# Rotating ring-disc electrode voltammetry for the evaluation of molybdenum dichalcogenide nanostructures

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# Abbreviations

#### General

- ${\bf A}$  Area
- a Tafel intercept
- Ag/AgCl Silver/ silver chloride
  - $\alpha\,$  Transfer coeficient or partition coefficient
  - $\beta\,$  Peak broadening
  - $\mathbf{C}$  Concentration
  - ${\bf D}\,$  Diffusion constant
  - ${\bf d}\,$  Lattice spacing
  - $\delta_d$  Hydrodynamic diffusion layer
  - $\delta_f$  Layer thickness
  - $\Delta G$  Gibb's free energy
  - $\Delta E$  Peak separation
    - $\mathbf{E}$  Energy
  - $\mathbf{E}_{1/2}$  Reaction half potential
    - e Elementary charge
  - EDXS Energy-dispersive X-ray spectroscopy
    - $\eta~$  Over potential or collection efficiency
    - ${\bf F}\,$  Faraday constant
  - ${\bf HER}\,$  Hydrogen evolution reaction
  - ${\bf I}~{\bf or}~{\bf i}~{\rm Current}$ 
    - J Exchange current density
    - ${\bf j}$  Mass flux
    - ${\bf K}\,$  Shape factor
    - ${\bf k}\,$  Reaction rate constant
    - $\mathbf{k}_B$  Boltzmann constant
      - $\lambda$  Wavelength
  - milli-Q Deionized water with a resistivity of  $18.2 \text{ M}\Omega \text{ cm}$ 
    - **n** Number of electrons or integer
    - $\nu\,$  Kinematic viscosity

- $\omega$  Angular frequency
- **OER** Oxygen evolution reaction
  - $\phi~$  Work function
  - ${\bf Q}$  Charge
  - ${\bf R}\,$  Ideal gas constant
  - $\mathbf{r}$  Radius
- **RDE** Rotating disc electrode
- **RHE** Reversible hydrogen electrode
  - $\rho~{\rm Density}$
- ${\bf rpm}$  Rotations per minute
- **RRDE** Rotating ring-disc electrode
  - ${\bf SHE}\,$  Standard hydrogen electrode
- ${\bf STEM}\,$  Scanning transmission electron microscopy
  - **T** Temperature
  - $\mathbf{t}$  Time
  - ${\bf TEM}\,$  Transmission electron microscopy
    - $\tau\,$  Mean crystalline size
    - $\theta\,$  Angle or Bragg angle
    - ${\bf TS}\,$  Tafel slope
  - **XRD** X-Ray diffraction
  - **XPS** X-Ray photoelectron spectroscopy
    - ${f Z}$  Vertical distance

#### Chemicals

- $\mathbf{H}^+$  Proton
- HCl Hydrogen chloride
- $HNO_3$  Nitric acid
- $\mathbf{H}_2\mathbf{O}_2$  Hydrogen peroxide
- $\mathbf{H}_2 \mathbf{SO}_4$  Sulphuric acid
- $KFe(CN)_6 \cdot 3H_2O$  Potassium ferrocyanide trihydrate
  - $\mathbf{KNO}_3$  Potassium nitride
    - InP Indium phosphide
    - ${\bf KCl}$  Potassium chloride

 $\mathbf{MoS}_2$  Molybdenum sulphide

- $\mathbf{MoS}_{x}\mathbf{Se}_{(2-x)}$  Molybdenum sulphoselenide
  - $\mathbf{MoSe}_2$  Molybdenum selenide
  - ${\bf MoXY}$  Molybdenum sulphoselenide compound
  - $\mathbf{NH}_4\mathbf{Cl}$  Ammonium chloride
  - $\mathbf{N}_{2}\mathbf{H}_{4}\cdot\mathbf{H}_{2}\mathbf{O}$  Hydrazine hydrate
- $Na_2MoO_4$ ·  $2H_2O$  Sodium molybdate dihydrate
  - $Na_2S \cdot 9H_2O$  Sodium sulfide nonahydrate
- $\mathbf{Na}_{2}\mathbf{WO}_{4} \cdot \ \mathbf{2H}_{2}\mathbf{O}$  Sodium tungstenate dihydrate
  - $\mathbf{OH}^-$  Hydroxide
    - ${\bf Se} \ {\rm Selenium}$

# 1 Introduction

#### 1.1 Motivation

The increasing energy demand of modern society is probably one of the biggest challenges we're facing. By 2050 the assumed global consumption will be about 40.8 TW.<sup>[1]</sup>. Therefore we have the need to find new renewable energy sources and/or storage methods to cope with the increasing demand. One popular approach is to use solar energy, which has the disadvantage that the energy production is highly fluctuating, depending on the weather. Furthermore there are limited storage options which can lead to a failure in energy gathering during peak times ( when a lot of energy is produced) to be efficiently utilised during times of high demand (such as winter).

One approach to this problem is to store the energy in chemical bonds, as plants do. A typical method is to split water into oxygen and hydrogen. The reverse reaction can then be performed to convert that stored energy into usable forms such as mechanical or electrical energy by using technologies such as combustion engines or fuel cells, respectively. The advantage of such a solution would be that the storage capability would enable society to store energy during peak times in production, which relieves the grid and energy can be produced in times of high demand. The production of hydrogen is currently too expensive to cope with the task of a large scale production due to the fact that platinum is used as a catalyst. Therefore scientists have started to search for alternatives and found that transition metal dichalcogenides have shown to be promising candidates.<sup>[2][3][4][5]</sup>

The following sections will therefore have a closer look at the hydrogen production, why transition metal dichalcogenides are promising catalysts, and introduce the goals and approach of this thesis.

#### 1.2 Water splitting and the hydrogen evolution reaction

One way to store energy in chemical bonds is the splitting of water into hydrogen and oxygen, shown in eq.1.1. The needed Gibb's free energy under standard conditions is  $\Delta G = 237.2 \text{ kJ mol}^{-1}$ . Using the Nernst equation (2.7) one can calculate the required potential per electron transfer which is  $\Delta E^0 = 1.23 \text{ eV}$  and corresponds to the wavelength of approx. 1000 nm. Therefore the splitting of water would be feasible using sunlight.

$$H_2 O \to H_2 + \frac{1}{2}O_2 \tag{1.1}$$

The process of water splitting is often divided into the two subreactions occuring at the different electrodes, namely the hydrogen evolution reaction (HER) and the oxygen evolution reaction (OER). By looking at the standard potentials one can see that the HER should take place without any applied potential (vs. standard hydrogen electrode (SHE)), while the OER takes place at 1.23 eV (vs. SHE). In reality, higher potential are needed to overcome the reaction barrier.<sup>[6]</sup> In this project, only the HER will be studied due to the limited time.

The energy to drive the HER is applied by an electrical potential. The needed potential to start the reaction is called overpotential. Instead of using electrical energy, it would revolutionary if one could use sun light directly which further reduces losses by avoiding energy conversion processes, which are never perfect. The HER will be discussed in more detail in sec.2.2.

#### **1.3** Why transition metal dichalcogenides?

Because high overpotentials are energetically inefficient, catalysts are often used to lower this energy barrier for the conversion. To be a good catalyst for a reaction the reactant  $(H^+)$  needs to be able to bind strong enough to the catalyst's surface for the reaction to occur but weak enough for the product  $(H_2)$  to diffuse away and freeing the reaction site for the next reactant. This principle has been found and first described by Paul Sabatier.<sup>[7]</sup> Platinum is currently the most used due to the fact that it reduces the needed overpotential to drive the reaction almost to 0 V, which can also be seen in fig.1.1. Nøskov et al. investigated the catalytic properties of different material regarding the HER and found that as already experimentally known platinum showed the best performance.<sup>[3]</sup>



Figure 1.1: Current density versus Gibb's free energy by Nøskov et al.<sup>[3]</sup>

Nøskov et al. predicted later on that  $MoS_2$  nanoparticles <sup>[4]</sup> would be a good catalyst for the HER using density function theory. They also investigated the actives of  $MoSe_2$  and  $WSe_2$  in 2014 and found that it was mainly the edge sites which acted as reaction center.<sup>[5]</sup> In the last years the investigation of transition metal dichalcogenides had a huge increase and are proving to be one of the most promising candidates for industrial applications.<sup>[8][9][10][11][12][13][14][15][16]</sup> The properties of  $MoS_2$  will be discussed in more detail in sec.2.1.2.

#### 1.4 Scope of this thesis

The aim of this thesis is to produce photocatalytic devices and characterise them using transmission electron microscopy (TEM) and X-Ray diffraction (XRD). To construct those devices, InP quantum dots (supplied by Geoffry Laufersky, Victoria University Wellington) and/or NiO with coumarin combined with a nanostructured MoXY electrocatalyst are used. The MoXY compounds are obtained by:

- Hydrothermal methods.
- Collaboration with Yuta Nakayasu (Tohoku University Japan), Geoff Waterhouse (Auckland University NZ) and/or Mark Waterland (Massey University NZ)

In a last step the fabricated devices are tested regarding their catalytic and photocatalytic properties using rotating ring-disk electrode (RRDE) voltametry to quantify the amount of produced hydrogen. For the photocatalytic measurements a solar simulator is combined with the RRDE.

### 2 Theory

#### 2.1 MoXY

Transition metal dichalcogenides such as MoXY compounds exhibit a similar 2d structure similar to graphene. The atoms are covalently bound into planar layers, with interlayer interactions being dependent on van der Waals forces. As  $MoS_2$  is the most studied compound of the transition metal dichalcogenide family, it's properties will be elaborated in sec.2.1.1 before the different dichalcogenides will be discussed in sec.2.1.2.

#### 2.1.1 Properties of $MoS_2$

The atomic structure of  $MoS_2$  has been historically controversial due to the fact that most scientists were not aware that different allotropes existed. The phase of  $MoS_2$  was often not reported and any phase which deviates from the 2H phase, as discussed later, was denoted as by  $1T.^{[17]}$ 

By today 2 polytypes (2H and 1T) are known which can build 5 allotropes of  $MoS_2$ , denoted by 2H, 3R, 1T, 1T' and 1T" as shown in fig.2.1. They all can occur within the same sample and have shown to be challenging to separate.<sup>[18]</sup>



(Top) Mo atoms are represented as teal spheres, S atoms as gold spheres. (Bottom) From left to right, relative stability in eV, lattice parameters a, b and α, Mo-Mo distance, and band gap E<sub>g</sub> (eV) based on Perdew-Burke-Ernzerhof (PBE) and Heyd-Scuseria-Ernzerhof (HSE) exchange-correlation functionals.

Figure 2.1:  $MoS_2$  allotropes with structural parameters predicted with DFT by Chou et al.<sup>[17]</sup> As the 2H phase is the thermodynamically most stable, all other phases are referenced with their relative stability towards the 2H phase.

#### The 2H and 3R phase

The 2H phase, also known as "molybdenite", is the thermodynamically most stable and therefore the most abundant in nature.<sup>[17]</sup> It is trigonal prismatic and has a hexagonal lattice projection. As a consequence of this orientation the electronic configuration introduced by the crystal-field splitting generates three degenerated states in the d-orbitals: the  $d_{z^2}$  state is the lowest and fully occupied, while the two upper levels are unoccupied and formed degenerately from the  $d_{x^2-y^2,xy}$  and  $d_{xz,yz}$  states respectively.<sup>[19]</sup> This semiconducting nature exhibits an indirect bandgap of 1.2 eV in it's bulk form.<sup>[20]</sup> As MoS<sub>2</sub> is exfoliaded it's bandgap changes up to a direct bandgap of 1.9 eV for a monolayer.<sup>[21][22]</sup> As a consequence of the direct bandgap transition, MoS<sub>2</sub> structures smaller than 5 nm are photoluminescent with the bandgap at the K-point of the Bernoulli zone.<sup>[22]</sup>

In Raman spectroscopy the 2H phase shows an  $E_{2g}^1$  and an out of plane  $A_{1g}$  peak at 380 cm<sup>-1</sup> and 404 cm<sup>-1</sup>, respectively.<sup>[23]</sup>

The 3R allotrope is build up from the 2H polytype and has a rhombohedral symmetry due to the different stacking order. It is also a natural occurring form often found in mineralogy, but is not of much technological interest, as the interesting properties of  $MoS_2$  do not occur in bulk material.<sup>[24]</sup>

#### The 1T-like phases

As the 1T' and 1T" phase are superstructures of the 1T phase, the mixture of the three phases are referred herein as "1T-like" phase in this thesis. "1T-like"  $MoS_2$  compounds have shown to be significantly more catalytic than the semiconducting 2H phase.<sup>[11]</sup>

The 1T phase is mainly obtained using lithium extrafolation.<sup>[25]</sup> In contrast to the 2H phase it is octahedral, has a triangular lattice projection and has two degenerate d-orbital electronic states in the d-orbitals. The  $d_{xy,xz,yz}$  is partially filled with two electrons, while the  $d_{x^2-y^2,z^2}$  state is empty.<sup>[19]</sup> The 1T phase is therefore metallic and the partially filled orbital is likely responsible for it being the least stable of the allotropes. As it is metastable and will convert into 2H if it is annealed at temperatures above 100 °C. Furthermore it is dynamically unstable and therefore tends to form the 1T' or 1T" phase.<sup>[17]</sup>

In contrast to the 2H phase, the 1T phase shows three Raman peaks often denoted by  $J_1$ ,  $J_2$  and  $J_3$  in the region of 100-350 cm<sup>-1</sup>.<sup>[18]</sup>

Interestingly, adsorbates and vacancies have shown to stabilise the metallic phase where as hydrogen adsorption causes a decay into the 1T' phase (often via the T" phase).<sup>[17][26]</sup>

The 1T' phase is a 2x1 superstructure of the 1T phase and has a zig-zag lattice projection. Furthermore, the structure has a lattice distortion which opens up a small bandgap.<sup>[17][26]</sup> Therefore the 1T' phase is semiconducting but behaves quasi-metallic due to the small band gap size.

In the Raman spectrum it shows five additional peak while the  $E_{2g}^1$  peak disappears.<sup>[26]</sup> Furthermore it is the most stable of the 1T-like phases, as shown by the relative stability in fig.2.1. DFT predictions have shown that it is even more stable than 2H when hydrogen is adsorbed to the surface.<sup>[26]</sup>

The 1T" phase consists of a 2x2 superstructure of the 1T phase. It is probably the least understood of all phases. It shows a rhomboidal structure where trimerized pockets of molybdenum-molybdenum clusters form.<sup>[17]</sup>

Despite many improvements to synthetic and post-processing procedures, it remains challenging to separate and characterize the different phases. The most common approaches are to use Raman spectroscopy and X-Ray photoelectron spectroscopy (XPS). By deconvolution of the 3d molybdenum XPS peak the 2H and 1T-like phase can be separated.<sup>[18]</sup> For further insight high resolution TEM/Scanning TEM (STEM) is needed.

#### 2.1.2 MoXY compounds

MoSe<sub>2</sub> has been shown to have the same allotropes as MoS<sub>2</sub>. In contrast to MoS<sub>2</sub> and MoSe<sub>2</sub>, compounds involving mixed dichalcogenides are significantly less understood. Studies have shown that by doping MoS<sub>2</sub> with selenium the electronic states in the MoXY compound can be altered, enabling the tuning of the bandgap for semiconducting MoS<sub>2</sub>.<sup>[19]</sup> Additionally, by mixing the dichalcogenides structures, three highly reactive sites can be formed. The hydrogen evolution can now occur at the sulfur, selenium or vacancy/defect sites. Furthermore, MoS<sub>1</sub>Se<sub>1</sub> compounds have also shown to be more catalytic than unmixed compounds.<sup>[12]</sup>

#### 2.2 Hydrogen evolution reaction (HER)

As mentioned previously the generation of hydrogen is theoretically energetically neutral as the reactant and product have the same energy level. However, in order for the transformation to happen, a reaction barrier has to be overcome. This is one of the sources of the needed overpotential to drive the reaction.

There is a common consensus that the HER consists of two main steps in an acidic environment. First a proton  $(H_{aq}^+)$  from the solution adsorbs to the catalyst surface and gets reduced to elementary

#### 2.3. ELECTROCHEMICAL METHODS

hydrogen ( $H_{ads}$ ) as shown in eq.2.1.<sup>[27]</sup>

$$H_{aq}^+ + e^- \to H_{ads} \tag{2.1}$$

This process is known as the discharge or Volmer reaction. This can then lead to two different processes for hydrogen generation via either the Heyrovsky reaction shown in eq.2.2 or the Tafel reaction shown in eq.2.3.<sup>[27]</sup>

 $H_{ads} + H_{aq}^+ + e^- \rightarrow H_{2(g)}$  (2.2)  $H_{ads} + H_{ads} \rightarrow H_{2(g)}$  (2.3) In the Heyrovsky reaction a proton in the solution reacts with an adsorbed hydrogen atom to form a hydrogen molecule by a reduction. In the Tafel reaction two adsorbed hydrogen atoms combine to form a hydrogen molecule.<sup>[27]</sup>

As the reactant is H<sup>+</sup>, it is not surprising that the HER is pH dependent. As Strmcnik et al. showed, the HER is not mass transport limited for pH values  $\leq 2$  and only become mass transport limited for pH values of 2.5 and higher.<sup>[28]</sup>

#### 2.3 Electrochemical methods

In order to test the compounds for the HER, the samples were characterised with a variety of electrochemical methods introduced in this chapter.

In all electrochemical measurements, a three or four electrode setup was used, consisting of one counter, one reference, and one or two working electrodes. All potentials are measured between the working and the reference electrode while the currents are measured between the working and the counter electrode.

The measurements can be divided into three different measurements: linear sweeps, cyclic voltammograms, and rotating ring-disc electrode measurements. The first two will be discussed in the following sections before the rotating ring-disc electrode measurements are introduced in sec.2.3.4 to 2.3.6.

#### 2.3.1 Linear sweep

In a linear sweep measurement, the potential of the working electrode is linearly changed from an initial state to a predetermined final value with a set scan speed while the current response is measured. Such a measurement is shown in fig.2.2. Linear sweep measurements are commonly used to test the catalytic behaviour of compounds and often called polarization curves. The two main figures of interest are the overpotential and the onset potential.

The overpotential is usually reported as the potential where the current density reaches  $10 \text{ mA cm}^{-2}$ . This value correspond to a 10 % efficient solar-to-fuel conversion device, which is an important benchmark.<sup>[29]</sup>

Unfortunately, there are four ways to calculate the onset potential as shown in fig.2.2. The first definition uses the intercept between the linear equations fit to the maximum slope and the baseline of the sweep, yielding the green intercept at a potential of -0.195 V. The second definition is shown as the blue line and gives the potential where the current density starts to deviate from the baseline. The third definition uses the potential where a current density of 0.5 or 2 mA cm<sup>-2</sup> is reached, shown in orange or red respectively. In this thesis the first definition will be used as it is the least dependent on the sample quality and user interpretations. Unfortunately, many papers do not report which definition they use, which makes the comparison of onset potentials unreliable.<sup>[10][16][30][31][32]</sup>

The current density response at an electrode as a function of the overpotential  $(\eta)$  is described by the Butler-Volmer equation shown in eq.2.4, where  $J_0$  is the exchange current density,  $\alpha$  is the transfer coefficient of the partial reaction, n is the number of electrons involved, F is the Faraday constant, Ris the ideal gas constant and T is the temperature.

$$J = J_0 \{ exp(\frac{\alpha_a n F \eta}{RT}) - exp(-\frac{\alpha_c n F \eta}{RT}) \}$$
(2.4)

Assuming that the proton adsorption is the rate determining step, the Gibbs free energy  $\Delta G_{H^+}$ of the process is negative and the pH is 0, one can derive the rate constant  $k_0$  as a function of the exchange current  $i_0$  using the Langmuir isotherm approximation.<sup>[33]</sup> The rate constant is shown in eq.2.5, where  $k_B$  is the Boltzmann constant and e the elementary charge.

$$k_0 = -\frac{i_0}{e} (1 + exp(-\frac{\Delta G_{H^+}}{k_B T}))$$
(2.5)

Similarly, for a positive Gibbs free energy,  $k_0$  can be calculated as shown in eq.2.6.<sup>[33]</sup>

$$k_{0} = \frac{i_{0}}{e} \frac{(1 + exp(-\frac{\Delta G_{H^{+}}}{k_{B}T}))}{exp(-\frac{\Delta G_{H^{+}}}{k_{B}T})}$$
(2.6)



Figure 2.2: Different onset potential definitions. The green line indicates the definition by the intercept. The red and orange line are defined when a value of 2 or  $0.5 \text{ mA cm}^{-2}$  is reached respectively. The blue line is defined when the current starts to deviate.



Figure 2.3: Cyclic voltamogramm of ferro/ ferri cyanide. The definition of the reaction half potential  $E_{1/2}$  and the peak separation  $\Delta E$  are shown in red and blue, respectively.

#### 2.3.2 Cyclic voltammogram

A cyclic voltammogram is basically a combination of two or more linear sweeps. In the first step the potential is increased into one direction while the current response is measured. Directly after the first linear sweep the direction of the scan is inverted. If a reactive species is on the electrode surface it can be oxidized and/or reduced yielding in a duck-shaped curve as shown in fig.2.3. An oxidation process yields a positive current while a reduction shows a negative current. If only one of the processes is occurring the second peak will be missing, which is typical for an irreversible process. Two figures are typically reported, namely the reaction half potential  $E_{1/2}$  and the peak separation  $\Delta E$ . As shown in fig.2.3, the reaction half potential lies at the average of the oxidation and reduction peak maxima. The distance between the two peaks determines the peak separation  $\Delta E$ .

The Nernst equation describes the reduction or oxidation potential of an electrochemical half cell as a function of the standard electrode potential  $E^0$ , the temperature T and the activity of the investigated species. The activity a species is usually approximated by its concentration C ( $C_O$  for the oxidised and  $C_R$  for the reduced species). Furthermore, R is the universal gas constant, n the number of electrons transferred, and F the Faraday constant.<sup>[34]</sup>

$$E = E^0 + \frac{RT}{nF} ln(\frac{C_O}{C_R})$$
(2.7)

In the case of an ideal Nernstian behaviour, the peak separation can be calculated to be 59 mV at  $25 \ ^{\circ}C.^{[34]}$ 

#### 2.3.3 Tafel equation

The Tafel equation describes the behaviour of an electrode for a reaction shown in eq.2.8 where n is the number of electrons involved, O is the oxidized, and R the reduced species.

$$O + ne^- \leftrightarrow R$$
 (2.8)

The exchange current density  $(J_0)$  is the flow of charge in an electrochemical system in a thermodynamic equilibrium, see eq.2.9.

$$J_0 = J_a - J_c \tag{2.9}$$

In a kinetic equilibrium  $J_0$  is 0, if a more negative potential is applied  $J_c$  increased and  $J_a$  decreases and vice versa for a more positive potential. Therefore with a high enough overpotential the cathodic or the anodic current density is neglectable and the Butler-Volmer equation (eq.2.4) can be simplified to eq.2.10 or eq.2.11.

$$J = J_a = J_0 \{ exp(\frac{\alpha_a n F \eta}{RT}) \}$$
(2.10)  $J = -J_c = -J_0 \{ exp(-\frac{\alpha_c n F \eta}{RT}) \}$ (2.11)

By reforming eq.2.11, one obtains the Tafel equation which describes a linear dependency of the applied overpotential as a function of the logarithm of the current density, shown in eq.2.12.

$$\eta = \frac{2.303RT}{\alpha_c nF} \log(J_0) - \frac{2.303RT}{\alpha_c nF} \log(-J_c) = a - b * \log(-J_c)$$
(2.12)

The slope of the Tafel equation is a typically reported for catalysts, as it provides information about the rate determining step. At low Tafel slopes  $30 \text{ mVdec}^{-1}$  the recombination reaction is rate-determining while at higher slopes of about  $120 \text{ mVdec}^{-1}$  the discharge/ Volmer reaction becomes the limiting factor for the HER.<sup>[34]</sup> Stephan Fletcher showed furthermore that the Tafel slope can be derived from first order principle.<sup>[35]</sup>

#### 2.3.4 Rotating disc electrode theory

In contrast to most electrochemical methods, a rotating disc electrode (RDE) voltammetry uses a rotating disc as the name suggest and is therefore not a stationary measurement. It is one of the few cases for which the diffusion and convection equation derived from the Navier-Stokes equation can be solved.

Consider a flat disk with a radius r and an angular frequency  $\omega$  immersed in solution with a density  $\rho$  and a kinematic viscosity  $\nu$ . If the concentration is only a function of the distance to the electrode and the bulk concentration of the solution  $C_B$ , then the convective diffusion equation can be simplified to eq.2.13, where Z is the vertical distance from the electrode and D is the diffusion constant.

$$\nu_Z(Z)\frac{dC}{dZ} = D\frac{d^2C_F}{dZ^2} \qquad \qquad for \ 0 \le Z \le \infty \qquad (2.13)$$

Assuming that all material that reaches the electrode surface undergoes a reaction, one can derive the following boundary conditions:

$$C = 0 \qquad \qquad for \ Z = 0 \qquad (2.14)$$

$$C = C_B \qquad \qquad for \ Z = \infty \qquad (2.15)$$

At the disc surface (Z = 0), the concentration of the reactant is 0 as everything undergoes the reaction which is assumed to be fast (which is the case for high enough potentials). In the solution far from the electrode  $(Z = \infty)$ , the concentration is given by the initial bulk concentration  $(C_B)$ . The concentration can then be determined using numerical calculations as a function of the distance to the disk surface giving:

$$C(Z) = \frac{C_B}{1.611(\frac{D}{\nu})^{\frac{1}{3}}\sqrt{\frac{\nu}{\omega}}} \int_0^Z exp\Big(\frac{1}{D}\int_0^t \nu_Z(y)dy\Big)dt$$
(2.16)

The current measured produced by the mass flux at the electrode can then be calculated using:

$$I = nF\pi r^2 D(\frac{\partial C}{\partial t})_{Z=0}$$
(2.17)

Giving the following expression which is known as Levich current.<sup>[36]</sup>

$$I_L = 0.62nF\pi r^2 D^{\frac{2}{3}} C_B \nu^{-\frac{1}{6}} \omega^{\frac{1}{2}}$$
(2.18)

The mass flux at the disk surface j is given by:

$$j = D(\frac{\partial C}{\partial Z})_{(Z=0)} = 0.62D^{\frac{2}{3}}C_B\nu^{-\frac{1}{6}}\omega^{\frac{1}{2}}$$
(2.19)

The hydrodynamic diffusion layer  $\delta_d$  can be calculated using  $\delta_d = \frac{DC_B}{j}$  giving:

$$\delta_d = 1.6D^{\frac{1}{2}}\nu^{-\frac{1}{6}}\omega^{-\frac{1}{2}} \tag{2.20}$$

A more detailed derivation can be found in appendix D.1. The rotation of the electrode has two significant outcomes. Due to the rotation, the transport of reactive species far away from the electrode is only defined by the convection. Close to the electrode it is defined by the diffusion. The distance where those two regimes meet is called the hydrodynamic diffusion layer  $\delta_d$  which is significantly smaller than in measurements where the solution is motion less.<sup>[36]</sup>

A typical RDE voltametry curve is shown in fig.2.4. To start with a potential is applied where no reaction occurs, in this case 0 V. The potential is then stepwise increased in one direction until a certain potential, here about -0.25 V, where the reaction starts to occur. As it is limited by the reaction rate at this point, it will increase until it reaches the limiting current (at around -0.7 or -0.85 V, respectively). At this point each reactant that reaches the electrode undergoes a reaction, therefore the current is limited by the mass transport, which can be described by the Levich current.

#### 2.3.5 Thin film coated rotating disc electrode

As the electrode will be coated with catalyst in the experiments the influence of a thin film will be discussed here. The approach to solve this was shown back in 1979 by Gough et al.<sup>[37]</sup>

Consider a RDE electrode covered with a thin film. The film has a thickness  $\delta_f$ , the concentration of the reactant in the film is  $C_f$ , and it's diffusion constant in the film is  $D_f$ . Furthermore, no convection is assumed in the film. The surface of the electrode is set to be at  $Z = -\delta_f$  and the solution interface is at Z = 0. Therefore the boundary conditions have to be adjusted.

In the film the diffusion equation is given by:

$$\frac{d^2 C_f}{dZ^2} = 0 \qquad \qquad for \ -\delta_f \le Z \le 0 \qquad (2.21)$$

The reaction is assumed to be fast enough so that the concentration at the electrode surface is:

$$C = 0$$
 for  $Z = -\delta_f$  (2.22)  
THe concentration in solution is given as before by eq.2.13 close to the electrode and far in the solution by eq.2.15.

At the thin film-solution surface, the mass must be conserved, therefore eq.2.23 holds.

$$D_f \left(\frac{dC_f}{dZ}\right)_{Z=0} = D\left(\frac{dC}{dZ}\right)_{Z=0}$$
(2.23)

Furthermore the partition coefficient  $\alpha$  at the membrane surface is defined as:

$$\alpha = \frac{C_f}{C} \tag{2.24}$$

With a similar approach as before, the convective diffusion equation can be solved. (For more details see appendix D.2)

The measured current is given by:

$$I_{meas} = nF\pi r^2 D^{\frac{2}{3}} C_B \nu^{-\frac{1}{6}} \omega^{\frac{1}{2}} \left(\frac{1}{1+\frac{D\delta_f}{\alpha D_f \delta_d}}\right) = I_L \left(\frac{1}{1+\frac{D\delta_f}{\alpha D_f \delta_d}}\right)$$
(2.25)

where  $I_L$  is the Levich current in absence of the membrane as given in eq.2.18.

By taking the inverse one can obtain

$$\frac{1}{I_{meas}} = \frac{1}{I_L} + \frac{1}{I_f}$$
(2.26)

Where  $I_f$  is the current in the thin film. Using eq.2.20 and eq.2.26 it can be rewritten as:

$$I_f = nFAC_B\alpha D_f \delta_f^{-1} = nFAC_f D_f \delta_f^{-1}$$
(2.27)

As one can see  $I_f$  is independent of the rotation speed. Therefore by using eq.2.26 one can plot the inverse of the current as a function of  $\omega^{-1/2}$ . As the Levich current  $I_L$  is proportional to  $\omega^{1/2}$ , the inverse of the Levich current will be proportional to  $\omega^{-1/2}$ . In the limit when the rotation speed increases towards infinity,  $\omega^{-1/2}$  goes towards 0,  $I_L^{-1}$  becomes neglectable, and the measured current is equal to  $I_f^{-1}$ . In other words  $I_f^{-1}$  is given by the intercept with the y axis in fig.2.5.



Figure 2.4: Example of a RDE voltametry curve. With increasing rotation speed the current increases.



Figure 2.5: Typical Koutechy Levich plot which is used to determine kinetic parameters.

#### 2.3.6 Rotating ring-disc electrode theory

A rotating ring-disk electrode (RRDE) is an electrode configuration which is an offspring of the RDE. The RRDE was first described by the Levich theory and lateron mathematically derived by Albery et al.<sup>[38][39][40][41][42]</sup> A scheme of a typical electrode is shown in fig.2.6.

During a measurement the electrode is rotated at a fixed rotation speed  $\omega$  which introduces convection in the solution. The amount of current flowing to the disk and the ring electrode is then determined by the mass transport of reactant to the electrode surface, as in the case of RDE. If a molecule reaches the disc surface, it can be reduced if the applied potential is negative enough. Afterwards, the convection of the rotating electrode causes the reduced species to move outwards to the ring, where it can be oxidized by a positive potential. This configuration enables the production of a molecule, such as H<sub>2</sub> and it's detection at the ring.

The most used technique is the RRDE voltametry, where the ring potential is kept at a fixed potential while the disc potential is stepped linearly into one direction. Typically produced ring and disc currents are shown in fig.2.7.





Figure 2.7: Typical RRDE curve.

At around 0.3 V the reactant gets oxidized and a positive current is measured. At the same time a negative current is observed at the ring, as the product from the disk is reduced by the applied constant potential. When the potential is high enough (around 0.6 V) the current starts to be constant and a limiting current is reached, as in the case for a normal RDE. The same can be seen for the ring current as the amount of product being brought to the ring becomes constant.

As one can see at the different current scales in fig.2.7, the ring current is significantly smaller as not all molecules reach the ring surface. Therefore the collection efficiency  $\eta$  is defined as:

$$\eta = \frac{-I_{lim}^{ring}}{I_{lim}^{disc}} \tag{2.28}$$

Albery et al.<sup>[38]</sup> showed that the collection efficiency for an electrode is defined by their geometrical configuration (radii of the disk and ring). According to the manufacturer, the electrode used in the experiments in this thesis has a theoretical collection efficiency of 25%.<sup>[43]</sup> In practice, the collection efficiency is usually determined experimentally by using a well known redox couple, for example ferro/ ferri cyanide.

RRDE voltametry is typically used to compare reaction path ways. For example, consider a molecule which can be oxidized at the disc and afterwards react with something in the solution or be detected at the ring. If the potential at the ring is different for the oxidized species and the reacted species, one can determine how much of the oxidized species reacts and compare the two reaction pathways.<sup>[44][45]</sup>

#### 2.3.7 Required setup

To measure two working electrodes at the same time a bipotentiostat is required. It is a combination of various resistors and operational amplifiers. The currents of the two working electrodes are fed into a IV converter (also known as current follower) and read out at it's output. The potential is measured between the first working electrode and the reference. This signal is used in a feedback loop and is connected to the control amplifier which controls the counter electrode. The second working electrode can be held at a set potential with respect to the first working electrode. <sup>[34]</sup>

#### 2.4 X-ray powder diffraction

X-ray diffraction (XRD), as the name implies, is a technique which uses X-rays and analyses their diffractive reflectance when introduced to a sample. If a sample is crystalline, the incoming X-rays will be diffracted at the lattice planes of the sample. According to Braggs law, constructive interference between the diffracted beams only occurs if the wavelength of the incoming beam is a multiple of the lattice spacing in the crystal, see eq.2.29 where n is an integer,  $\lambda$  the wavelength, d the lattice spacing, and  $\theta$  the angle of the incoming wave.

$$n\lambda = 2dsin(\theta) \tag{2.29}$$

Furthermore the diffracted wave will keep its wavelength due to elastic scattering and have a reflection angle of  $\theta$  with respect to the sample surface and therefore have a scattering angle of  $2\theta$ .

In contrast to diffraction of a single crystal, the use of a powder sample has some general factors to consider. It assumes that the powder consists of small crystals called crystallites. These are randomly oriented in the sample and therefore effects due to orientation and rotation will interfere. Often the sample is rotated during a measurement to minimize effects caused by texture. Due to the fact that the crystallites are very small, the reduced number of total lattice planes causes fewer signals that interfere resulting in a peak broadening described by the Scherrer equation (eq.2.30), where  $\tau$  is the mean size of the crystallites, K is the shape factor,  $\lambda$  the wavelength,  $\beta$  the peak broadening (FWHM), and  $\theta$  the Bragg angle. Hence the Scherrer equation can be used to determine the size of such crystallites.

$$\tau = \frac{K\lambda}{\beta\cos(\theta)} \tag{2.30}$$

Further effects that occur are the increase of background signal due to amorphous material, broadening in the peaks due to lattice defects, and different strain in the crystallites.<sup>[46]</sup>

# 2.5 Transmission electron microscopy and energy-dispersive X-ray spectroscopy

In transmission electron microscopy (TEM) submicroscopic samples can be observed using an electron beam. The electrons have a small Broglie wavelength which enables high resolution images up to an atomic resolution. The electron beam is generated in an electron gun which uses a potential to extract the electrons from the emitter, which are afterwards focused using various lenses and apertures in a high vacuum. When the electron beam reaches the samples, the electrons can pass through the material or be scattered. At the bottom of the microscope a detector records the transmitted electrons. Many TEMs can also be used to scan an image instead of taking the whole image at once. The scanning TEMs are called STEM and enable a higher resolution of the individual points.

When an electron from the beam scatters inelastically with an electron from an atom, it can excite the electron from the element into a higher energetic state. When the excited electron relaxes into his ground state, it emits a photon with the energy of the difference between the two states. Energy-dispersive X-ray spectroscopy (EDXS) analyses the emitted X-ray radiation of a sample. The electromagnetic emission spectrum is element specific and enables therefore the differentiation of elements. By combining an EDXS detector with an STEM a elemental map can be generated giving an insight into the material composition and its spacial distribution.

#### 2.6 X-ray photoelectron spectroscopy

X-ray photoelectron spectroscopy (XPS) or also called electron spectroscopy for chemical analysis (ESCA) is a technique in which an X-ray beam is irradiated on a sample which causes electrons of the surface to escape in such a way that the kinetic energy and the number of electrons are detected. The binding energy can be calculated using eq.2.31, where  $E_{binding}$  is the binding energy,  $E_{photon}$  is the energy of the incident photon,  $E_{kinetic}$  is the kinetic energy of the measured electrons and  $\phi$  is the spectrometer work function.

$$E_{binding} = E_{photon} - (E_{kinetic} + \phi) \tag{2.31}$$

Since the binding energy of a material is depending on its electron shell structure it is material specific. Furthermore, change of the chemical environment, for example metal-metal vonds versus metal-oxide bonds induces a chemical shift.

XPS is highly surface sensitive as only electrons in the top few nm are reaching the detector.<sup>[47]</sup>

## 2.7 Raman spectroscopy

In Raman spectroscopy the sample is illuminated with a laser of a known wavelength and the inelastically or Raman scattered light is collected using a lens and analysed by a monochromator. Depending on the vibrational, rotational, and other low-frequency modes of the sample, peaks are observed at certain wavelengths called Raman shifts. Those are material dependent and can be used as molecular fingerprint.<sup>[48]</sup>

# 3 Experimental

#### 3.1 Materials

All materials were used as provided by the supplier unless mentioned otherwise.

Sodium molybdate dihydrate (Na<sub>2</sub>MoO<sub>4</sub>· 2H<sub>2</sub>O), sodium sulfide nonahydrate (Na<sub>2</sub>S · 9H<sub>2</sub>O), elemental selenium (Se) powder, and a 5% (w/v) Nafion 117 solution were aquired through Sigma-Aldrich. The conc. hydrogen chloride (HCl) was supplied by AnalaR NORMAPUR while potassium chloride (KCl) and 70% nitric acid (HNO<sub>3</sub>) were from Pure Science. Ammonium chloride (NH<sub>4</sub>Cl) and the sulphuric acid (H<sub>2</sub>SO<sub>4</sub>) were obtained from Scientific & Chemicals Supplies. Hydrazine hydrate (N<sub>2</sub>H<sub>4</sub>) and potassium ferrocyanide trihydrate (K<sub>4</sub>Fe(CN)<sub>6</sub>·3H<sub>2</sub>O) were supplied by BDH Chemicals Ltd. And last but not least, hydrogen peroxide (H<sub>2</sub>O<sub>2</sub>) was supplied by Pronalys (ThermoFisher Scientific), the carbon black from Alfa Aesar, and the potassium nitride (KNO<sub>3</sub>) from Vickers Laboratories Ltd.

#### 3.2 Synthesis

#### $MoS_2$

 $MoS_2$  was produced using the approach published by Mokari-Manshadi et al.<sup>[49]</sup>.  $Na_2MoO_4 \cdot 2H_2O$  (730 mg, 3.0 mmol, 1 eq.) was dissolved in 30 mL milli-Q water and  $Na_2S \cdot 9H_2O$  (2.1 g, 9.0 mmol, 3 eq.) was added. 2.5 mL conc. HCl was added to adjust the pH to 1 which changed the clear solution to a dark red colour. The mixture was heated in a 100 mL Teflon-lined autoclave at 180 °C over the course of 25 h. The black precipitate of the solution was separated by centrifugation at 10'000 rotations per minute (rpm) for 10 min. and washed three times with milli-Q water. The isolated solid was dried under vacuum over night.

#### $MoS_2$ at 160 °C and at 200 °C

 $MoS_2$  as also obtained using the approach of Wang et al.<sup>[50]</sup>.  $Na_2MoO_4 \cdot 2H_2O$  (171 mg, 0.71 mmol, 1 eq.) was dissolved in 10 mL milli-Q water and 8 mL  $N_2H_4$  was added and the solution was stirred for 30 min. (2.7 g, 11 mmol, 16 eq.)  $Na_2S \cdot 9H_2O$  was dissolved in 10 mL milli-Q water and 10 mL concentrated HCl was added dropwise to obtain the yellowish solution. The two solutions were combined and stirred for 10 min. Afterward the mixture was transfered in a 100 mL Teflon-lined autoclave and heated in an oven overnight (15 h) at 160 °C or 200 °C, respectively. The black precipitate was filtered and dried under vacuum over night.

#### $\mathbf{MoS}_{0.5}\mathbf{Se}_{1.5}$

 $Na_2MoO_4 \cdot 2 H_2O$  (171.0 mg, 0.71 mmol, 1 eq.) was dissolved in a mixture of 10 mL milli-Q water and 8 mL  $N_2H_4$  and stirred for 30 min.  $Na_2S \cdot 9 H_2O$  (84.3 mg, 0.36 mmol, 0.5 eq.) and Se (84.5 mg, 1.07 mmol, 1.5 eq.) were dissolved in 10 mL milli-Q water and 10 mL conc. HCl and afterwards combined with the  $Na_2MoO_4$  solution and stirred for another 10 min. 22 mL milli-Q water were added to get a total volume of 60 mL which were poured into a 100 mL Teflon-lined autoclave and heated at 200 °C over night (16.5 h). The black precipitate was washed with milli-Q water, filtered, and dried under vacuum over night.

#### $\mathbf{MoSSe}$

 $Na_2MoO_4 \cdot 2 H_2O$  (171.0 mg, 0.71 mmol, 1 eq.) was dissolved in a mixture of 10 mL milli-Q water and 8 mL  $N_2H_4$  and stirred for 30 min.  $Na_2S \cdot 9 H_2O$  (170.5 mg, 0.71 mmol, 1 eq.) and Se (56.0 mg, 0.71 mmol, 1 eq.) were dissolved in 10 mL milli-Q water and 10 mL conc. HCl and afterwards combined with the  $Na_2MoO_4$  solution and stirred for another 10 min. 22 mL milli-Q water were added to get a total volume of 60 mL which were poured into a 100 mL Teflon-lined autoclave and heated at 200  $^{\circ}$ C over night (16.5 h). The black precipitate was washed with milli-Q water, filtered, and dried under vacuum over night.

#### $\mathbf{MoS}_{1.5}\mathbf{Se}_{0.5}$

 $Na_2MoO_4 \cdot 2 H_2O$  (171.0 mg, 0.71 mmol, 1 eq.) was dissolved in a mixture of 10 mL milli-Q water and 8 mL  $N_2H_4$  and stirred for 30 min.  $Na_2S \cdot 9 H_2O$  (255.7 mg, 1.07 mmol, 1.5 eq.) and Se (28.0 mg, 0.36 mmol, 0.5 eq.) were dissolved in 10 mL milli-Q water and 10 mL conc. HCl and afterwards combined with the  $Na_2MoO_4$  solution and stirred for another 10 min. 22 mL milli-Q water were added to get a total volume of 60 mL which were poured into a 100 mL Teflon-lined autoclave and heated at 200 °C over night (15 h). The black precipitate was washed with milli-Q water, filtered, and dried under vacuum over night.

#### $MoSe_2$

Following the procedure of Tang et al.<sup>[31]</sup> (483.0 mg, 2.0 mmol, 1 eq.) Na<sub>2</sub>MoO<sub>4</sub>· 2H<sub>2</sub>O was dissolved in 50 mL milli-Q water and (315.0 mg, 4 mmol, 2 eq.) elemental Se powder was dispersed in 10 mL N<sub>2</sub>H<sub>4</sub>. The Se solution was slowly added to the Na<sub>2</sub>MoO<sub>4</sub> under constant stirring at room temperature and afterwards transferred in a 100 mL Teflon-lined autoclave, where it was heated in an oven at 200 °C for 22 h. The black compound was collected by chentrifugation at 7000 rpm for 5 min, washed three times with milli-Q water, and collected by centrifugation at the same speed. The product was first air dried and then vacuum dried over night.

#### 3.3 Measurements

#### 3.3.1 Electrochemical measurements

All electrochemical measurements were obtained using a PINE WaveDriver bipotentiostat. The onset potential and overpotential were defined as mentioned in sec.2.3.1. Furthermore, the PINE gold or glassy carbon rotating ring-disc E6R1 electrode was used with disc diameter of 5.0 mm, an inner ring diameter of 6.5 mm and an outer ring diameter of 7.5mm. The modulated speed rotator from PINE was used to rotate the electrode. A platinum electrode was used as a counter electrode and a reversible hydrogen electrode (RHE) from ALS Co. Ltd., a single junction silver/ silver chloride (Ag/AgCl) reference electrode from PINE (F0DR-0021), or a silver wire pseudoreference as reference electrode. The silver wire was cleaned with nitric acid prior to use and the potential was calibrated using the ferro/ ferri cyanide redox couple if not otherwise mentioned. The other reference electrodes were cleaned by rinsing with milli-Q water. All solutions were degassed for at least 60 min. with N<sub>2</sub> prior to the measurement. The deposition of the catalyst is described in sec.4.2.2.

#### Electrode cleaning

The electrodes were cleaned by manual polishing using first a  $0.3 \ \mu m$  alumina suspension from Allied High Tech Products Inc. and afterwards a  $0.05 \ \mu m$  alumina suspension from Buehler. The electrodes were then sonicated for 10 min. in ethanol and afterwards in milli-Q water.

For the gold electrodes the cleanliness was checked by CV's in  $0.5 \text{ M H}_2\text{SO}_4$ , which were continued until the two peaks at 1.2 V and 1.4 V were observed, as discussed in sec.4.2.1.

#### Aqua regia

Aqua regia is a strongly acidic solution where 1 eq. of  $HNO_3$  is added to 4 eq. conc. HCl. It is used to remove metal contaminations and dissolves even noble metals such as platinum and gold.

#### Piranha solution

#### 3.3.2 Stylus profilometer

All stylus profilometer measurements were performed at the university of South Australia by Jing-Hong Pai on a Bruker DektakXT stylus profilometer using a stylus force of 3 mg. 4 samples were prepared and measured, all with a duplicate. Fig.3.1 shows a scheme of the sample and the measurement directions. The inner circle has the dimensions of the disk electrode (5.0 mm diameter) while the outer circle is the area of the whole electrode (15.0 mm diameter). All samples were prepared on glass microscope slides which were cleaned with water and soap, toluene, ethanol and acetone before deposition. For the first two samples, 17.5 µL and 35.0 µL Nafion solution were

deposited covering the area of the outer circle. For the other samples,  $1.0 \text{ mg MoS}_2$  or  $1.1 \text{ mg MoS}_1\text{Se}_1$  were dispersed in 1 mL of a mixture



Figure 3.1: Measurement directions

of 0.2 mL ethanol and 0.8 mL milli-Q water by sonication. The corresponding solution was deposited drop wise in the inner circle and dried in air. Afterwards 17.5  $\mu$ L Nafion solution was deposited covering the area up to the outer circle. All samples were initially dried in air and afterwards dried over night under vacuum before shipping to South Australia.

#### 3.3.3 XRD

All XRD spectra were recorded on a Pan analytic X'PertPro with Cu K $\alpha$  source ( $\lambda = 1.54$  Å) with an applied tension of 45 kV and current of 40 mA. The background correction was performed using the Highscore software, provided by PANanalytical. The reference patterns were taken from International Centre of Diffraction Data (ICDD) database. A K value of 0.9 was assumed for the mean crystalline size calculation.<sup>[51]</sup>

#### 3.3.4 TEM and EDXS

All TEM studies and EDS measurements were conducted using a JEOL 2100F TEM with a field emission gun operated at 200 kV. The TEM images were obtained using the Gatan software. The JEOL JED-2300 detector was used for the EDS measurement together with the Analysis Station software.

#### 3.3.5 Raman spectroscopy

All Raman spectra were obtained on a LabRAM HR800 Raman system with an excitation wavelength of 514 nm. The investigated samples were directly placed as powder on a cleaned microscopy glass slides.

#### 3.3.6 XPS

All XPS data were measured by Colin Doyle at the university of Auckland on a Kratos Axis Ultra<sup>*DLD*</sup> with Al K<sub> $\alpha$ </sub> X-ray source (1486.69 eV) at a power of 150 W (10 mA emission current, 15 kV acceleration potential). The pass energy was 160 eV for the wide survey, 80 eV for narrow survey and 20 eV for the core level measurements. The wide survey scan was obtained by averaging 5 scans at a rate of 180 s per scan, the narrow surveys were obtained by averaging 10 scans at a rate of a 180 s per scan and the core level scans were obtained over 30 averaged scans at a rate of 60 s per scan. All samples were deposited as powder on carbon tape for the measurement.

# 4 Results and discussion

#### 4.1 Compound synthesis and characterization

In this section the synthesis and the characterization of the used compounds are discussed. After discussing the individual results a final summary of the characterization results is given in sec.4.1.7.

#### 4.1.1 Synthesis

In the following differences between the reported and the used synthesis are pointed out. All compounds were obtained according to the procedures in sec.3.2.

#### $MoS_2$

The first compound named  $MoS_2$  throughout this thesis was synthesised according to the procedure of Mokari-Manshadi et al.<sup>[49]</sup>, except for the annealing step. Due to the fact that the available furnace could not reach a temperature of 750 °C and that the material started to decompose at lower temperatures (around 470 °C) the annealing step was omitted for this and all other samples.

The other  $MoS_2$  samples were prepared according to the procedure reported by Wang et al.<sup>[50]</sup> with the change that sodium molybdate instead of ammonium molybdate was used as precursor. The reaction still occurred in a good agreement with literature.

#### $\mathbf{MoSe}_2$

The  $MoSe_2$  compounds were obtained according to the procedure of Tang et al.<sup>[31]</sup> The annealing step was omitted for the same reason as mentioned for the  $MoS_2$ .

#### $MoS_xSe_{2-x}$

All mixed compounds were obtained by combining the procedure for  $MoS_2$  by Moraki-Manshadi et al. and the the one for  $MoSe_2$  using the respective ratios of precursors for the corresponding mixed compound.

#### 4.1.2 XRD results

Fig.4.1 shows a typical measured XRD signal. Although the signal was recorded over night with a scan time of about 500 s/deg, the number of counts is very low, indicating the average crystalline size to be small or amorphous. Furthermore, a strong background signal is measured, which indicates that most of the sample is amorphous. The peaks measured peaks are very broad, as shown in table 4.1 they are even below 1 Å supporting the theory that most of the sample is amorphous and the Scherrer formula might not hold.

Fig.4.2 shows an overview of all the samples after the background correction. The pure  $MoS_2$  samples were measured for approx. 2 h while all the other samples were measured overnight, leading to an improvement of the signal to noise ratio for the selenium containing compounds. The excact peak values are reported in table 4.1.

All samples show the (100) peak around 34 deg (indicated by the dashed brown line), but with increasing selenium concentration, the (110) peak moves from 57 deg for  $MoS_2$  to 55 deg for  $MoSe_2$  (indicated by the grey and green dashed line, respectively). This suggests an increasing lattice spacing due to the larger radius of Se compared to S. Furthermore, the  $MoS_2$ ,  $MoS_{1.5}Se_{0.5}$ , and  $MoS_{0.5}Se_{1.5}$  samples show the onset of the (002) peak at 14.7 deg. All mixed MoSSe compounds show the (103) peak at 42.8 deg.

The  $MoS_{0.5}Se_{1.5}$  measurement shows some traces of elemental selenium (see appendix for the sample holder, selenium, bulk  $MoS_2$  and  $MoSe_2$  XRD spectrum).



Figure 4.1: Measured XRD signal for  $MoS_{1.5}Se_{0.5}$ 



Figure 4.2: Background corrected XRD signal of all samples

Sample name	Peak position $(2\theta)$	Lattice plane	FWHM $(2\theta)$	d (nm)	Mean crystal size (nm)
	14.7	(002)	5.1	0.60	0.027
$MoS_2$	34.1	(100)	4.0	0.26	0.036
	57.9	(110)	2.8	0.16	0.057
MoS- @160 °C	33.8	(100)	6.6	0.26	0.022
M052 @100 C	57.0	(110)	5.9	0.16	0.027
	17.7	(002)	6.7	0.5	0.021
$MoS_2 @200 \ ^{\circ}C$	33.9	(100)	7.6	0.26	0.019
	57.2	(110)	4.7	0.16	0.034
	14.2	(002)	1.6	0.62	0.056
	34.2	(100)	8.4	0.26	0.017
$MoS_{1.5}Se_{0.5}$	42.9	(103)	3.4	0.21	0.044
	48.0	(105)	4.1	0.19	0.037
	56.6	(110)	4.7	0.16	0.033
	14	(002)	na	0.63	na
MoSt Set	21	na	na	0.42	na
Incoloci	34.4	(100)	5.6	0.26	0.026
	42.4	(103)	2.7	0.21	0.055
	47.8	(105)	1.6	0.19	0.095
	56.1	(110)	4.7	0.16	0.033
	13.4	(002)	4.5	0.66	0.031
$MoS_{0.5}Se_{1.5}$	34.1	(100)	8.4	0.26	0.017
	55.4	(110)	4.5	0.16	0.035
MoSoc	33.5	(100)	5.1	0.26	0.028
100065	55.0	(110)	5.7	0.17	0.027

Table 4.1: XRD values

#### $\mathbf{MoS}_2$

The MoS<sub>2</sub> spectra can not be compared to the spectrum published Mokari-Manshadi et al.<sup>[49]</sup> as they annealed their compound at 750 °C , which increases the crystallinity of the MoS<sub>2</sub> significantly. Furthermore, no information about the compound before the annealing is provided. Generally, the obtained compound is in good agreement with the MoS<sub>2</sub> at 160 °C and 200 °C samples.

The background corrected XRD spectra of  $MoS_2$  at 160 °C and 200 °C compound are in good agreement with the reported spectra of Wang et al.<sup>[50]</sup>.

#### $\mathbf{MoS}_{x}\mathbf{Se}_{2-x}$

Depending on the selenium content, the mixed components show a peak shift of the (110) peak which is in agreement with literature.<sup>[30]</sup> Interestingly, the calculated change in the lattice spacing d is only on the order of 0.1 nm as shown in table 4.1.

#### $\mathbf{MoSe}_2$

The MoSe<sub>2</sub> background corrected spectrum is in good agreement with literature.<sup>[31]</sup>

#### 4.1.3 TEM results

#### General observations

Fig.4.3 shows typical TEM images of MoXY particles. All samples show particles, which have random shapes with no ordered structures and various sizes. Sometimes lattice fringes, such as shown in fig.4.3(a) and (b) can be observed. Those fringes indicate that the particle is composed of a layered structure which stand perpendicular to the surface of the TEM grid. The dimension of the lattice fringes will be discussed later using images with higher resolution.



<u>100 пт</u>

(a) Image of a typical particle  $(MoS_2)$ .



(b) Image of a typical particle  $(MoS_{1.5}Se_{0.5})$ .

(c) Typical particle ( $MoS_{0.5}Se_{1.5}$ ).

(d) Nanodot strucutes (MoSe<sub>2</sub>).

Figure 4.3: Image (a)-(d) show particles observed for the different compounds in the TEM. Their range can go from about hundred nanometer up to micrometer sized particles. One of the larger particles is shown in the left upper corner of image (a). A overview image of the same huge particle is shown in the appendix fig.B.1. In figure (c) small crystalline structures can be seen in the upper left part next to the particle. These small fragments have shown to be NaCl contaminations and are also observed in the EDXS spectra fig.C.12. Furthermore, the particle extends into more sheet like structures. Image (d) shows a particle composed of smaller dot-like structures.

In fig.4.3(c) smaller crystalline structures can be seen in the upper left corner next to the particle. These consists most probably of sodium chloride (NaCl) as sodium as well as chlorine are detected in this sample in the EDXS spectra in fig.C.12. NaCl is produced as a side reaction and can be removed by washing the product more thoroughly with water. No other samples showed the NaCl contamination indicating that they were rinsed well enough.

Figure 4.3(d) shows more dot-like structures that were observed for the  $MoS_2 @160 \ ^{\circ}C$ ,  $MoS_1Se_1$ ,  $MoS_{0.5}Se_{1.5}$  and the  $MoSe_2$  samples. Similar structures have also been reported in literature.<sup>[12][52]</sup> They are most probably exfoliated structures produced during the sonication step in the sample preparation. Generally, the high resolution images indicated a high crystalline phase in the dot-like structures.



(c) High magnification of a particle with a two times magnified selected area  $(MoS_{0.5}Se_{1.5})$ .

(d) Nanodot strucutes (MoSe<sub>2</sub>).

Figure 4.4: High resolution of the different structures shown in fig.4.3

Fig.4.4 shows the corresponding high resolution images to the ones in fig.4.3. In all the images, fine structured areas can be observed. Those are either lattice-like structures as shown in fig.4.4(b)-(d) or fringe-like structures shown in fig.4.4(a) and (b). Generally lattice like structures could only be observed in thin (eg. areas with a few. to mono-layer thickness) and not in big particles such as in fig.4.4(a). A zoom into bigger particles proved to be challenging to focus due to thermal expansion and the corresponding drift during the imaging process. Furthermore, as the technique images through the sample, the produced data is a summary of all the atoms with the same x,y- positions. Hence, different heights cannot be separated and information about the lattice can only be obtained from few- to mono-layered structures which are usually found around the bigger particles.

As the observed structure were mostly randomly oriented (4.4(c)) and showed to be rather amorphous, the resolution is limited by the point-by-point resolution limit of 0.23 nm for the JEOL 2100F TEM instead of 0.15 nm for lattice structures.<sup>[53]</sup> Due to this limit, the phase of the compounds could not be determined. Some areas show the honey comb structure which is typical for the 2H phase but as the crystalline regions are small no conclusive statements can be made from this data.

Also due to the limited resolution, only the lattice spacing for the (002) or (100) plane (table 4.1) are observable in the TEM. To measure these distance, small crystalline regions were identified as shown by the red rectangles in fig.4.5. The intensity was integrated along the shorter axis which produces a profile as shown in fig.4.6. The distance was always measured over three periods and divided by three to get the spacing. The obtained distances are summarized in table 4.2. The estimated error

was calculated using the systematic error of 0.23 nm for samples with less than 10 measurements and with the statistical error for samples with 10 or more measurements. All values with the exception of the (002) plane of the MoS<sub>2</sub> @200 °C and MoS<sub>1.5</sub>Se<sub>0.5</sub> are in well agreement with the XRD values. Only one suitable fringe-like structure was found for the MoS<sub>2</sub> @200 °C sample, therefore if this one deviates due to some experimental factors such as tilt, the measured size could be significantly increased or decreased. For the MoS<sub>1.5</sub>Se<sub>0.5</sub> 10 measurements were performed, therefore the statistical error was used for the error calculation. The fact that the range with the statistical error does not include the expected value from the XRD might indicate that more measurements would be needed to neglect the systematic error. Using the systematic error, the XRD expectation value would be well in the range of the measurement.

Another issue is due to the limited amount of images available. It was rate that the fringes were aligned well enough to measure the distance over 3 periods. Therefore, variations in the three dimensional orientations such as tilt have a big influence on the measurement.



Figure 4.5: High resolution image of sample  $MoS_{0.5}Se_{1.5}$ . The red rectangles indicate where the intensity was integrated to obtain profile images as shown in fig.4.6. Due to the all measurements shown have an estimated error of up to 0.08 nm which makes the third position after the decimal point insignificant.



Figure 4.6: Profile of the square labeled with 0.288 in fig.4.5. The intensity is integrated perpendicular to the lattice structure. The area within the dashed lines corresponds to the area shown in the TEM image.

To gain more insight into the structure of the sample one can use electron beam diffraction. Such experiments were conducted but during the process the investigated areas changed drastically by either getting more crystalline or by burning the carbon grid. Another way to get diffraction patterns is by applying the fast Fourier transformation on the high resolution images. This generally gave either no peaks or a change in the sample was observed with the increased imaging time. Therefore the obtained diffraction patterns are not part of this report.

In the following the obtained TEM images are compared the literature.

#### $\mathbf{MoS}_2$

Unfortunately, Mokari-Manshadi et al.<sup>[49]</sup> did not publish any TEM measurements of their compounds. The other two  $MoS_2$  compounds are in good agreement with the images provided by Wang et al.<sup>[50]</sup> at low magnifications. At high magnification they observe significant more lattice fringes with a spacing of 0.8 nm, which is significantly wider then in the  $MoS_2$  @160 °C and  $MoS_2$  @200 °C compounds measured in this work.

#### $\mathbf{MoS}_{x}\mathbf{Se}_{2-x}$

Gong et al.<sup>[30]</sup> reported similar structures to the ones observed. As in the case for the  $MoS_2$  compounds, they observed more fringe-like structures. This was as well observed by Xia. et al.<sup>[16]</sup>. In contrast

to Gong et al., they performed high resolution TEM giving showing crystalline planes with various orientations comparable to fig.4.4(c).

#### $MoSe_2$

Similarly to the other compounds, more lattice fringes were reported by Tang et al.<sup>[31]</sup>. In contrast to the observed MoSe<sub>2</sub> they observed highly crystalline structures while the dot-like structures as shown in fig.4.4(d) were only observed for modified compounds.

	Lattice	Average	Standard	Estimated	XRD	Number
Sample name	plane	size	deviation	error	value	of
	(nm)	(nm)	(nm)	(nm)	(nm)	measurements
MoS-	(002)	0.62	na	$\pm 0.08$	0.60	1
10052	(100)	0.27	0.01	$\pm 0.01$	0.26	18
MoS. @160 °C	(002)	0.89	na	$\pm 0.08$	na	1
M052 @100 C	(100)	0.30	0.04	$\pm 0.04$	0.26	32
MoS. @200 °C	(002)	0.69	na	$\pm 0.08$	0.5	1
M052 @200 C	(100)	0.25	0.01	$\pm 0.01$	0.26	12
MoSSo	(002)	0.68	0.04	$\pm 0.04$	0.62	10
10001.5000.5	(100)	0.26	0.01	$\pm 0.01$	0.26	13
MoSiSoi	(002)	0.70	0.03	$\pm 0.08$	0.63	9
Mosisei	(100)	0.25	0.03	$\pm 0.03$	0.26	14
MoSe - Set -	(002)	0.62	na	$\pm 0.08$	0.66	1
10000.5001.5	(100)	0.28	0.02	$\pm 0.02$	0.26	38
MoSo	(002)	0.69	0.03	$\pm 0.08$	na	9
100002	(100)	0.26	0.03	$\pm 0.03$	0.26	21

Table 4.2: Measured lattice spacing by TEM

#### 4.1.4 EDXS results

A representative EDXS spectrum is shown in fig.4.7. All EDXS spectra can be found in the appendix sec.C. For single dichalcogenide compounds, only the corresponding dichalcogenide peak is present. Furthermore, copper, carbon, and oxygen are detected, coming from the copper grid and carbon film. A small amount of chromium, iron, and silicon can be observed and attributed to the machine contamination. The last elements that are detected as contaminant, are sodium, chloride, potassium, and calcium. The sodium and chlorine are most likely contaminants from the synthesis, while the potassium and calcium probably come from the water used in the synthesis. In general the contaminant level is low with the exception of carbon, copper, and oxygen, which is expected due to the grid.

As one can see, the molybdenum and sulphur signals overlap. This is due to the fact that the  $K_{\alpha}$  peak of sulfur occurs at an energy of 2.309 eV while the  $L_{\alpha}$  of molybdenum occurs at 2.292 eV. The  $K_{\alpha}$  peak of molybdenum is located at 17.380 eV and was used to quantify the molybdenum content. As it is observed with a low intensity and the  $L_{\alpha}$  peak of molybdenum and the  $K_{\alpha}$  peak of sulphur overlap a quantification of the relative ratios has been unsuccessful and the results are not included here.

#### Comparison with literature and summary

Probably due to the fact that the molybdenum and sulfur peaks overlap, no EDXS data were reported in previously referenced literature. An STEM EDXS map has been publish by Gong et al. and showed a well overlapping molybdenum and sulphide signal.<sup>[30]</sup> Due to the overlapping signal of those two elements this would be very suspect if it was not observed, and gives no information about the quantity and distribution.



Figure 4.7: Measured EDXS signal for  $MoS_{1.5}Se_{0.5}$ .

#### 4.1.5 Raman spectroscopy

To get an insight on the phase of the  $MoS_2$  compounds Raman spectroscopy was conducted. The obtained spectra are shown in fig.4.8. Unfortunately, the material crystallised immediately under the beam exposure. At the very start no signal is recorded until the material crystallises. Furthermore, the typical  $E_{2g}^1$  and  $A_{1g}$  peak at 382 to 384 cm<sup>-1</sup> and 403 to 407 cm<sup>-1</sup> are very small. The various J peaks seem to be shifted. Furthermore more unidentified peaks are present. The crystallisation of the sample could be due to inefficient heat dissipation. Therefore it was tried to obtain a spectra with different magnification objectives to increase the exposed area and to change the excitation wavelength to white light but the crystallisation was still observed. Deposition of a thin film on a microscopy glass slide showed no peaks in the spectral range of interest. The same was observed for samples which were dispersed in water to increase the heat dissipation.



Figure 4.8: Measured Raman shifts for two  $MoS_2$  samples measured with a 20x magnification.

Due to the change in the sample during the examination the results are not reliable and no measurements were conducted for the remaining compounds. Others do not encounter any problems or do not report those.<sup>[9][11][18][15][50]</sup>

Further Raman analysis were not performed because of the limited time of the project.

#### 4.1.6 XPS results

In order to confirm the material composition XPS was conducted at the university of Auckland. In a first part the measured samples are described and the general outcomes are reported analysing the peak positions, before the peak deconvolution is discussed and the results are summarised.



Figure 4.9: Figure (a) shows the narrow survey spectrum while the core level spectra are shown in (b)-(e). The legend for all samples is given in (f).

The MoS<sub>2</sub>, all mixed compounds, and the MoSe<sub>2</sub> sample, were send to the university of Auckland to be characterised by XPS. The corresponding powder as obtained in sec.3.2 were sent via courier and the measurement details can be found in sec.3.3.3. Two overview scans were performed for every measurement, a wide spectrum from 0 to 1300 eV averaged over 5 scans and a narrow spectrum from 0 to 600 eV over 10 scans. Furthermore, core level scans were measured over 30 scans for the molybdenum 3d (240-220 eV), sulphur 2p (183-152 eV), selenium 3d (65-45 eV), and selenium Auger (310-277 eV) regions.

The wide survey scans are not included as they do not show any further information than the narrow survey scans with the exception of the Auger lines for molybdenum (1267 eV), oxygen (975 eV), and carbon (1226 eV).

The narrow survey scan is shown in fig.4.9(a). This survey shows the expected molybdenum, sulphur and/or selenium signals as well as carbon and oxygen. Furthermore, two unidentified peaks at 356 and 252 eV are present. Interestingly all molybdenum peaks are shifted about 1 eV towards higher energies, indicating a higher oxidation state than the elemental form. To contrast, all selenium Auger lines are shifted about 2 eV to lower energies, indicating a more negative oxidation state. The shift towards higher energies for molybdenum and lower energies for selenium indicated the formation of the corresponding molybdenum dichalcogenide compound.

It is obvious that the selenium signals are missing in the MoS<sub>2</sub> sample. The sulphide 2p region shows how the sulphide 2p peaks transforms with increasing selenium content in the mixed dichalcogenide compounds towards the Se 3p orbital peaks. The molybdenum 3d signal in fig.4.9(b) has two peaks for the MoS<sub>2</sub> and MoS<sub>0.5</sub>Se<sub>1.5</sub> compound while it seems to have 4 peaks for the other samples. The first two peaks are bigger and in the region for molybdenum sulfides and selenides. They also exhibit the expected peak splitting of 3.1 eV. The two other peaks observed correspond well with MoO<sub>3</sub> and also exhibit the peak splitting of 3.1 eV. Confirming this, the highest signal for the MoO<sub>3</sub> compound is observed in the MoS<sub>1.5</sub>Se<sub>0.5</sub> sample which also has the most intense oxide peak in the survey (at 532 eV). The broadening in the MoS<sub>2</sub> sample indicates that a part is oxidized to MoO<sub>2</sub> where the  $3d_{\frac{5}{2}}$  peak shifts from 228 to 229 eV. It is not surprising that MoS<sub>0.5</sub>Se<sub>1.5</sub> as the sample with the lowest oxygen peak intensity shows no contribution of MoO<sub>2</sub> or MoO<sub>3</sub>.

Fig.4.9(c) shows the core level region for the sulfur 2p peaks. The peaks at higher energies correspond to the selenium Auger lines and therefore are not observed in the MoS<sub>2</sub> sample. With increasing selenium content, the Se 3p signal overlaps with the S 2p signal until it only shows the Se 3p signal for the MoS<sub>2</sub>. The pure S 2p peak for the MoS<sub>2</sub> signal corresponds to sulphides and no peaks for SO<sub>2</sub> (167-168 eV) is observed.

The spectrum for the selenium core level region is shown in fig.4.9(d). Again no signal for the  $MoS_2$  compound is observed and the signal increases with increasing selenium content. The peak unfortunately does not show a doublet as expected. The broadening of the peak could be due to some unreacted elemental selenium still present in the sample. The peak maximum at 55 eV is typical for selenides while no peak for  $SeO_2$  is found around 59-60 eV.

The selenium Auger spectrum is shown in fig.4.9(e). The peak in the  $MoS_2$  corresponds with the C 1s peak. As also the carbon Auger line is observed, as mentioned before, this as expected. The observed peaks suggest that carbon contaminations are the main source for the peak at 285 eV for the  $MoS_2$ ,  $MoS_{1.5}Se_{0.5}$ , and MoSSe samples. For the samples with high selenium content, the Auger lines are yielding the main contribution.

#### Peak fitting and summary

Due to the late arrival of the XPS data and the limited time, the peak deconvolution has not been done yet. First observations indicated that the sample is most likely composed of the 2H phase but this has to be confirmed by the deconvolution. Hopefully this data will be available for the presentation.<sup>[18][54][55]</sup>

Furthermore the XPS data confirm the composition of the various MoXY compounds but also reveal that the  $MoS_{1.5}Se_{0.5}$ ,  $MoS_1Se_1$  and  $MoSe_2$  samples show a contribution of  $MoO_3$  indicating some of the material oxidised. In contrast to the selenium containing compounds  $MoS_2$  shows a broadening in the of the molybdenum core level peaks indicating that some part of the sample might have oxidised to  $MoO_2$ . Only the  $MoS_{0.5}Se_{1.5}$  compounds shows no contribution of  $MoO_2$  or  $MoO_3$ .

#### 4.1.7 Summary of all characterization results

The XRD, TEM, EDXS and XPS results are confirming that MoXY compounds are produced. Due to the overlapping peaks in the EDXS and XPS spectra as mentioned in the corresponding sections the exact composition could not be confirmed. The methods used in literature to confirm the composition for  $MoS_xSe_{(2-x)}$  compounds are Inductively Coupled Plasma Mass Spectrometry (ICP-MS)<sup>[16]</sup> or Inductively Coupled Plasma Optical Emission Spectrometry (ICP-OES).<sup>[30]</sup> As such a tool is difficult to acquire the theoretical concentrations from the reactant ratios were assumed in this thesis.

Both XRD and XPS spectra confirm the increasing selenium content as shown in fig.4.2 and 4.9.

The XRD and TEM investigation indicate that most of the sample is amorphous. Due to the limited resolution of the TEM and the change of material during the diffraction measurement as well as during the Raman spectroscopy measurements the phase of the material could not be determined. It is most likely that the main part of the sample is amorphous while the crystallites are in the 2H phase as this phase is the thermodynamically more favoured. As the materials were observed to change during the diffraction and Raman measurements, all samples were also annealed in a DZF-6020 vacuum oven from Zenithlab at 200 °C for 22 h. Unfortunately, the XRD instrument became out of commission after the annealed samples were produced, so the limited time remaining restricted further characterisation.

The XPS furthermore revealed that the  $MoS_{1.5}Se_{0.5}$ ,  $MoS_1Se_1$  and  $MoSe_2$  samples showed contribution of  $MoO_3$  as a contamination, while the  $MoS_2$  showed a contribution of  $MoO_2$ . Only  $MoS_{0.5}Se_{1.5}$  shows no oxide contribution in the Mo 3d spectra.

As it was unknown how long the measurements would take and only a limited time was available only the mentioned samples were sent. After it was clear that enough measurement time was available the MoS<sub>2</sub> at 160 °C and at 200 °C were sent for the measurement. Those results are still pending.

#### 4.2 Electrochemical investigations

This section describes the experimental findings of the compounds produced and characterized in sec.4.1. In a first section the experimental setup and the optimisations made are discussed, before the Nafion film is investigated, which turned out to be inevitable for the measurements. Afterwards the various challenges regarding RRDE voltammetry measurements are discussed before an overview of the catalytic properties for all compounds is given. At the end the most important findings are summarized.

#### 4.2.1 Experimental setup and optimizations

To carry on of previous work by Nann et al.<sup>[56]</sup>, the initial plan of the thesis was to first measure the electrocatalytic behaviour before moving on to the photocatalytic. Therefore the electrocatalytic behaviour was studied on gold electrodes, in order to be able to compare it with the photocatalytical measurements.

Several challenges were found as listed here which are discussed in further details in the following subsections and summarized at the end of this section.

- (a) Film deposition and bubble formation
- (b) Electrode cleanliness
- (c) Electrolyte solution and milder conditions
- (d) Reference electrodes and their stability
- (e) Gold electrode

#### (a) Film deposition and bubble formation

To deposit the catalyst on the electrode surface, usually an ink-based approach is used. Ink-based depositions are the most used in literature and mainly use ethanol, water, the catalyst, and sometimes carbon black with varying ratios.<sup>[30][31][50][57]</sup>

To start, a recipe from Yuta Nakayasu (Tohoku University Japan), who has worked previously in the group with MoXY compounds, was used consisting of 6 mg catalyst, 3 mL ethanol, 6 mg carbon black, and 100  $\mu$ L 5% (w/v) Nafion. For the measurement, 10  $\mu$ L of this ink were deposited on the electrode surface and dried at air. During electrochemical measurements this film showed damage due to the formation of bubbles of hydrogen, leading to the destruction of the film in usually less than 10 subsequent measurements. As the formed bubbles could not be removed from the centre of the film, it was assumed, that due to the drying process the film had a concave shape with a thinner film in the middle and an increased thickness at the edge. This effect could be overcome by depositing the ink in two steps: first 7  $\mu$ L were deposited and dried and afterwards 3  $\mu$ L. This solved the problem for the bubble in the middle but the film was still not stable enough to perform many (more than 10) measurements.

The second approach used a published recipe consisting of 1 mg catalyst, 200 µL ethanol, 800 µL water, and 80 µL 5% (w/v) Nafion, deposited in the 7 and 3 µL way. <sup>[50]</sup> As the first ink, this one also suffered from instability. Furthermore, the measured currents were drastically below literature values for the same catalyst in the same ink and solution as one can see in fig.4.10 and 4.11.



Figure 4.10: Linear sweep measurements of  $MoS_2 @$ 160 °C and @ 200 °C in 0.5 M H<sub>2</sub>SO<sub>4</sub>.



Figure 4.11: Literature linear sweep measurements for  $MoS_2$  at various temperatures from Wang et al.<sup>[50]</sup>

The measured values only to go -0.3 V vs. RHE due to the fact that more negative potentials have shown in previous measurements to destroy the film. The curves were measured using a Ag/AgCl reference and the potentials where afterwards converted to the RHE. It turned out lateron that the used Ag/AgCl reference was not accurate and the potentials should have been significantly more negative (about 0.2 V), than shown in fig.4.10. More about the stability of the reference electrode will be descussed in the third part of this section.

While current densities are drastically smaller in the measured curves than in literature, this could be due to the low conductivity in the Nafion. Due to the ink based approach one cannot be sure to have the catalyst on the electrode surface instead of somewhere in the film, eg. on the Nafion, which would decrease the conductivity. To improve the conductivity carbon black can be as an additional compound in the ink.<sup>[57]</sup>

This is an inconvenient solution as it makes the system more complex and unreproducible. Unfortunately, there are no suitable solutions in literature without Nafion on gold electrodes. As the Nafion layer is therefore inevitable, its properties and behaviour were investigated and summarized in sec.4.2.2 yielding to a more convenient solution for the catalyst deposition.

#### (b) Electrode cleanliness

In a first screening with the ink approach from Wang et al.<sup>[50]</sup> the obtained polarization curves showed not to be reproducible and seemed to move with every subsequent scan, usually to more negative potentials. Interestingly, even the blank gold electrode showed this behaviour, as shown in fig.4.12(a), where it was expected that the polarization curves should be identical as the surface should not be changed.



Figure 4.12: Fig.(a) 10 Linear sweep measurements of the blank gold electrode used for the electrocatalytic measurements in 0.5 M H<sub>2</sub>SO<sub>4</sub>. Fig.(b) and (c) show measured CVs of the blank gold electrode in 0.5 M H<sub>2</sub>SO<sub>4</sub>, while fig.(d) shows the literature CV.<sup>[58]</sup>

This led to the conclusion that the electrode surface was not clean enough and the standard procedure with manual polishing using 0.3 and 0.05 µm alumina suspension was not sufficient. Therefore, efforts were made to improve the procedure. Various ways are known in literature for cleaning gold surfaces.<sup>[59]</sup> The method chosen was the potential cycling in  $H_2SO_4$  and the protocol by Heiskanen et al.<sup>[60]</sup> as the other methods were either not available or regarded as too aggressive and may harm the Teflon or platinum in the RRDE. The method of Heiskanen et al. was only performed once as it did not offer the possibility to compare the cleaning outcome without the need of a subsequent measurement such as a ferro/ ferri cyanide CV, which would demand cleaning again. Therefore the focus was set on the CV in sulphuric acid.

Two such CV's are shown in fig.4.12(b) and (c). These were obtained with the same electrode, however the one in (b) shows the CV at the beginning of the cleaning and (c) the CV at the end. One can observe how two or three peaks emerge from the initial broad peak. The current density

drops as the electrode gets cleaner and the reduction peak around 0.4 V vanishes. The peak around 0 V is probably due to adsorption of  $O_2$ . The oxygen reduction peak around 0.95 V is distinct in all measurements while the oxidation peaks evolves during the measurement.

When comparing it to the literature CV shown in fig.4.12(d) it is obvious that the two peaks in the measured CV's show a wider peak splitting than the reference. If one continues cycling one observes that the peak at 1.2 V vanishes and a peak at 1.3 V evolves yielding a similar pattern to the one reported by Rand et al.<sup>[58]</sup> To check that the surface is actually clean, a CV of ferro/ ferri cyanide was performed straight after showing a peak splitting of more than 100 mV, where values below 100 mV are the often taken as the benchmark for a clean surface.<sup>[59]</sup>

As the cycling in 0.5 M  $H_2SO_4$  is very time consuming and did show a inadequate peak splitting for the control CV, a pragmatic approach was used. First the electrode was taken apart and the Teflon spacer was cleaned with aqua regia while the gold electrode was incubated in piranha solution (see sec.3.3.1 for aqua regia and piranha solutions). When the electrode was taken apart, the inner wire connecting to the disc electrode (marked orange in fig.4.13) was found to be rusted.



Figure 4.13: Scheme of a RRDE.<sup>[43]</sup>

The rust was cleaned off and the electrode was reassembled. After a subsequent measurement in 0.5 M H<sub>2</sub>SO<sub>4</sub> the electrode was taken apart revealing again to be rusted. The Teflon spacer was therefore exchanged with a new one which resolved the problem. As it was unknown how many times previous users have taken the electrode apart, it is likely that it got worn out and some of the solution leaked in, in-between the Teflon spacer and the disc electrode, causing the corrosion.

After the cleaning with aqua regia and piranha solution, the electrode showed consistent curves as expected. Therefore, the cleaning procedure from now on was chosen to be the traditional manual polishing with 0.3 and 0.05  $\mu$ m alumina suspension, with subsequent CV's (usually about 40) in 0.5 M H<sub>2</sub>SO<sub>4</sub>, until the two peaks at 1.2 V and 1.4 V were observed as shown in fig.4.12(c). Regardless the fact that the CV in H<sub>2</sub>SO<sub>4</sub> did not show the exact literature shape, this was performed to get a more consistent starting point.

For the measurements on the glassy carbon electrode only the manual polishing was used as no other cleaning procedures were found in literature.

#### (c) Electrolyte solution and milder conditions

As the initial motivation of this thesis was to combine the MoXY compounds with InP quantum dots using an approach as shown by Nann et al.<sup>[56]</sup>, milder conditions than the very acidic solution of 0.5 M H<sub>2</sub>SO<sub>4</sub> (which is the standard for electrocatalytic measurements of the HER) were desired. As the HER is highly dependent on the pH<sup>[28]</sup>, due to the consumption of H<sup>+</sup>, a simple calculation was performed, to estimate the time it needed to change the pH by 0.1, 0.5 and 1. Assuming all current produces hydrogen, the current density J to be 20 mA cm<sup>-2</sup>, with a disc electrode area of  $A = 19.6 \text{ mm}^2$ , and a solution volume V of 180 mL. The definition of the current  $I = J * A = \frac{dQ}{dt}$ , where Q is the charge and t is the time, and the definition of the pH as pH = -log(c), where c is the concentration of protons can be used with the relation  $\frac{dQ}{q_e} = dn$ , where n is the number of protons and  $q_e$  the elementary charge and the definition of the concentration as  $c = \frac{n}{N_A V}$ , where  $N_A$  is the Avogadro constant and V the solution volume, to derive eq.4.1, where x is the initial and a is the change in pH.

$$dt = -\frac{N_A V q_e}{JA} (10^{-(x+a)} - 10^{-x})$$
(4.1)
#### 4.2. ELECTROCHEMICAL INVESTIGATIONS

Eq.4.1 is plotted using the previously mentioned assumptions and shown in fig.4.14. The numbers on the side correspond to the time, were the pH is changed by 0.1 starting with a pH of 2, 2.5 or 3 respectively. It is obvious that for initial pH values of 4 and higher the pH cannot be regarded as constant for any reasonable measurement time. As a typical RRDE measurement takes approximately 5 min. a pH value of 2.5 offered a good trade off with approx. 45 measurement time.



Figure 4.14: Visualization of eq.4.1 assuming a current density J of 20 mA cm<sup>-2</sup>, an area A of 19.6 mm<sup>2</sup> and a volume of 180 mL .

The use of a buffer system, which would stabilize the pH in the region of interests is not feasible, due to the fact, that no buffer system was found, which does not have any redox peak. This is necessary, because if the applied potential is above the oxidation peak or below the reduction peak the buffer would react at the electrode generating a current and it would be impossible to distinguish between current produced by the buffer and by the HER. Furthermore due to the reaction of the buffer, the buffer system to stabilise the pH would be destroyed. Because of those two reasons, an unbuffered solution of 0.5 M KCl adjusted to a pH of 2.5 with HCl was used.

It is also interesting to see, that in literature no buffers are used, but they also do not discuss the limited measurement time, which shows that measurements at pH 4 and higher cannot be performed without a change of pH.<sup>[28][61]</sup>

#### (d) Reference electrodes and their stability

In this part the stability of the various reference electrodes used is discussed. Starting with the RHE and afterwards the Ag/AgCl reference electrode and then silver wire pseudo reference. As the RHE is only accurate for pH values < 2, an alternative had to be found for the measurements at pH 2.5.

### (d.1) Stability of the RHE

To prove the stability of the RHE, two different measurements were performed. First the CV of the platinum ring electrode was measured, before potassium ferro cyanide was added and a CV of this redox couple was measured (as ferro-/ ferri cyanide is a common internal reference).

A typical platinum CV can be seen in fig.4.15. The 4 peaks in the region of 0 to 0.3 V correspond to the adsorption and desorption of hydrogen, while the peaks at more positive potentials correspond to the oxygen adsorption and desorption.<sup>[58][62][63]</sup> The different peaks of the oxygen are less well defined as in literature, which could be due to the fast scan speed of 0.1 V s<sup>-1</sup>. The two oxidation peaks are usually called  $H_{A1}$  and  $H_{A2}$  or  $Q_{H}^{a}$ , while the corresponding reduction peaks are named  $H_{C1}$  and  $H_{C2}$ or  $Q_{H}^{c}$ . The third peak used for the stability evaluation is the desorption peak of oxygen, often called  $O_{C}$  or  $Q_{O}^{c}$ .<sup>[58][62]</sup>



Figure 4.15: CV at the platinum ring electrode in  $0.5 \text{ M H}_2\text{SO}_4$ .



Figure 4.16: Ferro-/ ferri cyanide CV in 0.5 M H<sub>2</sub>SO<sub>4</sub>.

The average potentials at which the peaks occur are shown in table 4.3. It can be seen that the adsorption peaks are shifted towards more positive potentials while the hydrogen desorption peaks occur at almost exactly the expected value. The shift in the  $H_{A1}$  and  $H_{A2}$  and  $O_C$  peak has also been observed by Will et al.<sup>[64]</sup> and is attributed to the surface roughness and cleanliness.

Table 4.3: Potential values for the different peaks in fig.4.15 and the literature potentials taken from Will et al.<sup>[64]</sup>

Peak	Average potential $\pm$ standard deviation [mV]	Literature value [mV]
$H_{A1}$	$148 \pm 2$	110
$H_{A2}$	$275\pm3$	240
$O_C$	$719\pm 6$	700
$H_{C1}$	$94 \pm 5$	100
$H_{C2}$	$228 \pm 3$	230

As a second proof for the stability, the CVs of the ferro/ ferri cyanide redox couple were investigated. A typical CV is shown in fig.4.16.  $E_{1/2}$  occurs at  $685 \pm 5$  mV which is 337 mV more positive than the expected standard potential  $(358 \text{ mV})^{[34]}$ , the average peak spreading is  $184 \pm 45 \text{ mV}$ , which is very high, indicating a rough or dirty surface. This is not unexpected as all the ferro/ ferri cyanide CVs were obtained after a measurement for the electrocatalytic behaviour as discussed in sec.4.2.4. Usually the ferro/ ferri cyanide redox couple is measured in a solution of 1 or 0.1 M potassium nitrate (KNO<sub>3</sub>) at pH 7, where the reaction half potentials fits the expectation. Due to a lack of literature regarding the pH dependence of ferro/ferri cyanide and the fitting of the peaks for platinum in sulphuric acid, the results suggest that the ferro or ferri cyanide undergoes a process or reaction which changes the standard potential to a more positive one. Nonetheless, for both the ferro/ ferri cyanide and the platinum CVs, the potential stayed constant for multiple scans within a standard deviation of 6 mV. Additionally, the fact that the  $H_{C1}$  and  $H_{C2}$  peaks are at the expected potentials and the shift in the  $H_{A1}$  and  $H_{A2}$  peaks is already known in literature, the result supports the correctness of the RHE reference. Furthermore, by changing the ring potential from 0.2 to -0.1 V, one observes a decrease in the measured positive current and achieves a negative current for -0.1 V, which is the expected behaviour for platinum and therefore also supporting the reliability of the RHE with an estimated error of  $\pm 6 \text{ mV}$ .

### (d.2) Ag/AgCl reference

The Ag/AgCl reference was used in the beginning for the measurements in 0.5 M  $H_2SO_4$  (due to the fact that the RHE did not fit the vessel with the quarz bottom) and for the first few measurements at pH 2.5. Unfortunately, it did turn out the potential was not at the expected literature value, as

shown in fig.4.17. The standard redox potential for the ferro/ ferri cyanide redox couple is at 0.358 V. Therefore it should be at 0.158 V vs a 3 M Ag/AgCl reference. Hence, the measured  $E_{1/2}$  is off by 132 mV.

As it is a know procedure to clean and restore the electrode, this was performed according to literature.<sup>[65]</sup> The measured CV afterwards is shown in fig.4.18. The process was unsuccessful as the measured  $E_{1/2}$  is 355 mV. This is probably due to the fact, that the cleaning step with nitric acid is challenging, as the electrode cannot be taken apart. As the attempt to restore the electrode was performed before any statistical values were available for the initial reference, no statement can be made about how stable the reference was at its shifted potential. Therefore, all experiments made previously with this electrode are not included in this thesis. The electrode after the restoration attempt was later used for the H<sub>2</sub>SO<sub>4</sub> cleaning steps due to it's simplicity to use. For the measurements at pH 2.5, the silver wire, described in the following section, was used due to the fact that it could be cleaned inebetween measurements in contrast to the Ag/AgCl reference.



Figure 4.17: 0.01 M ferro/ ferri cyanide CV in 1 M KNO<sub>3</sub>.  $E_{1/2} = 0.290$  V and  $\Delta E = 69$  mV.



Figure 4.18: 0.01 M ferro/ ferri (0.01 M ) cyanide CV in 1 M KNO<sub>3</sub> after restoration.  $E_{1/2} = 0.355$  V and  $\Delta E = 70$  mV.

### (d.3) Silver wire pseudo reference

The siler wire pseudo reference was used with a home-built glass tube with a porosity 4 silica frit (pore size 10-16  $\mu$ m) at the end. The frit proved to have a high permeability for any aqueous solutions, which is not surprising with its pore size, while the traditionally Vycor frits are used,<sup>[65]</sup> which have a pore size of 4-6 nm.<sup>[66]</sup>



Figure 4.19: Ferro/ ferri cyanide calibration CV vs the silver wire pseudo reference electrode at pH 2.5.  $E_{1/2} = 0.167$  V and  $\Delta E = 74$  mV.

As no Vycor frits were available, the tubing was used to have at least some separation and reproducibility regarding placement of the pseudo reference electrode. To remove any osmotic pressure, the same electrolyte as used in the measurement, was inserted in the glass tubing. Prior to all measurements, the silver wire was cleaned with HNO<sub>3</sub> and rinsed with milli-Q water. At the end of every measurement, a CV with the ferro/ ferri cyanide couple was performed, as shown in fig.4.19. The  $E_{1/2}$ was found to be 0.167 V varying  $\pm 4$  mV. The pseudo reference is therefore stable and the estimated error with this electrode is  $\pm 4$  mV. Since the ferro/ ferri cyanide couple moved significantly in a solution of pH 0 as discussed before and shown in fig.4.16, it is unclear, whether the potential correction to the SHE is accurate.

### (e) Gold electrode

Unfortunately, measurements of the blank gold electrode in the same electrolyte solution on different days were not reproducible, as shown in fig.4.20. All solutions were freshly prepared, therefore the two variables obviously changing were the electrode cleanliness (shown by the  $H_2SO_4$  CV in fig.4.21) and the pseudo reference electrode, which was cleaned prior to the measurement. The  $E_{1/2}$  for the measured potential correction to the SHE from the ferro/ ferri cyanide couple were 0.186 V (day 1), 0.192 V (day 2) and 0.188 V (day 3), therefore giving an average potential correction of 0.189  $\pm$  0.003 V. As the potential corrections of the reference electrode are relatively similar, the change of almost 200 mV is most likely due to the different state of cleanliness of the gold electrode. The cleaning CVs, as shown in fig.4.21, are very similar with the exception of the different peak ratios. It is useful to mention here, that the fine tuning of the peaks is finicky and practically not feasible or extremely time consuming.

The fact that the onset potential changes and not just the intensity of the current density suggests that the electrode surface is changed by processes such as to an oxide formation or contaminations. If only the morphology of the surface area changed, the current densities would increase or decrease, while the onset potential should stay the same. Therefore, it is more likely that it is the surface composition changing and an influence on measurements of a catalyst on such an electrode cannot be neglected, as oxides or contamination could increase the resistance at the electrode-catalyst interface. Problems with gold electrodes and the ferro/ ferri cyanide redox couple as reference have also been reported for impedance spectroscopy measurements and such systems start to be scrutinised.<sup>[67][68]</sup>



Figure 4.20: Polarisation curves of the blank gold electrode at different days. The different line styles indicate the single measurements.



Figure 4.21: Corresponding cleaning CV's in 0.5 M H<sub>2</sub>SO<sub>4</sub> for the different days using the Ag/AgCl reference as discussed previously.

#### Summary of experimental setup and optimizations

First, the catalyst deposition with an ink-based approach did not exhibit a good reliability and was found to be destroyed usually within few measurements. The comparison with a literature reported process for the same catalyst, with the same deposition technique and the same solution, exhibited significantly lower current densities. Therefore a new deposition technique was investigated as lateron discussed in sec.4.2.2.

Second, in order to achieve milder conditions for the photocatalytical measurements, the maximal measurement time was estimated. As no buffers can be used, due to their redox peaks within the water splitting window, a pH of 2.5 showed to offer the best compromise, with an estimated measurement time of 45 min and measurable limiting currents for the RRDE measurements. As an electrolyte solution 0.1 M KCl was used, adjusted to the pH of 2.5 with HCl.

Third, the stability of the used reference electrodes was investigated. The RHE showed to be accurate with an estimated error of  $\pm$  6 mV at a pH of 0. The Ag/AgCl reference electrode was observed to deviate strongly from the expected behaviour and no analysis was done on the stability of it as it was only used for the cleaning procedure in 0.5 M H<sub>2</sub>SO<sub>4</sub>. The silver wire pseudo reference showed stable reproducible measurements with an estimated error of  $\pm$  4 mV at a pH of 2.5. The conversion to the SHE using the standard redox potential of ferro/ ferri cyanide is yet to be proven, as the CV shifted significantly towards more positive potentials for the RHE at pH 0.

Last but not least, the gold electrode has shown to be extremely sensitive towards cleaning, with not reproducible subsequent polarization curves for the standard cleaning procedure. This was probably due to contaminations from previous users. After the electrode was disassemble and the Teflon spacer was cleaned in aqua regia and the gold disc electrode in piranha solution, consistent polarisation curves could be achieved for subsequent scans. Furthermore, it revealed that a part in the interior of the electrode was rusted, what could be resolved by cleaning and replacement of the Teflon spacer with a new one. Additionally a new cleaning procedure was established offering the possibility to compare the state of the electrode by the CV in sulphuric acid shown in fig.4.21. Unfortunately, the measurements obtained with the gold electrode showed a potential shift and therefore are not reproducible, probably due to oxidation or contaminations. Due to this irreproducibility and the fact that gold itself is catalytic towards the HER (see fig.1.1), it is not a good electrode to use for this study in the view of the author.

### 4.2.2 Nation layer

#### Nation layer thickness

In order to get an idea of the Nafion layer thickness, stylus profilometer measurements were performed as discribed in sec.3.3.2. The theoretical thickness was calculated to be 2.5 nm for 17.5 µL Nafion solution using eq.4.2, assuming the Nafion density  $\rho_{Nafion,dry}$  in it's dried state to be 1.98 g cm<sup>-3[69]</sup>, the area A to be the area of the whole electrode (176.7 mm<sup>2</sup>), and the concentration of the Nafion solution to be 0.05 g L<sup>-1</sup> (5% w/v).

$$h = \frac{V_{NafionSol} * C_{NafionSol}}{A * \rho_{Nafion,dry}}$$
(4.2)

Fig.4.22 shows one curve of each measured sample. It can be seen that the film is not homogeneous and tends to be thicker in the middle. Furthermore, the profiles do not indicate any deformation due to compression by the applied stylus force. The average values, shown in table 4.4, were calculated in the middle of each measurement as it represents the area where the reaction takes place (area of the disc). It is surprising that the theoretical and practical values differ approximately by a factor of 2000. As the tip of the stylus profiler is in direct contact with the film it is unlikely that the measurement overestimates the thickness, in fact it would be more likely for it to compress or deform the film. This suggest that either the concentration has increased due to the evaporation of solvent or a manufacturing error, that not all of the solvent evaporates and is incorporated in the film, and/or the density differs from literature values.

Due to the non-homogeneity of the sample and estimation of the  $MoS_2$  and MoSSe layer was not possible. Nonetheless, it can be generally seen that the MoSSe layer is thicker, which makes sense as the selenium atoms are larger than sulphur.



Figure 4.22: Measured profiles for the different sample. Representative one of each is shown.



Figure 4.23: Overview of the average value of the film thickness.

Table 4.4: Averaged thickness values

Sample	Thickness nm
17.5 µL S1	$4074.0 \pm 415.3 \text{ nm}$
17.5 µL S2	$3738.8 \pm 588.0 \text{ nm}$
35.0 µL S1	$6859.6 \pm 124.0 \text{ nm}$
35.0 µL S2	$6395.2 \pm 323.4 \text{ nm}$
$MoS_2 S1$	$3739.3 \pm 437.7 \text{ nm}$
$MoS_2 S2$	$4502.7 \pm 403.2 \text{ nm}$
$MoS_1Se_1 S1$	$4947.7 \pm 502.0 \text{ nm}$
$MoS_1Se_1 S2$	$5633.7 \pm 445.6 \text{ nm}$

### Influence of the Nafion layer on electrochemical measurements

To get an understanding of the limits of the electrode setup, the influence of the Nafion film was investigated. As the measured limiting current at the disk  $I_{lim}$  is related by  $\frac{1}{I_{lim}} = \frac{1}{I_L} + \frac{1}{I_f}$ , as shown in eq.2.26, the Levich current  $I_L$  is proportional to  $\omega^{\frac{1}{2}}$ , while the current of in the film  $I_f$  is independent of  $\omega$ . Therefore, by plotting  $I_{lim}^{-1}$  as a function of  $\omega^{-\frac{1}{2}}$ , one can determine the current through the film. If  $\omega^{-\frac{1}{2}}$  approaches zero,  $I_L^{-1}$  becomes zero. Therefore,  $I_f^{-1}$  is given by the intercept at  $\omega^{-1/2} = 0$ . By fitting the measurement points with a linear function, the intercept was determined. Such plots are also known as Koutechy-Levich plots and an example is shown in fig.4.24, where Dill is a 3.0:58.5 and Dil2 is a 3.0:137.0 dilution of the 5 % (w/v) Nafion solution in ethanol. For both dilutions, 17.5 µL were deposited on the whole electrode surface.

After it was observed that the gold electrode was sensitive to surface contaminations the measurements from fig.4.20 were included in fig.4.24, revealing that the second dilution (Dil2) behaved similarly as the blank gold electrodes and can therefore be neglected.

The values from the linear fit are shown in table 4.5. All the curves show comparable slopes. Also, the intercept of Dil2 is comparable to the gold measurement within the error margin while the Dil1 is clearly influenced by the film thickness.

Interestingly, all measured intercepts with the exception of Dil2 are positive. This means in the limit of an infinitely fast rotation, the process occurring at the electrode is an oxidation. Such an inversion of the current is not observed for similar measurements made on platinum electrodes.<sup>[69][70]</sup> The reason for this behaviour could not be determined yet and up to further investigations.



Figure 4.24: Koutechy-Levich plot of the blank gold electrode and the same electrode covered with a thin Nafion film.

Measurement	Intercept $[mA^{-1}]$	Slope [(rad/second ) <sup>1/2</sup> mA <sup>-1</sup> ]	$\mathbf{R}^2$
Blank gold	$0.064 \pm 0.009$	$-9.662 \pm 0.097$	0.9996
Dil1 Nation	$-0.016 \pm 0.014$	$-10.716 \pm 0.154$	0.9992
Dil2 Nation	$0.091 \pm 0.026$	$-10.361 \pm 0.279$	0.9971
Au Day 1	$0.007 \pm 0.011$	$-8.705 \pm 0.127$	0.9997
Au Day 2	$0.069 \pm 0.012$	$-10.383 \pm 0.139$	0.9998

Table 4.5: Linear fit values from fig.4.24

### New film deposition technique

Due to the observed results of the previous section, a new catalyst deposition method was established. 1 mg of the catalyst was dispersed in a mixture of 450  $\mu$ L ethanol and 550  $\mu$ L milli-Q water using sonication. This has been in literature to be the most efficient way to exfoliate MoS<sub>2</sub>.<sup>[71]</sup> The obtained dispersions for all unannealed compounds were black , while the annealed compounds with a Se concentration showed a reddish colour, which turned into an orange colour for the MoSe<sub>2</sub> compound, shown in fig.4.25.



Figure 4.25: Dispersion of the various materials. In the front are the annealed compounds and in the back the corresponding unannealed ones. The samples start on the left with  $MoS_2$  and the selenium content is increased towards the right.

77.3 nmol of each catalyst was deposited for the measurements in sec.4.2.4 and dried in a desiccator. 77.3 nmol were chosen as it corresponded to the used amount by Chaoliang et al.<sup>[12]</sup>. After the catalyst was fully dried, 17.5  $\mu$ L of the diluted Nafion solution (Dil2) was deposited on the whole electrode surface to achieve a homogeneous coverage at the disc and the film was dried under vacuum over night. Before the measurement, the Nafion film was removed from the platinum ring (reasons for this will be discussed in sec.4.2.3) using paper tissue (Kimwipes) and a tooth pick first with n-hexane, then ethanol, and afterwards with the corresponding electrolyte.

Recently, similar deposition techniques were also reported by Voiry et al.<sup>[11]</sup> and Chaoliang et al.<sup>[12]</sup>

### 4.2.3 RRDE measurement optimisation

In this section, the various aspects of the RRDE measurements are discussed:

- (a) Collection efficiency of the ferro/ ferri cyanide redox couple
- (b) RDE and RRDE for the investigation of the HER
- (c) RRDE with a film

### (a) Collection efficiency of the ferro/ ferri cyanide redox couple

As already mentioned in sec.2.3.6, RRDE voltammetry is traditionally used to compare different reaction pathways. This thesis evaluates to use the technique for a detection application. To get an idea of the experimental collection efficiency, the ferro/ ferri cyanide redox couple (0.01 M, in 1 M KNO<sub>3</sub>) was used for a calibration. The obtained collection efficiencies for different rotation speeds can be seen in table.4.6

Table 4.6: Collection efficiency for the ferro/ ferri cyanide redox couple for different rotation speeds at a scan rate of 50 mV:

$\omega$ [rpm]	250	500	1000	1250	1500	1750	2000
$\eta \ [\%]$	26	26	26	25	25	25	25

With increasing rotation speed, the collection efficiency decreases slowly. This is probably due to the higher convection force, decreasing the time a species has at the ring before it is transported further into the solution. Another reason could be the increase in turbulence with increasing rotation speed. Those turbulences can be caused by scratches in the electrode surface or at the edge of the disc, the Teflon spacer, or the ring. Regardless, the measured collection efficiencies are very stable at 25-26% this is consistent with the expectation of 25% provided by the manufacturer.

### (b) RDE and RRDE for the investigation of the HER

The HER has already been studied using RDE voltammetry<sup>[28][61][72]</sup>, but RRDE voltammetry has not been used to the authors knowledge. In contrast to the ORR which has been studied using RDE and RRDE voltammetry.<sup>[73][74][44][75]</sup>

As mentioned in sec.2.2 the HER is dependent on the pH of the system. For pH values  $\geq 2.5$  the HER becomes mass transport limited by the transportation of H<sup>+</sup>.<sup>[28][61]</sup> In order to be able to use RRDE for quantification applications, limiting currents must be achieved, as this is a premiss needed to derive the collection efficiency defined by eq.2.28. Therefore, all measurements in this section were performed at a pH 2.5, for the reasons discussed in sec.4.2.1.

For an ideal system, every  $H^+$  that reaches the electrode surface will undergo a reaction and a certain percentage (collection efficiency) will be detected at the ring electrode surface. If some of the current measured is due to material degradation, the collection efficiency will differ from the expected value and one can quantify how much of the current is decomposing the material and therefore how much of the current is producing hydrogen. For an ideal catalyst that does not decompose, the maximum current measured will be equal to the one defined by the collection efficiency of the electrode.

In a first step, the reaction was studied on a blank gold electrode. The main challenge was fast identified to be the formation of hydrogen bubbles, which tend to accumulate first on the disc surface and then at the Teflon spacer. Investigations on the Teflon spacer revealed that it was positioned below the hight of the disc and ring electrode. Therefore, bubbles that are transported outwards get stuck due to buoyancy. To exchange the Teflon spacer, the electrode was disassembled as discussed in sec.4.2.1 revealing that part of the inside was rusted. After the rust was cleaned, a new Teflon spacer was inserted and the electrode was reassembled resulting in a Teflon spacer that was now higher than the disc and ring electrode. The spacer was therefore mechanically polished down. This decreased the previous problem of bubble agglomeration, but did not solve it. The main problem is most likely the hydrophobicity of the Teflon surface.



Figure 4.26: Point-by-point RRDE measurement at different rotation speeds.



Figure 4.27: RRDE measurement at 1000 rpm using a lean stream of nitrogen generated by the bubbler shown in fig.E.1.

In literature, a point-by-point solution is suggested to solve this problem.<sup>[61]</sup> However, this did not work out for our setup as shown in fig.4.26. The bubbles agglomerated at the Teflon spacer and did therefore not reach the ring electrode, especially for higher applied potentials. Additionally, the bubble removal procedure with rotating the electrode at 1600 rpm did not efficiently remove the bubbles. Finally, due to the limited time for a measurement as discussed in sec.4.2.1, only a limited number of individual points can be measured limiting the resolution.

The next approach used was to have a lean stream of nitrogen constantly flowing on to the electrode surface, shown in fig.4.27. This resulted in either a full coverage of the electrode surface (M1 at -0.7 V) or no change in comparison with no stream (M2 decreasing ring current). It is believed that problems arose because a homogeneous constant stream could not be achieved, mainly due to the limitation of

the valve, as well as due to the dependency of the pressure in the initial pipes.

A better result was achieved by using a long syringe needle and occasionally directing the nitrogen below the electrode. The short pulse of nitrogen caused the accumulated bubbles to move outwards and afterwards the produced hydrogen could be detected before the nucleation of new bubbles started again, as shown in fig.4.28. The nitrogen pulses are clearly visible by the decrease of the corresponding current and there seems to be no significant delay between the measured disc and ring currents. Always directly after a pulse, the current was found to produce a linear relation for the limiting current shown by the red lines.



Figure 4.28: RRDE measurement at 1000 rpm using a syringe needle to flush away the accumulated bubbles.

Table 4.7: Collection efficiency of the HER on blank gold electrodes for various rotation speeds:

$\omega$ [rpm]	1000	1500	2000
$\eta$ [%]	19	18	16

The corresponding collection efficiency of those measurements are shown in table 4.7. As expected they are lower than the corresponding ferro/ ferri cyanide values due to the fact that the bubble geometry limits the availability at the ring surface. What was also observed is that the potential of subsequent scans shifted towards more negative potentials but the limiting currents stayed similar (only a change in the first decimal space). This therefore enables the measurement on a blank electrode yielding a limiting ring current which is more significant than others published for the OER.<sup>[75]</sup>

### (c) RRDE with a film

In order to be able to measure a catalyst, a Nafion film has to be deposited on top of the catalyst as described in sec.4.2.2. To get a good uniformity, the film is deposited on the whole electrode. This has the draw back that the film blocks the access to the ring electrode and measurements without film removal have shown to have a decreasing ring current responses for subsequent measurements. Ethanol, acetone, isopropanol, and hexane were tried as solvents to remove the film using tissues (Kimwipes) and a toothpick. All solvents by have proven to be inefficient and only the combination of hexane with a high potential (1.7 or 1.9 V) applied for 15 s , denoted by High V, showed removal of the film, as shown in fig.4.29.

As this was the most successful procedure found it was used for measuring the catalytic compounds. Such a measurement is shown in fig.4.30. It was generally observed that the same subsequent measurement did not yield the same ring currents. In between the measurements the same potential was applied as in the cleaning procedure, due to the fact that without this step the current was observed to decrease due most likely adsorption of contaminants. One reason for the increasing current with a high voltage applied as cleaning step, could be that the ring electrode becomes cleaner in subsequent measurements. Due to the limited measurement time for the pH-stability, only few measurements could be made giving no obvious results.

Interestingly accumulated hydrogen bubbles were now observed on the disc surface instead of on the Teflon spacer. This suggest that the remaining Nafion on the spacer reduces the hydrophobicity which enables bubbles to move outwards freely. The agglomeration at the disc is most likely due to the electrode surface roughness. Unfortunately, no profilometer data is available on the appearance of the film with the thinner Nafion layer.

Due to the limited time of the Masters thesis, no further research was performed to optimise this measurement.



Figure 4.29: RRDE measurements at 1000 rpm after different cleaning procedures.



Figure 4.30: Subsequent RRDE measurements at 1000 rpm.

### 4.2.4 Analysis of the catalytic behaviour

In this section, the catalytic behaviours of the synthesised compounds in 0.5 M H<sub>2</sub>SO<sub>4</sub> are discussed and analysed. In a first part, the polarization curves are presented and discussed, afterwards a RRDE voltammetry measurement was performed to confirm the formation of hydrogen, and in the last part polarization curves were measured again, to investigate whether the RRDE measurements damaged the film.

All compounds were deposited with the new technique as described in sec.4.2.2. The measured polarization curves are shown in fig.4.31 and the all values are summarized in table 4.8 and 4.9.

From fig.4.31 it is obvious that the glassy carbon electrode is not catalytic, as expected. Platinum is showing the best catalytic behaviour with a overpotential of only  $-38 \pm 6$  mV which is below the literature value of -59 mV.<sup>[76]</sup> This might be due to a different gas for the degassing step. The used gas was not mentioned by Li et al. but the usage of H<sub>2</sub> instead of N<sub>2</sub> is not uncommon.<sup>[11][12]</sup>

All the initial compounds perform significantly better than the corresponding annealed ones. This is most likely due to degradation and/ or oxidation during the annealing process, as the dispersions shown in fig.4.25, display a reddish or orange colour for selenium containing compounds. Therefore, the annealed compounds will not be discussed in further details.

Table 4.8 and 4.9 show the obtained values for all materials. The onset potentials obtained at a scans speed of 50 mV s<sup>-1</sup> and 5 mV s<sup>-1</sup> are consistent within the error of the experiment. The overpotentials on the other hand tend to be more negative for the measurements obtained at 5 mV s<sup>-1</sup>. Due to the slower speed of the measurement more hydrogen is produced, which is afterwards blocking the electrode surface and therefore decreasing the measured current. Due to this, the potential needed

to achieve 10 mA cm<sup>-2</sup> increases and the measured Tafel slope decreases. Due to the decreased Tafel slope, the corresponding exchange current density is increasing for all measurements performed at 5 mV s<sup>-1</sup>, as eq.2.12 defines  $J_0 = 10^{a/TS}$ , where *a* is the Tafel intercept and *TS* the Tafel slope.

From all compounds, the mixed dichalcogenides performed better than the pure molybdenum sulphides and selenide.  $MoS_{1.5}Se_{0.5}$  showed the best performance with a onset potential of -192 mV  $\pm$  6 mV and an overpotential of -218 mV  $\pm$  6 mV (at 50 mV s<sup>-1</sup>). In contrast,  $MoS_1Se_1$  has shown to be the best performing in literature.<sup>[12][16]</sup> As both determined the atomic ratios, this suggests that our compound may not have the assumed composition.

Furthermore, the materials of Xia et al.<sup>[16]</sup> were obtained in a similar fashion using slightly different precursors. In contrast to Xia et al., the used MoXY compounds were prepared as described in sec.4.2.2 and showed a significant improvement in the catalytic behaviour. The best performing compound from Xia et al. was  $MoS_1Se_1$  with an overpotential of -271.3 mV while it was -218 mV for  $MoS_{1.5}Se_{0.5}$ . This improvement is most likely due to exfoliation during the sonication step. Chaoliang et al.<sup>[12]</sup> could achieve an even lower overpotential of -140 mV due to the lithium exfoliation, which enables the preparation of high-percentage 1T-phase MoXY samples.



Figure 4.31: Linear sweep measurement for all compounds at a scan speed of 50 mV s<sup>-1</sup> in 0.5 M  $H_2SO_4$  on a glassy carbon electrode. The initial compounds are shown in straight lines while the annealed ones are displayed dashed. All compounds were directly measured against the RHE.

After the initial polarization curves, RRDE voltammetry measurements were performed to confirm that the current is due to the reduction of  $H^+$ . Fig.4.32 shows such a curve in the region of the onset potential. The onset of the ring and disc current occur synchronously, confirming the formation of hydrogen. The full measurement is shown in fig.4.33. The magnitude of the disc current is steadily decreasing as expected while the current at the ring seems to decrease. This is likely due to the fast nucleation of hydrogen on the electrode, which causes the formation and growth of bubbles. With increasing bubble density less hydrogen reaches the ring electrode as only a fraction of the bubbles is in contact with the ring surface. The formed bubble then shields the area for not nucleated hydrogen molecules, which causes the current to decrease further.

Table 4.8: Electrocatalytic properties for all measured compounds. OnP stands for onset potential,
OP for overpotential, TS for Tafel slope, aRRDE for after the RRDE measurement and S1 and S2 for
scan speed 50 mV s <sup><math>-1</math></sup> and 5 mV s <sup><math>-1</math></sup> respectively.

Property	Mo	$S_2$	$MoS_2$ (	⊉ 160 °C	MoS <sub>2</sub> @	$200 ^{\circ}\mathrm{C}$	$MoS_{1.5}Se_{0.5}$		
Annealed	No	Yes	No	Yes	No	Yes	No	Yes	
OnP [mV] S1	-196	-228	-190	-280	-209	-242	-192	-300	
OnP [mV] S2	-199	na.	-184	-286	-209	-247	-193	-295	
OP [mV] S1	-246	-280	-394	-812	-246	-299	-218	-442	
OP [mV] S2	-258	na.	-286	-951	-249	-332	-222	-456	
$J_0  [mA  cm^{-2}]  S1$	-169.7	-290.1	-5.0	-502.2	-229.7	-55.0	-404.2	-516.2	
$J_0  [mA  cm^{-2}]  S2$	-1571.9	na.	-589.5	-3007.9	-2555.1	-1281.4	-11103.4	-3660.7	
TS $[mVdec^{-1}]$ S1	-74	-80	-165	-117	-72	-104	-61	-101	
TS $[mVdec^{-1}]$ S2	-56	na.	-61	-92	-54	-65	-44	-80	
OnP aRRDE [mV] S1	-205	an.	-195	na.	-213	na.	-195	-321	
OnP aRRDE [mV] S2	-203	na.	-186	-301	-211	-260	-194	-311	
OP aRRDE [mV] S1	-249	na.	-286	na.	-252	na.	-223	-488	
OP aRRDE [mV] S2	-248	na.	-285	-1430	-251	-362	-224	-491	
$J_0 \text{ aRRDE } [\text{mA cm}^{-2}] \text{ S1}$	-423.5	na.	-26.4	na.	-239.0	na.	-757.4	-571.8	
$J_0 \text{ aRRDE } [\text{mA cm}^{-2}] \text{ S2}$	-3540.1	na.	-887.7	-3162.3	-3375.2	-1873.8	-15347.8	-2363.2	
TS aRRDE $[mVdec^{-1}]$ S1	-67	na.	-109	na.	-74	na.	-58	-103	
TS aRRDE $[mVdec^{-1}]$ S2	-51	na.	-58	-100	-53	-66	-43	-83	

Table 4.9: Electrocatalytic properties for all measured compounds. On P stands for onset potential, OP for overpotential, TS for Tafel slope, aRRDE for after the RRDE measurement and S1 and S2 for scan speed 50 mV s<sup>-1</sup> and 5 mV s<sup>-1</sup> respectively.

Property	MoS	$S_1Se_1$	MoS <sub>0</sub>	$.5$ Se $_{1.5}$	Mo	$\mathrm{oSe}_2$	Pt	GC
Annealed	No	Yes	No	Yes	No	Yes	No	No
OnP [mV] S1	-207	-327	-217	-353	-220	-322	-9	-652
OnP [mV] S2	-208	-327	-218	-345	-223	-315	-19	na.
OP [mV] S1	-266	-498	-249	-657	-253	-395	-38	-1008
OP [mV] S2	-238	-547	-253	-762	-256	-402	-44	na.
$J_0 [{\rm mA cm^{-2}}] {\rm S1}$	-363.6	-1045.7	-82.9	-339.7	-41.5	-3162.3	-1.6	-399.9
$J_0 [{\rm mA cm^{-2}}] {\rm S2}$	-15848.9	-11253.4	-1204.1	-2716.2	-705.5	-8522.3	-1.6	na.
TS $[mVdec^{-1}]$ S1	-66	-103	-86	-145	-97	-82	-42	-206
TS $[mVdec^{-1}]$ S2	-45	-78	-62	-106	-66	-72	-34	na.
OnP aRRDE [mV] S1	-212	-362	-218	-356	-225	-329	na.	na.
OnP aRRDE [mV] S2	-209	-354	-217	-351	-224	-326	na.	na.
OP aRRDE [mV] S1	-237	-1143	-249	-802	-254	-418	na	na
OP aRRDE [mV] S2	-236	-1339	-253	-860	-253	-418	na.	na.
$J_0 \text{ aRRDE } [\text{mA cm}^{-2}] \text{ S1}$	-1081.2	-827.6	-165.2	-784.8	-87.5	-1721.7	na.	na.
$J_0 \text{ aRRDE } [\text{mA cm}^{-2}] \text{ S2}$	-20805.7	-5809.7	-1117.9	-2470.9	-508.0	-6709.1	na.	na.
TS aRRDE $[mVdec^{-1}]$ S1	-59	-146	-78	-133	-86	-89	na.	na.
TS aRRDE $[mVdec^{-1}]$ S2	-44	-106	-62	-112	-68	-75	na.	na.

This limit occurs already at very low currents (around 60 to 120  $\mu$ A) while the disc current continues increasing to mA-ranged values. If one is continuously using the nitrogen flow to flush away hydrogen bubbles on the surface as previously discussed, the measured currents reach higher values, but the signal to noise ratio increases significantly. In literature, the formation of bubbles is usually prevented by using hydrogen instead on nitrogen in the degassing process.<sup>[11][12]</sup> This is not applicable for the suggested measurements in this thesis due to the fact that if the solution was saturated, the

ring electrode would also oxidise the hydrogen from the solution and the origin of the measured current could not be determined.

If another way was found, so that the measured current would not be limited by the bubble formation, the current should increase similarly to the disc current, until the area of the platinum ring surface becomes the limiting factor. As no mass transport limited currents are reached, a quantification of the produced hydrogen is not possible using RRDE.



Figure 4.32: RRDE measurement of the  $MoS_{0.5}Se_{1.5}$  compound in 0.5 M  $H_2SO_4$  at 1000 rpm. The region around the onset of the reaction is shown revealing a synchronous increase in ring and disc current.



Figure 4.33: RRDE measurement of the  $MoS_{0.5}Se_{1.5}$  compound in 0.5 M  $H_2SO_4$  at 1000 rpm.

An alternative suggested by this thesis is to confirm the formation of hydrogen as shown in fig.4.32 and calculate the reaction rate using eq.2.5 and 2.6. Using these equations,  $k_0$  can be calculated from the exchange current density given by the Tafel plot and the Gibbs free energy is either given by literature or calculated using DFT.<sup>[8][12][77]</sup>



Figure 4.34: Tafel plot obtained in 0.5 M  $H_2SO_4$  for subsequent platinum measurement and for one  $MoS_{1.5}Se_{0.5}$  measurement at 5 mV s<sup>-1</sup>.



Figure 4.35: Polarization curves in 0.5 M  $H_2SO_4$  before and after the RRDE voltammetry measurement of compound  $MoS_{0.5}Se_{1.5}$ . The straight line corresponds to the initial compound while the dotted represents the annealed one.

As one can see in table.4.8 and 4.9 the measured exchange current density is significantly higher for all measured compounds than for the platinum. A reason for this is most likely the reaction is not at its thermodynamic equilibrium. This also manifests in the Tafel plot as shown in fig.4.34. It was generally observed that the changes from the cathodic and anodic branchs were moving to more negative potentials, as shown for the platinum measurements (M1 and M2). The steep part shown in the Pt M1 and  $MoS_{1.5}Se_{0.5}$  curve is most likely due to the fact that the measurement was not taken at its thermodynamic equilibrium. The platinum measurements were the only ones where a shift of the subsequent measurements reached a typical Tafel curve (Pt M2); all other samples exhibit the huge increase as shown for  $MoS_{1.5}Se_{0.5}$ . As the system is not at the thermodynamic equilibrium, the Tafel equation does not hold and therefore the incredible high calculated exchange current densities in table 4.8 and 4.9 are not correct. A possible solution could be to perform a second separate measurement where hydrogen is used in the degassing step instead of nitrogen.

To confirm that the catalyst film is still present after the RRDE measurement, polarisation curves at the same speed as before were performed. The measurements for the  $MoS_{0.5}Se_{1.5}$  are shown in fig.4.35 for the initial and annealed compounds. The initial compound shows almost the identical curve while the current was decreased for the annealed compound, which can also be seen in table 4.8 and 4.9. This was observed for all the measured samples and indicates that the lifetime of the annealed compound is very limited. As both of them were covered with the same amount of Nafion film it is unlikely that it is due to damage in the film.

### 4.2.5 Summary

The investigation of the Nafion film revealed that it was about 2000 times thicker than expected. This is probably due to solvent evaporation or a manufacturing error. An investigation of the influence of the film thickness on electrochemical measurements revealed that a 3:137 dilution of the initial Nafion solution could be neglected. Interestingly, in the limit of an infinitely fast rotation of the electrode an oxidation seems to occur. Similar studies on platinum did not show such a behaviour, and an explanation has still to be found.

A new deposition technique was established, where the catalyst was directly deposited on the electrode surface and coated with the diluted Nafion solution. This let to a tremendous increase in the film stability.

Regarding the RRDE measurements the experimental collection efficiency was determined as 25-26 % using the ferro/ ferri cyanide redox couple, which is in good agreement with the theoretical collection efficiency provided by the manufacturer. Afterwards the collection efficiency of the HER on a gold electrode was determined to be 16-19 %, after some challenges due to bubble formation were overcome. Unfortunately, the Nafion film deposited to fix the catalyst on the electrode revealed to have a crucial role. Due to the film the detection at the ring is limited and measured currents were not reproducible. A removal with hexane and an high positive applied potential enabled the detection of hydrogen at the ring. Unfortunately, subsequent scans had different ring currents and further work is needed to achieve reliable results.

The catalytic properties of all samples were investigated on glassy carbon in 0.5 M H<sub>2</sub>SO<sub>4</sub> and compared to literature. The measured compounds showed an increase, compared to similarly produced materials, but do not outperform lithium exfoliated samples.  $MoS_{1.5}Se_{0.5}$  showed the best performance, while in literature  $MoS_1Se_1$  are the best performing compounds. This suggests that the assumed atomic ratio might not be correct. The Tafel slopes and exchange current densities were calculated, yielding lower Tafel slopes and higher exchange current densities for the measurements at lower scan speeds. This and the observed Tafel curves indicate that the measurements were not conducted at the thermodynamic equilibrium, which leads to wrong values for both, Tafel slope and exchange current density.

RRDE voltammetry measurements proved that the generated current is due to the HER. It was also shown that the deposited catalysts remained on the electrode during the RRDE voltammetry measurement.

### 5 Conclusion

### 5.1 Summary

This section summarises the results obtained during the Masters thesis.

In a first step, MoXY compounds were obtained using a hydrothermal method. The compounds showed XRD spectra, which were in good agreement with literature. Furthermore, the XRD indicated that a most of the samples are amorphous. TEM investigations confirmed the amorphous structures with smaller crystalline areas. Electron beam diffraction revealed that the materials were not stable during the investigation, therefore these results are not included. A change in material was also observed during the Raman measurements. These differ from the expected values and the explanation has yet to be found.

While EDXS was used to confirm elemental compositions, XPS ws found to be more useful as the sulphur  $K_{\alpha}$  and molybdenum  $L_{\alpha}$  signals overlap in the EDXS spectra. While XPS measurements gave good agreement with the XRD results, it also revealed some contamination most likely due to oxidation to MoO<sub>3</sub> for the MoS<sub>1.5</sub>Se<sub>0.5</sub>, MoS<sub>1</sub>Se<sub>1</sub> and MoSe<sub>2</sub> samples and of MoO<sub>2</sub> for MoS<sub>2</sub>. Only MoS<sub>0.5</sub>Se<sub>1.5</sub> does not show any oxidation signals. Due to the limited availability of the XPS, only the mentioned compounds were measured with this technique. When it was clear that enough measurement time was available, also the MoS<sub>2</sub> at 160 °C and at 200 °C were sent to Auckland. These results are still pending.

As a change in material was observed in during the Raman and the electron beam diffraction measurements all compounds were annealed at 200  $^{\circ}$ C in a vacuum furnace.

As initial electrochemical measurements were unsuccessful with an ink-based approach, a new deposition method was established where the catalyst was directly deposited on the electrode and covered with a thin Nafion film. It was proven, that the Nafion film used can be neglected and has no influence regarding the measurement. A new cleaning procedure was established, which yielded more reproducible measurement than before, furthermore the Ag/AgCl reference electrode was found to be incorrect and a blank silver wire was investigated and used as an alternative for the measurements at pH 2.5 with an estimated error of  $\pm 4$  mV. The RHE was found to be accurate with and estimated error of  $\pm 6$  mV.

RRDE measurements were conducted and the collection efficiency was determined (using the ferro/ ferri cyanide redox couple) to be in good agreement with the the manufacturer specifications. Hydrogen could be detected at the platinum ring and the setup was improved, enabling the determination of the collection efficiency on a blank gold electrode to be 16-19% at a pH of 2.5, depending on the rotation speed.

Unfortunately, the deposition of the film was found to have a crucial influence on the on the detection of hydrogen. A procedure was established to remove the Nafion film from the ring electrode, which enable the detection of hydrogen. But the results are not consistent and further work is needed to get a collection efficiency for a film-covered electrode.

Last but not least, all compounds were measured on a glassy carbon disc electrode in  $0.5 \text{ M H}_2\text{SO}_4$ , revealing that all unannealed compounds perform significantly better. Furthermore,  $\text{MoS}_{1.5}\text{Se}_{0.5}$  was found to be the best catalyst. Using RRDE voltammetry, it could be confirmed that the onset is due to the production of hydrogen and not the degradation of catalyst. It was also shown that the catalyst was still intact after the RRDE voltammetry measurements.

It was found that the exchange current densities calculated using the Tafel equation are most likely incorrect, due to the fact that the reaction was not at its thermodynamic equilibrium. Furthermore, the scan speed has an influence on the obtained Tafel slopes, giving lower slopes with slower scan speeds. This carried over into the calculation for the exchange current density and therefore another error source.

### 5.2 Future work

For the future there are still various challenges left.

Regarding the material synthesis and characterisation it is still unclear, why the obtained MoXY compounds have shown to be unstable towards the electron beam during the diffraction measurement and under the Raman laser. Furthermore, a lithium exfoliation approach should increase the catalytic properties significantly, as it favours the 1T-phase. Additionally, an approach with mixing the 2H and 1T phase would potentially offer a good alternative to the InP quantum dots, due to the similar conduction and valance bands. That a mixture of 2H and 1T-phase compounds can be used for photocatalysis has just been shown for  $MoS_2$  in 2016 and for MoXY compounds this year.<sup>[9][14]</sup>

Regarding the RRDE measurement setup, there has been a big improvement from not measuring limiting currents to the determination of the collection efficiency of the HER on a gold electrode. In order to use it in combination with catalysts there is still some work to be done.

First, a more efficient way for the removal of the Nafion film must be found which enables reproducible and consistent measurements. Second, more measurements are needed for the collection efficiency to be able to do a statistical evaluation of the reproducibility. And third, a method to replace the needle approach with some solution, which would enable automation would be a big improvement.

Regarding the silver wire pseudo reference, the conversion to the SHE has still to be proven, as the ferro/ ferri cyanide redox couple shifted in very acidic conditions to more positive potentials. This could probably be done with a standard reference electrode, such as a double junction Ag/AgCl or a saturated calomel electrode.

Last but not least, more work has to be done to measure the Tafel plot at its thermodynamic equilibrium. This might be achieved by long term measurements where a catalyst is usually measured over a couple of thousand scans. This would furthermore give insight into the long term stability, which is currently lacking. Alternatively, measurements in hydrogen saturated solution could be an alternative.

### 5.3 Closing words

To close let's have a look at the initial aim of the thesis presented in sec.1.4.

The aim of producing photocatalytic devices was not reached, due to the various struggles in the measurement setup, which would have made it impossible to characterise the produced devices in a scientific manner. Therefore, the focus shifted to the improvement of the measurement method.

The used catalysts were all obtained using hydrothermal methods. Samples provided by Yuta were only measured in an initial screening, where the results were not reproducible and the Ag/AgCl reference electrode was found to be unreliable. As they did not perform significantly better and due to the restricted time available, only the already characterised hydrothermally produced compounds were measured. Furthermore, more characterisation techniques were used, namely EDXS, XPS, and Raman spectroscopy.

RRDE voltammetry was improved to the point, where hydrogen could be detected, and a collection efficiency could be determined for the blank gold electrode. This has shown not to be directly applicable for the film covered electrode. Therefore more work has to be done.

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Universität Basel



Philosophisch-Naturwissenschaftliche Fakultät

**Erklärung zur wissenschaftlichen Redlichkeit** (beinhaltet Erklärung zu Plagiat und Betrug)

Bachelorarbeit / Masterarbeit (nicht Zutreffendes bitte streichen)

Titel der Arbeit (Druckschrift):

RING-DISC ELECTRODE POLANNG FOR THE EVALUATION OF OLTAMM MOLYBDENUM DICHALCOGENIDE NAVOSTRUCTURES

Name, Vorname (Druckschrift):

AMPORT TANJA

Matrikelnummer:

-052-890

Hiermit erkläre ich, dass mir bei der Abfassung dieser Arbeit nur die darin angegebene Hilfe zuteil wurde und dass ich sie nur mit den in der Arbeit angegebenen Hilfsmitteln verfasst habe.

Ich habe sämtliche verwendeten Quellen erwähnt und gemäss anerkannten wissenschaftlichen Regeln zitiert.

Diese Erklärung wird ergänzt durch eine separat abgeschlossene Vereinbarung bezüglich der Veröffentlichung oder öffentlichen Zugänglichkeit dieser Arbeit.

🗆 ja 🛛 nein

Ort, Datum:

DELLINGTON 16.8.18

Unterschrift:

Dieses Blatt ist in die Bachelor-, resp. Masterarbeit einzufügen.

# Appendices

# A XRD spectra

Fig.A.1 shows the various simulated reference spectra from the ICDD and their corresponding identification number.



Figure A.1: XRD of important compounds from the ICDD as well the measurement from the blank sample holder.

# B TEM images

The big particle mentioned in the results and discussion is shown in fig.B.1.



Figure B.1: Area of the EDXS spectra of sample  ${\rm MoS}_2$ 

### C EDXS spectra

The EDXS spectra for all measured compounds are shown in this section. A part of the axis is skipped from 13.0 to 16.7 eV as it does not show any peaks.



4000  $\frac{x^{s}}{5}$  3000  $C K_{\alpha}^{2}$   $C K_{\alpha}^{2}$  $C K_{$ 

Figure C.1: Area of the EDXS spectra of sample  $MoS_2$ 

Figure C.2: EDXS spectra of sample  $MoS_2$ 



Figure C.3: Area of the EDXS spectra of sample  $MoS_2 @ 160 °C$ 



Figure C.4: EDXS spectra of sample  $\rm MoS_2$  @ 160  $^{\rm o}\rm C$ 





Figure C.5: Area of the EDXS spectra of sample  $MoS_2 @ 200 \ ^{\circ}C$ 

Figure C.6: EDXS spectra of sample  $\rm MoS_2$  @ 200  $^{\circ}\rm C$ 





Figure C.7: Area of the EDXS spectra of sample  $MoS_{1.5}Se_{0.5}$ 

Figure C.8: EDXS spectra of sample  $MoS_{1.5}Se_{0.5}$ 



Figure C.9: Area of the EDXS spectra of sample  $\rm MoS_1Se_1$ 



Figure C.10: EDXS spectra of sample  $MoS_1Se_1$ 



Figure C.11: Area of the EDXS spectra of sample  $MoS_{0.5}Se_{1.5}$ 



Figure C.12: EDXS spectra of sample  $MoS_{0.5}Se_{1.5}$ 



Figure C.13: Area of the EDXS spectra of sample  $MoSe_2$ 



Figure C.14: EDXS spectra of sample MoSe<sub>2</sub>

### D Derivation for RDE

### D.1 Rotating disc electrode theory

Rotating disc electrode voltametry (RDE) uses a disk which is rotated with a frequency  $\omega$ . It is one of the few cases for which the diffusion and convection equation derived from the Navier-Stokes equation can be solved. In contrast to most electrochemical methods, where the solution is motionless, the solution has a constant laminar flow at the electrode surface. Therefore reactions are no longer diffusion but mass transport limited. In the following the theory describing this behaviour is presented.

Consider a flat disk with a radius r, an angular frequency  $\omega$  immersed in solution with a density  $\rho$ and a kinematic viscosity  $\nu$ . If the concentration is only a function of the distance to the electrode and the bulk concentration of the solution is  $C_B$ , then the convective diffusion equation can be simplified to eq.D.1

$$\nu_Z(Z)\frac{dC}{dZ} = D\frac{d^2C_F}{dZ^2} \qquad \qquad for \ 0 \le Z \le \infty \qquad (D.1)$$

Furthermore we assume that all material that reaches the electrode surface undergoes a reaction therefore we obtain the following boundary conditions:

$$C = 0 \qquad \qquad for \ Z = 0 \qquad (D.2)$$

$$C = C_B$$
 for  $Z = \infty$  (D.3)

After the first integration of eq.D.1  $\frac{dC}{dZ}$  is given by:

$$\frac{dC}{dZ} = a_1 exp\left(\frac{1}{D} \int_0^Z \nu_Z(y) dy\right) \tag{D.4}$$

After the second integration one obtains:

$$C(Z) = a_1 \int_0^Z exp\Big(\frac{1}{D} \int_0^t \nu_Z(y) dy\Big) dt + a_2 = a_1 J + a_2$$
(D.5)

where the current density is  $J = \int_0^Z exp\left(\frac{1}{D}\int_0^t \nu_Z(y)dy\right)dt$ . Using boundary condition D.2 one sees that  $a_2$  must be zero. To solve eq.D.5 we distinguish two regimes, close to the electrode and far in the solution. Close to the electrode the concentration will be mainly depending on the diffusion while the diffusion can be neglected in the bulk solution. The layer in which the concentration is diffusion limited is called hydrodynamic diffusion boundary layer denoted by  $\delta_d$ . In the region close to the electrode surface  $\nu_Z$  can be approximated by the numerical solution of  $\nu_Z \approx -0.51 \sqrt{\frac{\omega^3}{\nu}} y^2$  which vields:

$$J_1 = \int_0^{\delta_d} exp\Big(-\frac{\omega^{\frac{3}{2}}t^3}{5.88D\nu^{\frac{1}{2}}}\Big)dt$$
(D.6)

By substituting with  $u = \frac{\omega^{\frac{1}{2}}t}{(5.88)^{\frac{1}{3}}D^{\frac{1}{3}}\nu^{\frac{1}{6}}}$  we obtain:

$$J_1 \approx \frac{1.81D^{\frac{1}{3}}\nu^{\frac{1}{6}}}{\omega^{\frac{1}{2}}} \int_0^{2(\frac{\nu}{D})^{\frac{1}{3}}} exp(-u^3)du$$
(D.7)

As the integration rapidly decreases we can approximate the upper limit with infinity. The solution of this integral is then a gamma function of the form:

$$J_1 \approx \frac{1.81D^{\frac{1}{3}}\nu^{\frac{1}{6}}}{\omega^{\frac{1}{2}}} (\frac{1}{3}\Gamma(\frac{1}{3})) = 1.611D^{\frac{1}{3}}\nu^{\frac{1}{6}}\omega^{-\frac{1}{2}}$$
(D.8)

In the bulk of the solution  $\nu_Z$  can be approximated by  $-0.89\sqrt{\nu\omega}$ . Therefore we get:

$$J_2 = \int_{\delta_d}^{\infty} exp(-\frac{0.89\sqrt{\nu\omega}}{D}t)dt = \frac{D}{0.89\sqrt{\nu\omega}}exp(-\frac{0.89\sqrt{\nu\omega}}{D}\delta_d)$$
(D.9)

In the case of  $\nu \gg D J_2$  can be neglected and we determine  $a_1$  using eq.D.5 and eq.D.8 applying the boundary condition in eq.D.3:

$$a_{1} = \frac{C_{B}}{1.611(\frac{D}{\nu})^{\frac{1}{3}}\sqrt{\frac{\nu}{\omega}}}$$
(D.10)

Now we can rewrite eq.D.5.

$$C(Z) = \frac{C_B}{1.611(\frac{D}{\nu})^{\frac{1}{3}}\sqrt{\frac{\nu}{\omega}}} \int_0^Z exp\Big(\frac{1}{D}\int_0^t \nu_Z(y)dy\Big)dt$$
(D.11)

The current measured produced by the mass flux at the electrode can then be calculated using:

$$I = nF\pi r^2 D(\frac{\partial C}{\partial t})_{Z=0} \tag{D.12}$$

Giving the following expression which is known as Levich current.<sup>[36]</sup>

$$I_L = nF\pi r^2 D^{\frac{2}{3}} C_B \nu^{-\frac{1}{6}} \omega^{\frac{1}{2}}$$
(D.13)

The mass flux at the disk surface j is given by:

$$j = D(\frac{\partial C}{\partial Z})_{(Z=0)} = 0.62D^{\frac{2}{3}}C_B\nu^{-\frac{1}{6}}\omega^{\frac{1}{2}}$$
(D.14)

 $\delta_d$  can be calculated using  $\delta_d = \frac{DC_B}{j}$  giving:

$$\delta_d = 1.6D^{\frac{1}{2}}\nu^{-\frac{1}{6}\omega^{-\frac{1}{2}}} \tag{D.15}$$

### D.2 Thin film coated rotating disc electrode

Let's consider a RDE electrode covered with a thin film. The film has a thickness  $\delta_f$ , the concentration of our reactant in the film is  $C_f$  and it's diffusion constant  $D_f$ . Furthermore no convection is assumed in the film. The surface of the electrode is set to be at  $Z = -\delta_f$ . The solution interface is at Z = 0. In the film the diffusion equation is given by:

$$\frac{d^2 C_f}{dZ^2} = 0 \qquad \qquad for \ -\delta_f \le Z \le 0 \qquad (D.16)$$

In the solution the concentration C is given by eq.D.1. The reaction is assumed to be fast enough so that the concentration at the surface is:

$$C = 0$$
 for  $Z = -\delta_f$  (D.17)  
At the membrane-solution surface the mass must be conservated therefore eq.D.18 holds.

$$D_f \left(\frac{dC_f}{dZ}\right)_{Z=0} = D\left(\frac{dC}{dZ}\right)_{Z=0} \tag{D.18}$$

The partition coefficient  $\alpha$  at the membrane surface is defined as:

$$\alpha = \frac{C_f}{C} \tag{D.19}$$

By integrating eq.D.16 we get the following equation, where  $a_1$  and  $a_2$  are constant in respect with Z.

$$C_f(Z) = a_1 Z + a_2$$
 (D.20)

With the first boundary condition given in eq.D.17 it follows

$$a_2 = a_1 \delta_f \tag{D.21}$$

As we saw in sec.D.1 in the solution the concentration is given by:

$$C = a_3 \delta_d + a_4 \tag{D.22}$$

where  $\delta_d = 1.6D^{\frac{1}{3}}\nu^{\frac{1}{6}}\omega^{-\frac{1}{2}}$ . Using eq.D.3 gives  $a_3$  by:

$$a_3 = \frac{C_b - a_4}{\delta_d} \tag{D.23}$$

At the film solution interface Z = 0 C is given by the partition coefficient in eq.D.19. Therefore  $a_4$  is:

$$a_4 = \frac{C_f}{\alpha} \tag{D.24}$$

Furthermore eq.D.18 may be evaluated using eq.D.20, eq.D.23 and eq.D.24.

$$D_f a_1 = D \frac{C_b - \frac{C_f}{\alpha}}{\delta_d} = D \frac{C_b - \frac{a_1 Z + a_2}{\alpha}}{\delta_d}$$
(D.25)

As Z = 0 at the interface the  $a_1$  term on the right side vanishes. Using eq.D.21 the following relation can be obtained for  $a_1$ :

$$a_1 = \frac{C_B}{\delta_d} \left( \frac{1}{\frac{D_f}{D} (1 + \frac{D\delta_f}{D_m \alpha \delta_d})} \right)$$
(D.26)

Hence the solution for eq.D.16 is:

$$C_f = \frac{C_B D}{\delta_d D_f} \left( \frac{Z + \delta_f}{1 + \frac{D \delta_f}{D_f \alpha \delta_d}} \right) \tag{D.27}$$

As we know  $C_f a_4$  is can be calculated using eq.D.24.

$$a_4 = C_B \left(\frac{1}{\frac{D_f \delta_d \alpha}{\delta_f D} + 1}\right) \tag{D.28}$$

Using eq.D.23  $a_3$  is given by:

$$a_3 = \frac{C_B}{\delta_d} \left( \frac{1}{1 + \frac{\delta_f D}{D_f \delta_d \alpha}} \right) \tag{D.29}$$

The measured current  $I_{meas}$  is given by:

$$I_{meas} = nF\pi r^2 D_f (\frac{\partial C}{\partial Z})_{Z=-\delta_f}$$
(D.30)

Evaluating this expression using eq.D.27 gives

$$I_{meas} = nF\pi r^2 D^{\frac{2}{3}} C_B \nu^{-\frac{1}{6}} \omega^{\frac{1}{2}} \left(\frac{1}{1 + \frac{D\delta_f}{\alpha D_f \delta_d}}\right) = I_L \left(\frac{1}{1 + \frac{D\delta_f}{\alpha D_f \delta_d}}\right)$$
(D.31)

where  $I_L$  is the current in absence of the membrane as also given in eq.D.13.

### D.2. THIN FILM COATED ROTATING DISC ELECTRODE

By taking the inverse one can obtain

$$\frac{1}{I_{meas}} = \frac{1}{I_L} + \frac{D\delta_f}{I_L \alpha D_M \delta_d} = \frac{1}{I_L} + \frac{1}{I_f}$$
(D.32)

Where  $I_f$  is the current in the thin film. Using eq.D.15 and eq.D.32 it can be rewritten as:

$$I_f = nFAC_B \alpha D_f \delta_f^{-1} = nFAC_f D_f \delta_f^{-1} \tag{D.33}$$

# E Varia

The home-built bubbler used for the degassing step is shown in fig.E.1.



Figure E.1: Bubbler used in the electrochemical experiments.