of 30, 50 and 70 °C, respectively. Sluggish electrode reaction requires higher overpotential to run the reaction. The onset potentials for acidic electrolyzers are significantly lower [2,4,5] due to different reaction mechanism and kinetics compared to alkaline media. Even though methanol oxidation in alkaline media has shown enhanced kinetics it might be that the anion exchange membrane as such is not alkaline enough to show this behavior but would require addition of alkaline salt to the electrolyte solution.

5.2 PEM electrolyzer activity

While the alkaline membrane electrolyzer has its own advantages, PEM electrolyzers are widely researched and exploited in electrolyzers as the Nafion membrane has very high proton conducting rate making it a compelling option. In addition, the membrane is highly stable both chemically and mechanically, and the acidic environment of the membrane provides propitious conditions for the HER.
5.2.1 Molybdenum carbide

The electrolyzer cell results (Fig. 15a) confirm the performance of molybdenum carbide catalyst in a realistic electrolyzer system. The cell performance increases when temperature is increased as the potential to reach 10 mA·cm⁻² current decrease from 609 mV to 452 mV and the current densities at 1 V are 130, 188, 267, 345 and 422 mA cm⁻² for 30, 40, 50, 60 and 70 °C, respectively. The obtained current at 1 V potential at 70 °C is about 80 % of the current (515 mA·cm⁻²) measured with a similar MEA (Fig. 15b) with platinum cathode (1.43 mg·cm⁻² loading), though the HER current of Mo₂C is rising steeper with increased overpotential than the current with the Pt catalyst. At the straight part of the polarization curve, the cell resistance is dominated by the ohmic losses. This implies that the Mo₂C electrode has higher ion conductivity of protons, as it is a major contributor in the ohmic losses in PEM cells [110]. This might be due to better contact between the catalyst particles and the electrolyte.

Fig. 15. The polarization curves of the methanol electrolyzer cell with the 50 wt% Mo₂C/C catalyst at chosen temperatures (a) and comparison of the 50 wt% Mo₂C/C catalyst and platinum as the cathode catalyst for the electrolyzer cell at 70 °C. (Pub. II)

The electrolyzer cell was analyzed with constant voltage of 0.8 V and at 30 °C temperature for four weeks to verify long-term usability. The measurement was divided to one-week period, which consisted of constant potential measurement followed by a potential scan. Small potential activation was observed at the beginning of the first week but there forward the constant potential measurements we relatively stable (Fig. 16a). At the beginning of weeks 2-4 temporal activation is seen due to the small downtime and potential sweep between the constant potential measurements. However, the currents stabilize to same level, 56-58 mA·cm⁻², every week, though some variation in the currents at the
end of the weeks can be observed. The potential scans (Fig. 16b) performed before the measurements and after each week verify the stability of the cell over the four weeks measurement period. While there are small variations in the currents, overall the performance level stays constant. These results imply that the 50 wt% Mo₂C/C catalyst is stable in typical conditions in the electrolyzer.

Fig. 16. Constant potential electrolyzer cell measurement with the 50 wt% Mo₂C/C catalyst at 0.8 V and 30 °C (a) and polarization curves of the electrolyzer cell before the long-term measurements and after each measurement week at 30 °C. (Pub. II)

5.2.2 N-FWCNT

The performance of the N-FWCNT-8 catalyst was studied in a PEM electrolysis cell. The polarization curves for the hydrogen production are presented in Fig. 17a. The polarization curves reveal an onset potential for the hydrogen evolution in the range of 300 mV to 500 mV and expected temperature dependent behavior; at higher temperatures mass transport and reaction kinetics are enhanced, and higher current densities are obtained. The maximum current densities achieved at the studied temperatures are 130, 180, 250, 310 and 380 mA cm⁻² for 30, 40, 50, 60 and 70 °C, respectively. The onset overpotential is higher than for the Pt/C cathode (Fig. 17b), as expected based on the half-cell polarization curves (Fig. 5a). Nevertheless, when potential is increased the hydrogen production of the N-FWCNT cell increases steeper than with Pt/C. As earlier noted with Mo₂C, this implies that the N-FWCNT electrode has higher ion conductivity of protons than the Pt electrode. Similar phenomenon has been also observed with a N-FWCNT fuel cell cathode [111].
Figure 17. Polarization curves for the PEM MeOH electrolysis cell with the N-FWCNT-8 cathode at temperature range of 30 to 70 °C (a) and comparison to platinum cathode electrolyzer at 70 °C (b). (Pub. III)

The stability of the N-FWCNT catalyst is tested by chronoamperometry at 0.75 V (Fig. 18) for one week at a time and total of five weeks. The performance of the cell slightly decreases during the constant operation but recovers to a higher current level after cut-off indicating reversible losses resulting e.g. from mass-transfer effects. Nevertheless, the measured currents slightly reduce every period and the currents at the end of each one-week period are approximately 11.3, 10.9, 10.8, 10.0 and 9.7 mA cm\(^{-2}\). Irreversible losses during the long-term measurements can include contribution from several different degradation mechanism including chemical and structural changes in the cathode and anode catalysts, the electrode layers or in the membrane.
Figure 18. Constant potential electrolyzer cell measurement with N-FWCNT-8 at 0.75 V and 30 °C. (Pub. III)

5.3 Comparison of degradation

With the studied Mo$_2$C catalyst, it is impossible to see any significant degradation during the 4 weeks experiments. The chronoamperometric measurement shows similar performances each week and there is no evident trend in the polarization curves measured after each one week set. Electrolyzer current with N-FWCNT catalyst decreased from the end of first week 11.3 mA cm$^{-2}$ to end of fifth week 9.7 mA cm$^{-2}$. This drop of 1.6 mA cm$^{-2}$ accounts for 14 % of the original current and over the period of 28 days results in an average of 0.5 % loss in 24 h.

Currently electrolyzer counter as state-of-the-art systems are showing 0.4 to 5 μV/h degradation in constant current measurements [112]. 5 μV/h degradation rate over 60 000 operation hours would account for 0.3 V additional required overvoltage at the end of operation. From the stability perspective Mo$_2$C catalyst is an interesting choice for further research as significant degradation cannot be observed. N-FWCNT will need improvement in stability before consideration for commercial electrolyzers.
It is surprisingly rare that electrochemically researched catalysts are tested also in an electrolyzer cell even though it is the only method to validate the catalyst usability in realistic conditions. One research tested Mo-based catalysts in a PEM water electrolyzer cell over 24 h period [113]. For two of the researched catalysts the drop after the initial stabilization was around 10 % of the current. Surprisingly, the third catalyst was stable over the 24 h period with even slightly increased performance over time. Another interesting finding in the research was that two catalyst with similar activities in an electrochemical cell yielded results different from each other in the electrolyzer cell. This was suspected to occur because of poor catalyst-membrane interfacial contact or poor catalyst conductivity, highlighting the importance of electrolyzer tests in catalyst research.
6. Conclusions

The basic principles of methanol-water solution electrolysis with an alkaline membrane cell is introduced and verified in this research. This method is interesting due to potential savings by enabling lower power consumption than conventional water electrolyzers and enabling the utilization of low-cost membrane materials instead of expensive proton exchange membranes. In addition, for further research alkaline media is better suited for the use on non-precious metal catalyst for hydrogen evolution.

In Pub. I hydrogen production by alkaline membrane methanol electrolysis has been reported for the first time. The article has been acknowledged e.g. in a book [114] covering current themes on energy and environment.

While there is still need for improvement in the stability and ion conductivity of the membrane and the ionomer, this novel method opens a new area for investigation in hydrogen production and enables alternative material choices to produce commercially viable methanol electrolyzers.

Molybdenum carbide nanoparticles and nitrogen functionalized carbon nanotubes are interesting alternatives for noble metal catalysts which are widely used to catalyze the HER in acidic electrolyzers. Both catalysts have their own advantages even though they still lack behind in performance comparing e.g. to platinum catalysts. Mo$_2$C has simple synthesis route and thus is scalable for industrial applications which is relevant in the search for new catalyst materials for real applications. As the catalyst materials are abundantly available and cheap there is a potential to develop the electrolyzer cell in a manner than can utilize higher loadings of the catalyst and raise the performance. This is contrary approach than with platinum as it is scarce and expensive raw material. While N-FWCNTs are also based on earth-abundant elements the catalytic activity is lower than with Mo$_2$C nanoparticles. Pub. III was only the second time that the activity of nitrogen functionalized carbon nanotubes towards the HER has been reported and thus, there are still plenty of opportunities to better understand and optimize the catalytic features of the tubes. Both catalysts showed reasonable stability in a long-term electrolyzer experiments.
The effect of pH on the HER currents and the possibility to extract information of the reaction mechanism have not been widely used previously. This is an interesting approach to better understand what really happens on the electrode surface. Usually only Tafel slope analysis have been used to understand the HER mechanism but its usability is limited. This pH analysis gives another alternative or supplementary approach.

Research of catalysts with various temperatures, pHs and electrolytes has risen the awareness that great care should be taken when comparing results with different catalysts. Pub. II was referred by a review article [98] especially for the research done with varying conditions.

The combination of experimental and computation analysis in Pub. III yielded information that would not have been able to provide without this combination. The experimental research could not answer the question why the N-FWCNT catalyst is active even though earlier calculations showed no activity. Without the experimental research showing that the catalyst is active for the HER the computational researcher would not have had a reason and a direction how to find right conditions for the calculations proving the effect of nitrogen functionalization towards the HER.

To continue with the research, next interesting topics would be to use charge transfer resistance obtained from impedance spectroscopy. This might be relevant addition to the methods used for reaction mechanism analysis in additional to the traditional Tafel slope and pH analysis. It has been used in situation when the log $i$ vs. potential does not form an unambiguous slope.

Another aspect would be to further develop the concept of pH variation as a tool to analyze the HER reaction mechanism. This should be done as controlled and well-known environment as possible. Current catalyst research practicalities are widely different from one research group to another. The more tools there are to analyze the reaction and thus understanding the underlying phenomenon, the better comparisons can be done between different researches.
References

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