

DEVELOPMENT OF NANOSTRUCTURED REDOX
COUPLE $\text{Ni}(\text{OH})_2/\text{NiOOH}$ -Ni BASED RECEPTOR
ELEMENTS FOR DETECTION OF FORMALDEHYDE
IN ALKALINE MEDIA

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RAZVOJ NANOSTRUKTURIRANIH RECEPTORSKIH
ELEMENTOV ZA DETEKCIJO FORMALDEHIDA V ALKALNIH
MEDIJAH NA OSNOVI REDOKS SISTEMA $\text{Ni}(\text{OH})_2/\text{NiOOH-Ni}$

Doktorska disertacija

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Abstract

The present dissertation deals with the electrochemical synthesis of Ni-based electrodes, i.e. receptor elements that enable fast, completely repeatable and feasible testing of formaldehyde (HCHO) by monitoring their oxidation ability in alkaline media. The main objectives of this work were to electrochemically synthesise 2-D films and 1-D nanowires based on metallic Ni and catalytically active $\text{Ni}(\text{OH})_2/\text{NiOOH}$ surface species.

It was shown that electro-catalytic oxidation of HCHO is highly dependent on the surface composition of Ni-based electrodes, the formation and crystallinity of which can be controlled by electrodeposition conditions (pH, substrate, etc.). A detailed electrochemical study supported with X-ray diffraction (XRD) and Fourier-transform infrared spectroscopy (FT-IR) analysis showed that $\text{Ni-Ni}(\text{OH})_2/\text{NiOOH}$ electrodes can be prepared via direct electrodeposition or indirect processing which includes the electrodeposition of Ni/NiO and subsequent KOH-transformation of catalytically inactive NiO to active $\text{Ni}(\text{OH})_2/\text{NiOOH}$.

Direct synthesis is only possible by using strongly acidic conditions in an electrochemical deposition. Directly deposited $\text{Ni}(\text{OH})_2/\text{NiOOH}$ -Ni film, i.e. “fine-grained” Ni film, was prepared from NiSO_4 electrolyte (pH = 2.5) by applying a constant potential of -1.0. The pH of 2.5 was adjusted by adding H_2SO_4 . Fine-grained Ni film was electrodeposited on Au substrate that exhibits preferential crystallographic orientation in (1 1 1) direction. XRD confirmed the presence of electrodeposited Ni ($\text{Ni}^{2+} + 2e^- \rightarrow \text{Ni}^0$) with the same texture in (1 1 1). Also, XRD and FT-IR confirmed the presence of crystalline hexagonal $\alpha\text{-Ni}(\text{OH})_2$ which chemically precipitates on the surface of metallic Ni due to the massive production of OH^- in water splitting reaction ($\text{H}_2\text{O} + 2e^- \rightarrow \text{H}_2 + 2\text{OH}^-$).

The indirect preparation of Ni-based receptor elements was introduced in the case of “coarse-grained” Ni film and Ni nanowires. The “coarse-grained” Ni film was electrodeposited from NiSO_4 solution (pH = 5.5) by applying a constant potential of -1.0. Also, “coarse-grained” Ni film was electrodeposited on Au (1 1 1). The XRD and FT-IR confirmed the presence of metallic Ni (with the preferential (1 1 1)-orientation), and NiO_2 which is mainly present due to the rapid passivation of metallic Ni upon exposure to air or aqueous solutions. The XRD analysis revealed the absence of $\text{Ni}(\text{OH})_2$ as the mechanism of electrodeposition was different due to the increase of electrolyte pH. The Ni nanowires were electrodeposited from $\text{NiSO}_4\text{-H}_3\text{BO}_3$ electrolyte into Al_2O_3 template that was covered by isotropic Au at the bottom. The XRD revealed the presence of isotropic Ni and NiO after the removal of the template.

After electrodeposition of “coarse-grained” Ni film and Ni nanowires, the surface transformation, i.e. KOH-modification (from inactive NiO_x to catalytically active $\text{Ni}(\text{OH})_2/\text{NiOOH}$) was introduced. A comprehensive study of surface transformation was performed using cyclic voltammetry under controlled experimental conditions that include: the potential range (up to 1.0 V or 0.6 V), scan rate (10, 200 or 400 mV s^{-1}) and a number of cycles (1–50). Each surface transformation of KOH-modified electrodes was supported by testing the catalytic ability towards HCHO oxidation and by means of analysis (XRD, FT-IR or TEM). It has been shown that inactive NiO_x is completely transformed to active $\text{Ni}(\text{OH})_2/\text{NiOOH}$ by using the following parameters in KOH-modification process: potential range up to +0.6 V, the scan rate of 200 mV s^{-1} , and 50 cycles. XRD confirmed the presence of crystalline hexagonal $\alpha\text{-Ni}(\text{OH})_2$ that has grown on a preferentially (1 1 1)-oriented fcc Ni in coarse-grained Ni film substrate, while the presence of amorphous $\text{Ni}(\text{OH})_2$ on the surface of the isotropic Ni nanowires substrate was proven by TEM and FT-IR.

It was shown that the KOH-modified Ni-based electrodes are able to electro-catalyze an HCHO oxidation, due to the formation of an active $\text{Ni}(\text{OH})_2/\text{NiOOH}$ surface layer. Based on a comparison of the output current density (current / electrochemically active surface, determined by the ‘oxalate method’) and the electrochemical detection potential, it was shown that KOH-modified Ni nanowires exhibit better catalytic properties for HCHO

detection in comparison to KOH-modified fine- and coarse-grained Ni films. The better catalytic activity was attributed to the amorphous nature (TEM, FT-IR) of thin $\text{Ni(OH)}_2/\text{NiOOH}$ surface layer and its low work function, due to electron doping from under layered Ni. On the other hand, the HCHO electrochemical oxidation of KOH-modified Ni films resulted in lower output-current densities and higher onset overpotential attributed to the $\alpha\text{-Ni(OH)}_2/\gamma\text{-NiOOH}$ surface layer.

The catalytic properties of KOH-modified Ni-based electrodes were supported by a study of sensory properties by determination of the following parameters: limit of detection, linear range, sensitivity, and selectivity. It is worth mentioning that the developed HCHO detection platform that is based on KOH-modified Ni nanowires surpasses other Ni-based nanostructured electrodes and has limits of detection ($8\text{ }\mu\text{mol L}^{-1}$) comparable to those achieved with noble metals ($5\text{--}10\text{ }\mu\text{mol L}^{-1}$). Thus, it shows great potential for the successful implementation in future HCHO sensing applications.

Povzetek

V tem doktorskem delu smo se osredotočili na elektrokemijsko sintezo Ni-osnovanih katalizatorjev, t. i. receptorskih elementov, ki kažejo velik potencial za hitro in cenovno ugodno določanje toksičnega formaldehida (HCHO) v alkalnih vodnih raztopinah in so hkrati primerni za nadaljnjo uporabo v senzoričnih napravah. Pripravljeni so bili receptorski elementi različnih dimenzij, 2-D filmi in 1-D nanožice, katerih sestava je temeljila na osnovi Ni in katalitično aktivnih $\text{Ni(OH)}_2/\text{NiOOH}$ površinskih mest (t. i. $\text{Ni-Ni(OH)}_2/\text{NiOOH}$ receptorski elementi).

Tekom študije je bilo pokazano, da je elektrokemijska katalitična reakcija HCHO oksidacije v veliki meri odvisna od sestave in kristaliničnosti površine vsakega posameznega Ni receptorskega elementa. Sama sestava in tudi kristaliničnost sta lahko v veliki meri nadzorovano pripravljene v samem elektrokemijskem nanosu z izbiro primerne substrata ali pH raztopine. Podrobna študija elektrokemijskega nanosa, ki je bila podprta z različnimi analiznimi tehnikami (rentgensko difrakcijo – *angl.* XRD, vibracijsko spektroskopsko metodo – *angl.* FT-IR ali transmisijskim elektronskim mikroskopom – *angl.* TEM), je pokazala, da so lahko katalitično aktivne površinske specije ($\text{Ni(OH)}_2/\text{NiOOH}$) tvorjene prek direktne elektrokemijske priprave ali posredno. Le-ta zajema elektrokemijski nanos Ni/NiO osnovane elektrode in kasnejšo pretvorbo neaktivne NiO površine do aktivne $\text{Ni(OH)}_2/\text{NiOOH}$ v procesu KOH modifikacije.

Izkazalo se je, da je direktna sinteza možna le z uporabo raztopine s kislim pH-jem. Direktni nanos Ni-Ni(OH)₂ filma, t. i. »drobno-zrnat« Ni film, je bil izveden pri konstantnem potencialu -1,0 V iz raztopine NiSO₄, katere pH je bil uravnan na 2,5 z dodatkom konc. H₂SO₄. Drobnozrnat Ni film je bil nanešen na Au substrat s kubično kristalno strukturo in prednostno orientacijo v (1 1 1) smer. XRD analiza je potrdila prisotnost elektrokemijsko nanešenega kovinskega Ni ($\text{Ni}^{2+} + 2e^- \rightarrow \text{Ni}^0$) s kubično kristalno strukturo in enako prednostno orientacijo (1 1 1) kot Au substrat. Prav tako sta XRD in FT-IR analizi potrdili prisotnost Ni(OH)_2 . Le-ta je bil prisoten na površini zaradi reakcije razklopa vode ($\text{H}_2\text{O} + 2e^- \rightarrow \text{H}_2 + 2\text{OH}^-$) pri močno negativnem potencialu, ki je vodila do znatne produkcije OH⁻ in posledično do kemijskega obarjanja slabo topnega kristaliničnega $\alpha\text{-Ni(OH)}_2$ na površini kovinskega Ni.

Posredna priprava Ni osnovanih receptorskih elementov je bila vpeljana pri pripravi »grobno-zrnatega« Ni filma in Ni nanožic. »Grobno-zrnat« Ni film je bil pripravljen elektrokemijsko pri konstantnem potencialu -1,0 V iz raztopine NiSO₄ (pH = 5,5). Tudi grobo-zrnat Ni film je bil nanešen na Au substrat s kubično kristalno strukturo in prednostno orientacijo v (1 1 1) smer. XRD in FT-IR analizi sta potrdili prisotnost kovinskega Ni s kubično kristalno strukturo (prednostno (1 1 1)-orientiran) in NiO₂, ki je bil v večini prisoten na površini zaradi hitre pasivacije kovinskega Ni pri izpostavljenosti zraku ali vodnim raztopinam. Z analizo smo tudi ovrgli možnost prisotnosti Ni(OH)_2 na površini, saj se pod temi eksperimentalnimi pogoji ni oboril na površini zaradi drugačnega mehanizma elektrokemijskega nanosa. Ni nanožice so bile pripravljene iz NiSO₄-H₃BO₃ elektrolita v Al₂O₃ predlogo, ki je bila na spodnji strani zapolnjena z Au (izotropne kristalne strukture). XRD analiza, ki je bila narejena po odstranitvi Al₂O₃ predloge v močni bazi, je potrdila prisotnost kovinskega Ni (z izotropno kristalno strukturo) in NiO.

Prav zaradi prisotnosti Ni oksidov smo »grobno-zrnat« film in Ni nanožice v naslednjem koraku elektrokemijsko tretirali v raztopini KOH z uporabo ciklične voltametrije. Ta eksperimentalni korak je bil vpeljan z namenom, da neaktiven površinski Ni oksid pretvorimo v katalitično aktivne $\text{Ni(OH)}_2/\text{NiOOH}$ specije. Obsežna študija pretvorbe površinskega NiO do $\text{Ni(OH)}_2/\text{NiOOH}$ v procesu KOH modifikacije je bila izvedena pri različnih eksperimentalnih pogojih. Le-ti so vključevali študijo potencialnega območja (do +1,0 V ali do +0,6 V), študijo hitrosti preleta (10, 200 ali 400 mV s⁻¹) in študijo števila ciklov (1–50). Elektrokemijska analiza katalitičnih lastnosti v HCHO alkalni raztopini, ki je bila

podprta z XRD, FT-IR ali TEM analizo, je pokazala, da maksimalno pretvorbo površine iz katalitično neaktivnega NiO do katalitično aktivnega Ni(OH)₂/NiOOH dosežemo pri sledečih pogojih KOH modifikacije: območje potencialov le do +0,6 V, 200 mV s⁻¹ in 50 ciklov. Z XRD analizo smo potrdili prisotnost heksagonalnega α-Ni(OH)₂ na površini kovinskega Ni pri »grobno-zrnati« Ni elektrodi, medtem ko smo prisotnost amorfnega Ni(OH)₂ na površini izotropnega Ni pri Ni nanožicah potrdili šele po TEM in FT-IR analizah.

Tekom študije smo uspeli za vsako posamezno elektrodo (drobno- ali grobo-zrnat Ni filma ali Ni nanožice) poiskati eksperimentalne pogoje, ki so omogočili pripravo katalitično aktivne površinske komponente Ni(OH)₂/NiOOH, ki je ključna za elektrokemijsko (t. i. amperometrično) detekcijo HCHO. Glede na to, da so bili izhodni signali detekcije (električni tok) normalizirani na predhodno določeno elektrokemijsko aktivno površino (določena z »oksalatno metodo«), nam je bila omogočena primerjava teh treh različno dimenzioniranih elektrod. Na podlagi primerjave izhodne gostote električnega toka (tok/elektrokemijska aktivna površina) in elektrokemijskega potenciala detekcije smo ugotovili, da KOH modificirane Ni nanopalčke izkazujejo najboljše katalitične lastnosti pri detekciji HCHO v primerjavi z »drobno-zrnatim« Ni filmom in KOH modificiranim »grobno-zrnatim« Ni filmom. Te odlične katalitične lastnosti (povečana gostota električnega toka in znižan vnos energije, ki je potreben za potek reakcije – manj pozitiven elektrokemijski potencial) Ni nanopalčk so bile pripisane nastanku tankega sloja površinskih aktivnih vrst Ni(OH)₂/NiOOH in njihovi amorfnosti naravi (dokazano s TEM analizo). Po drugi strani pa je glavni razlog za slabše katalitično obnašanje Ni filmov kristalna struktura površinskih komponent, in sicer α-Ni(OH)₂ in γ-NiOOH (dokazano z XRD analizo).

Odlične katalitične lastnosti KOH modificiranih Ni nanopalčk so bile podprte s študijo senzoričnih lastnosti, pri kateri smo vsem trem elektrodam določili sledeče parametre: linearno območje, meja detekcije, občutljivost, selektivnost. Prek teh študij je bilo dokazano, da KOH modificirane Ni nanopalčke dosežejo najnižjo mejo detekcije, najnižjo občutljivost, dobro ponovljivost in zelo dobro selektivnost. Ne samo, da so ti rezultati presegli lastnosti »drobno-zrnatega« in »grobno-zrnatega« filma, hkrati je treba poudariti, da so bili s tako nizko mejo detekcije (8 μmol L⁻¹) preseženi vsi do sedaj objavljeni rezultati v literaturi, pri katerih so bili kot receptorski element za detekcijo formaldehida uporabljeni različno strukturirani in dopirani receptorski elementi na osnovi žlahtnih kovin ali Ni/Fe/Co.

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Abbreviations

0-D	... Zero-dimensional
1-D	... One-dimensional
2-D	... Two-dimensional
3-D	... Three-dimensional
A	... Area
AAO	... Anodic aluminium oxide
A_{ecsa}	... Electrochemically active surface area
A_{geom}	... Geometrically determined surface area
<i>aq</i>	... Aqueous phase
BSE	... Backscattered electrons
CA	... Chronoamperometry
CE	... Counter electrode
CV	... Cyclic voltammetry
DFT	... Density function theory
fcc	... Face-centred cubic
FEG-SEM	... Field emission gun scanning electron microscopy
FT-IR	... Fourier transform infrared spectroscopy
HCHO	... Formaldehyde
ICDD	... The Powder Diffraction File
iR	... Ohmic drop
LOD	... Limit of detection
LSV	... Linear sweep voltammetry
OCP	... Open circuit potential
PC	... Polycarbonate
PVD	... Physical vapour deposition
RE	... Reference electrode
<i>s</i>	... Solid-phase
SAED	... Selected area diffraction
SE	... Secondary electrons
SHE	... Standard hydrogen electrode
TEM	... Transmission electron microscope
WE	... Working electrode
XRD	... X-ray diffraction

Symbols

$j_{1^{st}}$	... Current density in the 1 st cycle
$j_{50^{th}}$	... Current density in the 50 th cycle
j_m	... Migratory flux
∂	... Derivation
$\emptyset$	... The external electric field at the electrode/solution interface
Δj	... Change in current density
$\propto$	... Proportional
c	... Concentration
E	... Potential
e^-	... Electron
E_0	... Standard electrode potential
E_{aq}	... Solution potential
E_e	... Equilibrium potential
E_{off}	... Relaxation potential
E_{on}	... Deposition potential
$E_{p,a}$	... Anodic peak potential
$E_{p,c}$	... Cathodic peak potential
E_s	... Potential of the electrode in the solid phase
F	... Faraday constant
h	... Planck's constant
i	... Overall current
i_0	... Exchange current
i_L	... Diffusion limited current
i_{lim}	... Diffusion limiting current
i_{ox}	... Oxidation current
$i_{p,a}$	... Anodic peak current
$i_{p,c}$	... Cathodic peak current
i_{red}	... Reduction current
k	... Rate constant
k_{ox}	... The heterogeneous rate constant for the electron transfer for oxidation
k_{red}	... The heterogeneous rate constant for the electron transfer for reduction
n	... Number of electrons exchanged
R	... Gas constant
T	... Temperature
t	... Time
t_{off}	... Relaxation time
t_{on}	... Deposition time
v	... The velocity of solution species
η	... Over-potential
D	... Diffusion coefficient
J	... The flux of solution species
j	... Current density
m	... Sensitivity
u	... Ionic mobility
x	... Position

Chapter 1

Introduction

The global demand for nanotechnology has become one of the most interesting forefront fields in natural sciences. This demand is growing further as the nanoscale materials have found to have numerous applications in the real world applications [1, 2]. With the progressed realisation of nanoscale systems properties in originating from their small size and multifunctionality, they lead to many breakthroughs in different areas, e.g. materials, nanoelectronics, environmental science, biology, medicine, agricultural and food science, etc. Furthermore, by mimicking the nature, it is possible to control the development of nanomaterials in order to fabricate new devices and tools with outstanding and innovative properties that are originating from the nanoelements [2, 3]. The inherent versatility of nanomaterials is mostly attributed to the controllable shapes and sizes extending over different dimensions. According to the distribution and shape-controlled manufacturing, the nanomaterials can be considered as: zero-dimensional (0-D), one-dimensional (1-D), two-dimensional (2-D) and three-dimensional (3-D). Typical 0-D nanomaterials are measured within the nanoscale (no dimension) and mostly include nanoparticles (quantum dots, fullerenes). The most common representatives of 1-D nanomaterials are nanowires, nanotubes, nanorods or narrow sheets. 2-D nanomaterials exhibit a planar structure forming a network or a sheet, while 3-D nanomaterials are created by a combination of 0-, 1- or 2-D nanostructures [2, 4]. Such nanomaterials have been shown to have numerous attractive physical, chemical and electronic properties that are markedly different from the bulk material and offer the possibilities for improved performances [5].

For the construction of a nanoscale system, two main approaches can be employed, top-down and bottom-up [2]. The top-down approach is based on patterning on a large scale while reducing the lateral dimensions or removing the unnecessary parts until the desired, nanoscale shape is achieved. The top-down methods are lithographic (semi-conductive chips and components) and non-lithographic technologies, mainly used for the development of the materials in the size range from micro- to nanometers. The bottom-up approach is based on the arrangement and linking of the elemental constituents, atoms or small molecules, to assembly the desired nanoscale materials. The bottom-up methods are, e.g. molecular beam epitaxy, lithography (dip pen and nanoimprint), self-assembly, chemical synthesis and electrochemistry [3]. Especially the latter plays an essential role in many areas of applied technology and science, as extensive range applications of electrochemical principles can be found in (nano)material development, such as electrochemical deposition of polymers, metals and their alloys, electrochemical formation of oxide films and semiconductors, corrosion protection, etc. [6].

1.1 Basic Concepts of the Electrochemistry

Electrochemistry is the study of the charge transfer (electron) across the interface between conductive electrodes in a solid phase (*s*) – usually metals and the reactants – a solution phase (*aq*) [7]. In principle, the electron transfer can occur homogeneously in a solution or heterogeneously in an interfacial region between electrode and solution. To ensure the electro-neutrality, two (or even more) electron transfer reactions take place, i.e. reduction and oxidation (Figure 1.1) [8]. The oxidation is determined by the loss of the electrons, whereas the reduction is distinguished by the gain of the electrons [9].

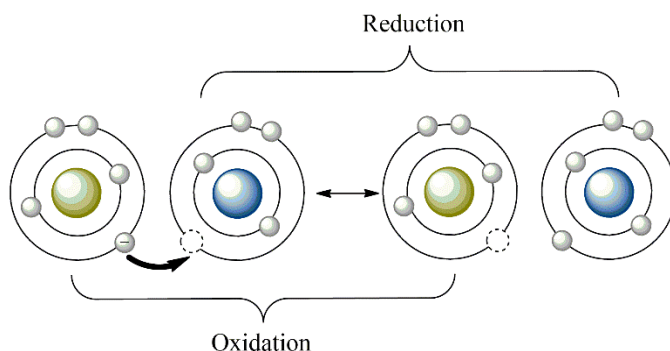


Figure 1.1: Schematic representation of oxidation and reduction reaction.

The reduction and oxidation can proceed once an electrode (a source of electrons for reduction or a sink of electrons for oxidation) is inserted into a solution, as illustrated by the following reduction reaction (1.1):



Where O and R are the oxidised and the reduced species, respectively, and n is the number of the transferred electrons between O and R . For electron transfer to successfully occur, the energies of the electron highest filled orbitals of donor and acceptor must be in correspondence. This means that for a reduction, the highest filled orbital electrons from the electrode must have minimum energy so that transfer occurs, while for oxidation, the lowest unoccupied level in the electrode must have maximum energy to receive the electrons from species in the solution [8]. The first occurrence corresponds to a negative potential and the second to a positive potential (both in volts) [8]. If the reaction is heterogeneous, the electron transfers between two different phases (s and aq). Consequently, the charge separation among these two phases arises between the electrode and solution, and the reaction moves towards equilibrium since the charge separation creates a potential difference on the interface. If E_s is a potential of the electrode (in solid phase) and E_{aq} is a solution potential, the equilibrium potential (the potential drop across the electrode/solution interface) is given by: $E_e = E_s - E_{aq}$ [8, 9]. However, direct measurements (i.e. experimentally) of the E_e at a single interface are not feasible, since the measurements of potential difference require a complete electrical circuit. To resolve this problem, electrochemists are using an electrochemical cell composed of two half-cells. Provided no current flows through the cell, the potential rapidly reaches an equilibrium value that depends upon the relative concentrations of O and R . Nernst showed the mathematical expression of the potential established at the electrode under equilibrium conditions by the following equation (1.2) [7-9]:

$$E_e = E^0 + \frac{RT}{nF} \ln \frac{[O]}{[R]} \quad (1.3)$$

Where E_e is an equilibrium potential [V], E^0 is a standard electrode potential [V] for the case where the half-cell of interest has a unit activity of all its potential determining ions, and the potential is measured relative to the standard hydrogen electrode – SHE. $[O]$ and $[R]$ are the concentrations [mol L^{-1}] of the oxidised and reduced species at the electrode surface, which, under equilibrium conditions, are the same as their bulk values. R is the gas [8.314 J mol K^{-1}]. F is the Faraday constant [96,485 C mol $^{-1}$], and T is the temperature [$^{\circ}\text{C}$] [8, 9]. Equilibrium electrochemical measurements enable determination of several thermodynamic parameters, e.g. enthalpies, entropies, energies, solution concentrations/activities, pH, etc.

The measurements of electrochemical processes become more complicated once the current passes through the electrochemical cell. The current can flow as a consequence of the spontaneous processes, which correspond to the transformation of the energy obtained in a chemical reaction into electron movement – i.e. galvanic cell. Also, the

current is allowed to pass through the cell by supplying electrical power from an external voltage source which enables the conversion of electrical energy into chemical, i.e. electrolysis.

1.1.1 Electrolysis

Electrolysis is a process when by the application of a potential that is different in value of equilibrium potential (E_e), the current induces the exchange of electrons between the electrode and the solution [8, 9]. The electrode-solution interface itself is composed of the electrical double layer (Figure 1.2), meaning that it is composed of the electrical charge at the surface of the electrode itself and the charge of the ions dispersed in a solution at a short distance from the surface [6]. The first layer termed as an inner Helmholtz plane consists of the desolvated ions and the solvent molecules. The second layer termed as an outer Helmholtz plane consists of the solvated ions. There, the ions are surrounded by the solvent molecules and cannot approach closer than the distance of the outer Helmholtz layer [7, 8].

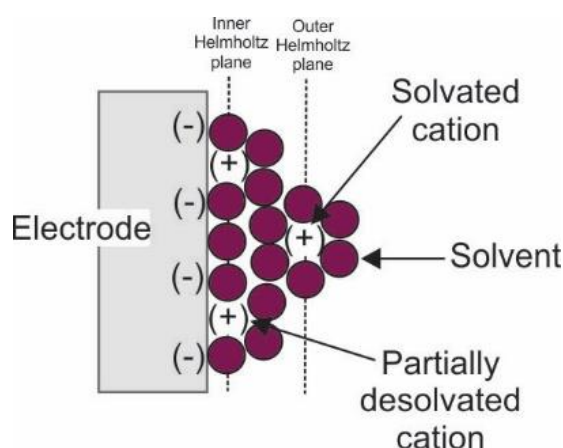
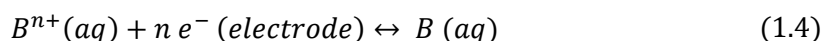


Figure 1.2: Scheme of the electrical double layer.

Electrolysis is usually performed in the electrolytic cell, which is composed of a two- or three-electrode system. The two-electrode configuration includes a cathode (i.e. working electrode, WE) at which reduction occurs and an anode (i.e. counter electrode, CE) at which oxidation occurs, while in a three-electrode system also a reference electrode (RE) is included. The RE provides a stable potential by which the WE potential can be monitored [6, 10]. During the electrochemical experiments, the reduction or the oxidation occurs at one electrode, usually at the WE. When the potential is measured between the WE and RE, the voltage drop might be observed which is equivalent to the product of the current passing through the electrolytic cell (i) and the solution resistance (R). For the systems, where the iR is small (< 2 mV), the two-electrode system can be used, but if the iR is large (> 2 mV), a three-electrode configuration must be used. The three-electrode configuration reduces the iR because the majority of the current flows between WE and CE. Furthermore, the iR effect can also be reduced by positioning the RE as close as possible to the WE.

To study the mechanisms of electrolysis, we consider the case of a reduction where the ions in solution (B^{n+}) may accept an electron (e^-) from the electrode without chemical transformation, an example being (1.4):



For the reductive electrolysis, the magnitude of the current passing through is given by 1.5 [7]:

$$i = AFj \quad (1.5)$$

Where A is the electrode area (cm^2), F is the Faraday constant, and j is the flux of B^{n+} reaching the electrode surface ($\text{mol cm}^{-2} \text{s}^{-1}$). It follows that the observed electrolytic current is dependent on the:

- 1.) Transport of the solution ions (B_{bulk}^{n+}) to the region where the reaction occurs (towards the surface of the electrode), i.e. **mass transport** (Figure 1.3, step 1),
- 2.) Rearrangement of the B_{surface}^{n+} ions (Figure 1.3, step 2-4),
- 3.) Reorientation of the solvent dipoles (Figure 1.3, step 2-4) in outer and inner Helmholtz plane (Figure 1.2),
- 4.) Alterations between the B_{surface}^{n+} ion and the ligands which surround these ions (Figure 1.3, step 2-4),
- 5.) Heterogeneous **electron transfer** between solid electrode and B_{surface}^{n+} ions, i.e. **electrode kinetics** (Figure 1.3, step 5).

However, the mass transport and the electron transfer are two major processes that govern the overall reaction rate and the slowest one will be the reaction rate-determining process [8, 9].

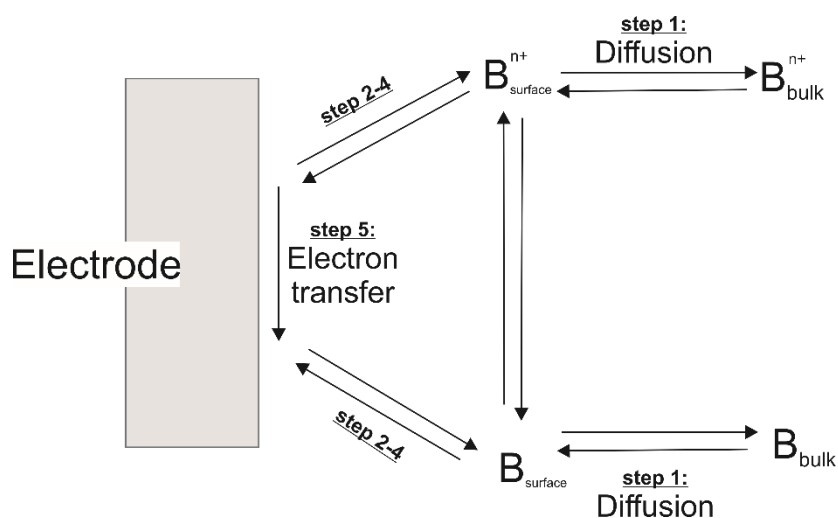


Figure 1.3: The scheme of processes involved in an electrode reaction.

1.1.1.1 Mass transport

Mass transport is the movement of species in solution; thus, the solution species can be charged or neutral. Mass transfer can be accomplished in three different ways or a combination of the following modes:

- 1.) Convection [7, 9]: the movement of the solution species induced by mechanical force, e.g. external (stirring, gas bubbles formation or pumping) or natural (density gradient) forces. As a result of the electrode reaction, the concentration of products near the electrode is different from those of the reactants in bulk solution. Mathematically, concentration changes ($C_{B^{n+}}$) [mol L^{-1}] in time (t) [s] resulting from movement of species (B^{n+}) with a velocity v_x [cm s^{-1}] and are given by:

$$\frac{\partial C_{B^{n+}}(x, t)}{\partial t} = -v_x \frac{\partial C_{B^{n+}}(x, t)}{\partial x} \quad (1.6)$$

In practice, the effect of mechanical convection can be minimised by using quiescent conditions (e.g. not stirring), while natural convection typically becomes significant perturbation in electrolysis conducted with electrodes of conventional size (mm or larger) on the time scale 10–20 s and longer. Generally, it is undesirable since it is difficult to predict.

- 2.) Migration [9]: the external electric field ($\frac{\partial \phi}{\partial x}$) [V cm^{-1}] at the electrode/solution interface is capable of exerting an electrostatic force on the species at the interfacial

region. As a result, the migration of ions (B^{n+}) to an electrode occurs. The migratory flux (j_m) [$cm\ mol\ L^{-1}s^{-1}$] is proportional to the concentration of the ions ($C_{B^{n+}}$) [$mol\ L^{-1}$], the electric field and ionic mobility (u) [$cm^2\ V^{-1}s^{-1}$] (1.7):

$$j_m \propto -uC_{B^{n+}} \frac{\partial \phi}{\partial x} \quad (1.7)$$

The interplay of the migration in any electrochemical reaction gives rise to a complex physical transport process which is hard to control or interpret. For example, it will cause a change in the concentration of solution ions local to the electrode, and as a result, the electrical potential in the solution will be changed. To simplify this problem, the electrochemical experiments should be performed under conditions where migration can be neglected. This might be done by addition of high concentration of inert background electrolyte that removes the electrode/solution interface, to maintain near electrical neutrality.

- 3.) Diffusion [7, 8]: is a movement of solution species against a concentration gradient. Diffusion arises from an uneven concentration distribution without the effect of the electric field. The rate of diffusion depends on the concentration gradients. Fick proposed two laws for diffusion that describe the relationship between the flux of species and the concentration of the substance as a function of time (t) [s] and position (x) [cm] (1.8):

$$-J(x, t) = D_{B^{n+}} \frac{\partial C_{B^{n+}}(x, t)}{\partial x} \quad (1.8)$$

where $J(x, t)$ [$mol\ cm\ s^{-1}L^{-1}$] is the flux of the species B^{n+} , and $D_{B^{n+}}$ is a diffusion coefficient [cm^2s^{-1}]. The variation of the concentration of the species B with time due to the diffusion was described by Fick's second law, which is 1.9:

$$\frac{\partial C_{B^{n+}}(x, t)}{\partial t} = D_{B^{n+}} \left(\frac{\partial^2 C_{B^{n+}}(x, t)}{\partial x^2} \right) \quad (1.9)$$

From the experimental point of view, electrochemists are usually concerned with the change in concentration at a point (when more than one direction needs to be considered) as a function of time. The Fick's second law of diffusion and the diffusional equation must be extended to describe each direction.

Since the electroactive species have to be transported to the electrode surface for electrolysis to occur, it follows that the maximum current is limited by the rate at which solution species reach the electrode/solution interface. Once the electrode is connected to the potential source, the B^{n+} react with the electrons, as shown in 1.4. Consequently, the concentration gradient is created perpendicular to the electrode in the region between the electrode surface ($B_{surface}^{n+}$) and bulk solution (B_{bulk}^{n+}). The induced gradient acts to force a flux of fresh bulk B^{n+} towards the electrode surface (1st Fick law, 1.8) and as a result, a diffusion layer is created in the region close to the electrode surface, where $[B_{surface}^{n+}] \neq [B_{bulk}^{n+}]$. Electrolysis proceeds and the diffusion layer becomes thicker.

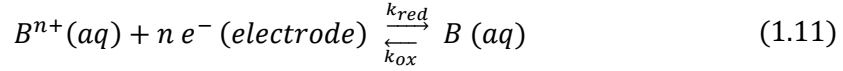
With time the concentration of electroactive species (B^{n+}) at the electrode surface goes to zero and maximising the diffusion current. No further increase in the current can be achieved. This is the reason why the maximum current is called the limiting current. The expression for the diffusion-limited current (i_l) is derived from Fick's second law of diffusion, and it is known as a Cottrell equation (1.10). The equation predicts the variation of the current in time, when a potential is applied under conditions of large overpotential, $\eta = E - E_e$ (η is an extent to which the reaction is driven beyond the equilibrium potential [7]). By this, the depletion of electroactive species happens at the electrode surface. The equation for diffusion-limited current is given as 1.10:

$$i_l(t) = \frac{nFAD_B^{0.5}C_B}{\pi^{0.5}t^{0.5}} \quad (1.10)$$

where D_B is a diffusion coefficient [$cm\ s^{-1}$], C_B [$mol\ L^{-1}$] is a concentration of the electroactive species converted at the electrode, A is an electrode area [cm^2], and n is the number of transferred electrons [7, 9].

1.1.1.2 Electrode kinetics

The Butler-Volmer equation is a fundamental equation to study the electrode kinetics and may be used to predict the current when the mass-transfer limitations are eliminated. If we consider a half-reaction of first-order occurring at an electrode (1.11):



Where k_{red} and k_{ox} are first-order rate constants [$cm\ s^{-1}$] for the electron transfer in the reduction and oxidation electrode reactions, respectively. The current flowing in the reductive or oxidative step is proportional to their heterogeneous rate constant (1.12):

$$\begin{aligned} i_{red} &= -nFA k_{red}[B^{n+}], \text{ and} \\ i_{ox} &= nFA k_{ox}[B] \end{aligned} \quad (1.12)$$

Where F is the Faraday constant [$96,485\ C\ mol^{-1}$], A is the electrode's area [cm^2], i_{red} and i_{ox} are the reduction and oxidation currents [A], respectively. By definition, the i_{red} is measured in negative values, while the i_{ox} is positive. Thus, the overall current (i) [A] can be written as the difference of the oxidation (i_{ox}) and reduction (i_{red}) current (1.13) which tells that the current flows across interface:

$$i = i_{ox} + i_{red} \quad (1.13)$$

It has been established that when the applied potential (E) [V] is equal to the equilibrium potential (E_e) [V], no current will flow through the cell. In other words, when an electrochemical cell is at equilibrium, the system contains a cathodic current balanced by an equal and opposite anodic current, $i_{red} = i_{ox}$. Whether or not any current flows will depend on the kinetics of the particular electrode reaction under investigation. As already mentioned, for electrolysis to occur, a potential different to that of E_e (i.e. overpotential, η) has to be applied to the WE. Butler-Volmer model displayed the relationship between applied η and electrode kinetics, where the rate constant for the forward (reductive) and backward (oxidative) reactions can be written as (1.14):

$$\begin{aligned} k_{red} &= k_0 e^{\frac{-\alpha F \eta}{RT}}, \text{ and} \\ k_{ox} &= k_0 e^{\frac{(1-\alpha) F \eta}{RT}}, \end{aligned} \quad (1.14)$$

Where T is the temperature [$^{\circ}C$], F and R are the Faraday [$96,485\ C\ mol^{-1}$] and gas [$8.314\ J\ mol\ K^{-1}$] constants, respectively. The k_0 is the standard rate constant [$cm\ s^{-1}$], independent of η . The α is a transfer coefficient, which is a dimensionless parameter with values between 0 and 1 and can be calculated from the slopes of the linear region of Tafel plots (Figure 1.4). From this, a Butler-Volmer equation (1.15) has been developed and can be used when the mass-transfer limitation is eliminated. This can be achieved in a well-stirred solution where diffusion to the electrode is no longer the limiting factor in the experiment. Thus, the observed current for kinetic control of the electrode reaction is proportional to the difference between the rate of the oxidation and reduction reactions (1.15) [7, 8]

$$i = i_0 \left[e^{(1-\alpha)\frac{F\eta}{RT}} - e^{-\alpha\frac{F\eta}{RT}} \right] \quad (1.15)$$

Where i_0 [A] is the exchange current which represents the current in the absence of net electrolysis and at zero η . It can be derived experimentally from the Tafel plot (Figure

1.4) that is composed of an anodic branch for positive η and a cathodic branch for negative η . It can be used to calculate the i_0 from the intercept of the y-scale.

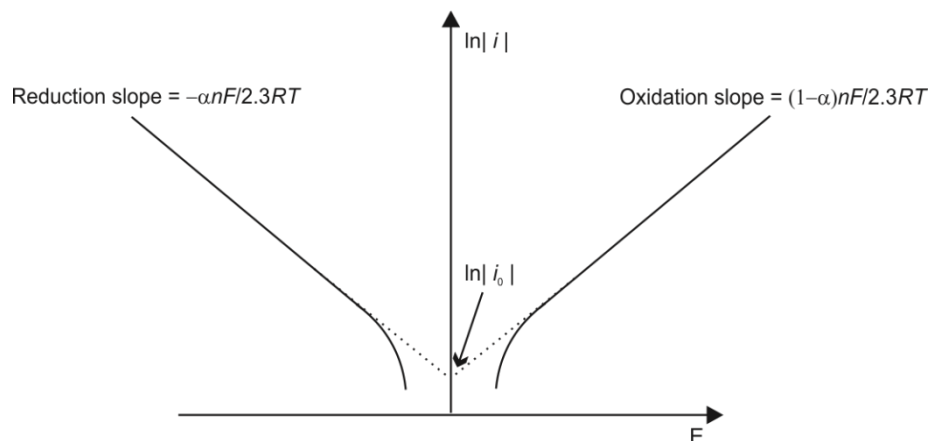


Figure 1.4: Tafel plot.

The Tafel equation (1.16) predicts how the applied η links to the current that passes through the electrolytic cell according to the following equation:

$$\eta = \frac{RT}{\alpha F} \ln(i_0) - \frac{RT}{\alpha F} \log(i) \quad (1.16)$$

The utility of 1.16 equation is limited by reversibility and diffusion. When the i_0 is large ($k_0 \gg D$), very small or no applied η is required to drive the reaction. The slope of the Tafel slope increases due to the more significant backward reaction and changing the relative concentrations at the electrode surface. In this case, the current flows in both directions (cathodic and anodic). Such a system is reversible. When very large η is applied ($k_0 \ll D$), the slope deviates below the prediction of the Tafel equation due to the mass-transport limitations. Such a system represents irreversibility of the reactions. These are relative terms and signify the time-scale of the electrode kinetics relative to the transport of material in and out of the interfacial region [7, 9].

1.1.2 A study of the electrode reactions

The measurements of the electrode currents as a function of a voltage applied to the electrolytic cell can provide remarkably detailed information about the mechanism of the redox reactions. The methods available for studying the electrode processes are the potential sweep methods, pulse techniques, impedance methods and steady-state methods [7, 8].

Linear sweep voltammetry and cyclic voltammetry are the most widely used techniques for quick and straightforward studies of basic principles of the electrochemical reactions. As stated, they are usually used to investigate the mechanism of electrochemical reactions, to analyse the species presented in a solution and offer a rapid location of the redox potentials of the electroactive species, or semi-quantify reaction rates [8].

1.1.2.1 Linear sweep voltammetry

Linear sweep voltammetry (LSV) is usually the first technique employed in any electrochemical investigation since it is easy to perform and provides quick information about the electrochemical reactions. The experiments are conducted with stationary electrodes and rely on the diffusion of species to the electrode surface. In LSV, the potential scan is done in one direction (positive or negative). As it is represented in Figure 1.5, A, the scan begins when the potential is swept from E_1 towards E_2 ; when the equilibrium at the surface starts to alter, the current begins to flow. The current is increasing as the potential is swept further from its initial value, therefore, when the equilibrium potential is shifted further to the E_2 side and thus oxidising more reactants. The current peak ($i_{p,a}$) is observed at the potential of $E_{p,a}$, and can be attributed to the oxidation of solution species. Once the

diffusion layer becomes thicker, the flux of species to the electrode becomes slower. As a result, a current starts to drop. In fact, the drop in current follows the same behaviour as that predicted by the Cottrell equation (1.10). The current observed in this forward scan (from E_1 to E_2) is positive.

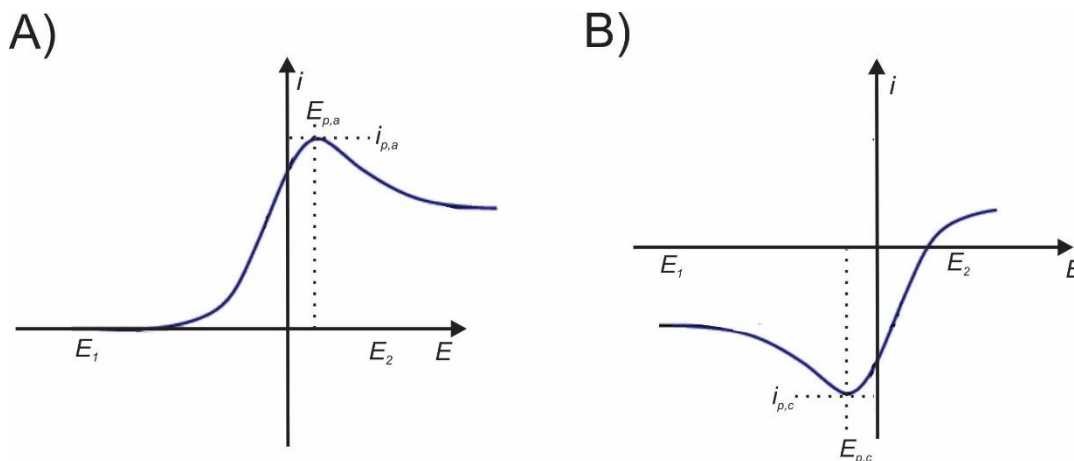


Figure 1.5: A typical linear sweep voltammogram.

If the scan is performed in the opposite direction, i.e. negative (Figure 1.5, B), the current increases exponentially with potential or time as the Butler-Volmer equation (1.15) suggests. The maximum current ($i_{p,c}$) occurs at the potential of $E_{p,c}$ and represents the reduction of solution species at the electrode surface. Further potential scanning to E_1 causes a decrease in the current value due to the diffusion limitation of solution species. The current observed in a direction from E_2 to E_1 is negative [9]. However, this technique can be extended by the sweeping potential in two directions (positive and negative), i.e. cyclic voltammetry [8, 9].

1.1.2.2 Cyclic voltammetry

Cyclic voltammetry is very similar to LSV, however, the voltage is swept between two values; for example, from E_1 to E_2 and then the scan is reversed and the potential is swept back to E_1 . A typical cyclic voltammogram for the reversible system is shown in Figure 1.6.

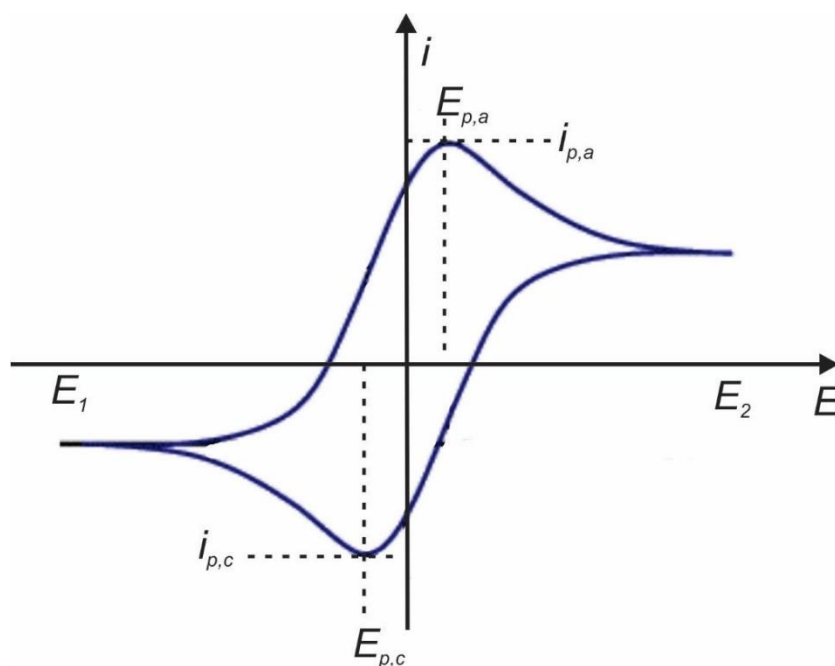


Figure 1.6: Cyclic voltammogram for a reversible electron transfer reaction [11].

The peak potentials and the peak sizes in Figure 1.6 reflect the reversible system. It means that the heights of the forward and reverse current peaks are of the same magnitude and are separated by a potential of 59 mV (25°C), independently of the scan rate. If n electrons are transferred in a reversible electrode process, the separation can be given by the following equation (1.17):

$$|E_{p,a} - E_{p,c}| = 2.218 \frac{RT}{nF} \quad (1.17)$$

The potentials of forward and reverse peaks are voltage sweep-dependent in the reversible system, and this contrast is diagnostic of the nature of the electrode kinetics. When the rate of the electron transfer decreases, no peak appears on inverting the scan direction. This case is known as an irreversible system (Figure 1.7, A, green curve). The terms of reversible and irreversible refer to limiting cases, according to the electrode kinetics (fast or slow), and relative to the mass transport conditions of the electrode of interest. Intermediate cases, i.e. quasi-reversible systems, depend on both the forward and reverse electron transfer rates and the rate of mass transport (Figure 1.7, A, red curve) [8, 9, 11]. Regardless of reversibility, the absolute magnitudes of the peak currents for both, forward and reverse, scans depend on the voltage sweep rate ($k_{\text{reversible}} > k_{\text{quasi-reversible}} > k_{\text{irreversible}}$).

The LSV and CVs were described for a single scan rate. If the scan rate is altered, the current response changes [11]. From Figure 1.7, B, it is apparent that with the increased scan rate, the total current increases for all the reaction types. This fact can be correlated with a thickness of the diffusion layer and the time taken to record the scan. If the scan rate is slow, the diffusion layer will grow much further from the electrode. As a result, the flux of solution species to the electrode surface is smaller [9].

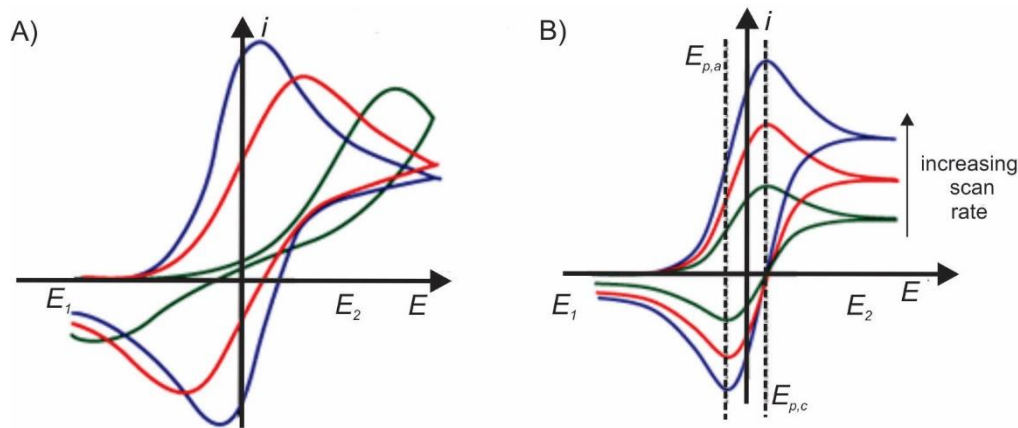


Figure 1.7: a) Cyclic voltammogram for a reversible (blue), a quasi-reversible (red) and an irreversible (green) electron transfer reaction [11], and b) the effect of scan rate on current [11].

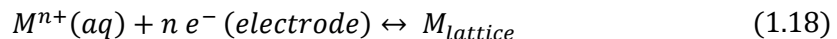
1.2 Applications of Electrochemistry

Once the electrode reactions and processes are understood, the knowledge can be used for studying complex systems in biochemistry, developing new electrode materials (metallic or non-metallic), measuring the concentration of electroactive organic and inorganic compounds, etc.

1.2.1 Development of a nanostructured metal-based electrode materials

The electrochemical deposition can be used to synthesise nano-sized materials. It has many advantages such as industrial applicability, rapidity, low cost, free-from porosity, high purity, and ability to produce structural features with sizes ranging from nm to μm , or to produce coatings on various substrates, etc. Electrodeposition is a unique technique in which different types of nanomaterials can be processed, including metals, polymer, ceramics. In this thesis, we are mainly focused on the electrodeposition of metallic nanomaterials.

Electrodeposition of metals is the electrolysis process, which consists of three-electrode configuration electrochemical cell (Figure 1.8) for applying a controlled potential or current [12]. The three-electrode cell contains a RE, anode as a CE and cathode as a WE. However, in the electrodeposition of metals, we are mainly interested in a cathode reaction (reduction), which presents a reaction of charged particles (electrons and metal ions) at the interface between a substrate and a liquid solution as it is presented by 1.18 [9, 13]:



In the process of a reduction reaction, several types of important subjects are involved:

- Metal-solution interface (structure of a double layer) as a position for the deposition and a concentration of metal ions in solution [12, 13],
- Growth and nucleation of nanostructures on the conductive substrate (electrode) that is affected by various parameters, including the applied η , the crystal structure of the substrate, lattice orientation and crystallographic mismatch, specific free surface and adhesion energy, etc. The nucleation can be either instantaneous or progressive. If the nucleation process is instantaneous, all the nuclei form instantaneously on the substrate and subsequently grow with the increasing time of the electrodeposition. On the other hand, in the case of progressive nucleation, the number of formed nuclei is a function of the electrodeposition time. In contrast to instantaneous nucleation, the nuclei grow gradually and overlap [9, 12],
- Mechanisms and kinetics; the rate of the deposition process is defined as the number of moles of M^{n+} depositing per time [s] second and per unit area [cm^2] of the electrode surface (1.19):

$$rate = k[M^{n+}] \quad (1.19)$$

Where k is the rate constant and $[M^{n+}]$ is the activity of M^{n+} ions $[mol\ L^{-1}]$. The rate constant is interpreted on the basis of the statistical mechanism, and is given by the expression (1.20):

$$k = \frac{k_b T}{h} \left(-\frac{\Delta G_e^\ddagger}{RT} \right) \quad (1.20)$$

Where k_b is a Boltzmann constant $[1.38 \times 10^{-23} m^2 kg\ s^{-2} K^{-1}]$, T is the absolute temperature $[K]$, h is the Planck constant $[6.62 \times 10^{-34} m^2 kg\ s^{-1}]$, $\Delta G_e^\ddagger$ $[J\ mol^{-1}]$ is the electrochemical activation energy and R is a gas constant $[8.314\ J\ mol\ K^{-1}]$. The electrochemical activation energy is a function of the electrode potential: $\Delta G_e^\ddagger = f(E)$. These equations show why understanding and development of electrochemical depositions depend on statistical mechanisms [13].

- d) Properties of deposited metals that reveal chemical, electrical, magnetic and physical properties of the deposited metals and their alloys [13].

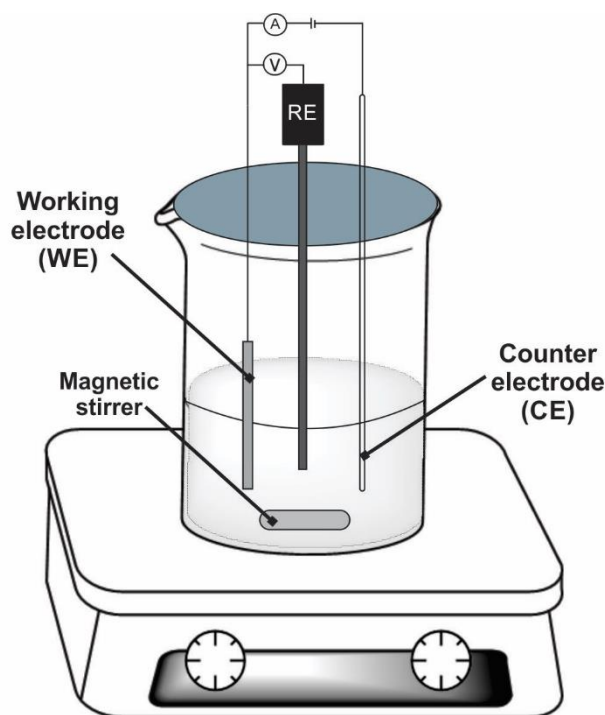


Figure 1.8: Scheme of the three-electrode configuration electrochemical cell for deposition of metals.

The major challenge with using the electrodeposition process to synthesise nanostructures is the preparation or usage of a suitable substrate since the electrodeposition strongly depends on the surface characteristics of the substrate. Therefore, the shape, the dimensionality and the size of metal deposits are affected by the substrate.

The bath composition and deposition parameters control the chemical composition, morphology and porosity of the deposits. The substrate can be flat, which enables, e.g. the electrodeposition of 2D-thin films. In contrast, using a porous template as a surface of the cathode, various desired nanostructures, e.g. nanowires, nanotubes, etc., can be synthesised for an extensive range of applications.

1.2.1.1 Template-assisted electrodeposition

The template-assisted electrodeposition is one of the most used procedures to control the shape and the size of nanostructures by using templates that contain cylindrical pores of uniform diameters, monodisperse nanocylinders of the desired non-conductive and inert electrode material [9, 12, 14]. The most commonly used templates are polycarbonate (PC) and anodised aluminium oxides (AAO) membranes.

The PC membranes are prepared by a track-etched method that entails bombarding of a non-porous sheet with nuclear fission fragments to create a damage track in the material that is later removed by chemical etching. Usually, they consist of randomly distributed cylindrical pores with a uniform diameter (from 10 nm-400 nm) and pore density around 10^9 per cm^2 . In recent years, the PC templates have been used for deposition of metal-based and metal oxides-based nanowires or nanotubes. However, the common problem of the PC templates is correlated with the frequent pore fusion [9, 14, 15].

AAO membranes are prepared by a two-step anodization process of pure aluminium films utilising acids. As a result of this process, the structure of the aluminium oxide film consists of a uniform array of parallel alumina cells packed hexagonally and containing nearly cylindrical pores [7]. The pore diameter depends on the voltage used in the anodization process and can vary in the range from 10-200 nm. These templates have been considered as the ideal templates since they possess many advantages, such as thermal stability, good mechanical strength, uniform pore distribution, and high pore density (10^9 – 10^{11} pores/ cm^2) [2, 9, 16].

Electrodeposition into the pores (Figure 1.9) of AAO or PC templates requires that one side of the membrane is covered by a conductive layer, usually in the thickness from 100–1000 nm. The conductive layer is produced by plasma or vacuum deposition of metals that can be either the same or different from that one which will provide the final template structure. In the electrodeposition process, the template is placed in an electrochemical cell where it acts as the cathode and the open side of the template is exposed to the electrolyte. The electrodeposition is based on the progressive filling and growth of the pores starting at the bottom conductive layer and proceeding progressively toward the open end of the pores. Final products are solid nanoparticles, typically nanowires or hollow structured, i.e. nanotubes or nanocapsules [7, 9]. The deposition can be carried out under potentiostatic conditions where the constant potential is applied, or galvanostatic conditions where the constant current is applied.

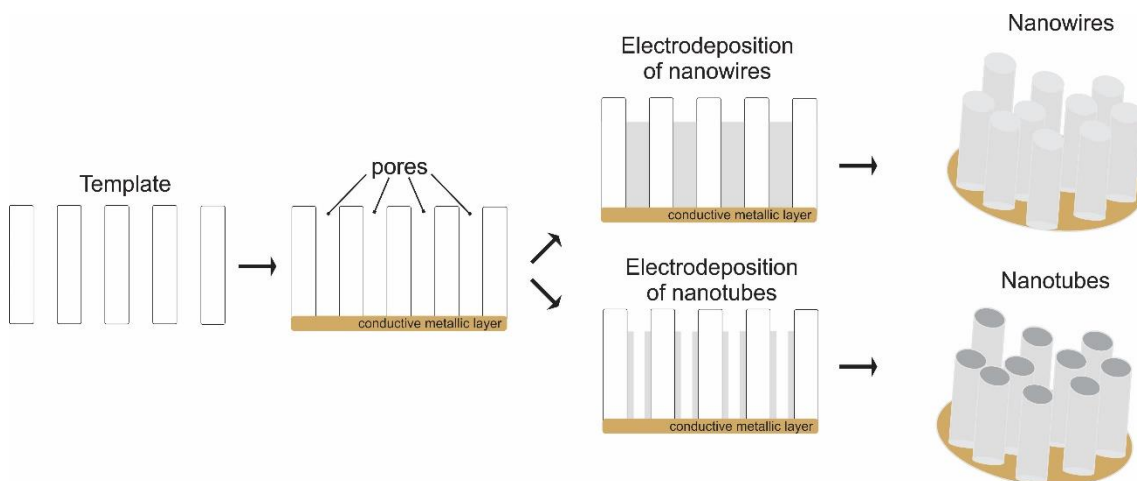


Figure 1.9: Nanotubes and nanowires synthesis by the template-assisted method.

Electrodeposition into the porous templates is more complicated than the one on the flat electrodes. There is a large field of parameters that influence the deposition process and thus affect the quality of the deposits:

- a) The thickness of conductive metallic layer; if the conductive layer is thin or the bottom layer is not completely covered, electrodeposition can also occur at the backside and forms a thick metal layer, as it is shown in Figure 1.10. As a result, the

deposition is difficult to control, and the fabricated nanowires/nanotubes are not homogeneous [9]. Thus, a conductive layer should be thick enough to completely cover one side of the pores [9].

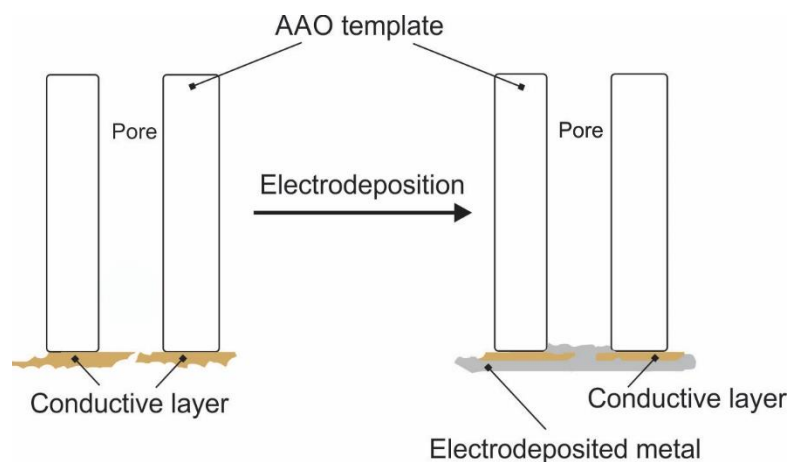


Figure 1.10: Schematic illustration of electrodeposition when the bottom part of the template is not completely covered.

- b) By using the sputtering technique for the preparation of conductive layer, metals in the form of nanoparticles can penetrate inside the template, as presented in Figure 1.11. As a result, the deposition will start on the conductive nanoparticles and lead to the formation of junctions after prolonged electrodeposition. In order to avoid the formation of the junctions, and to deposit morphologically uniform nanowires/nanotubes, the wetting of the template should be introduced before the electrodeposition [9].

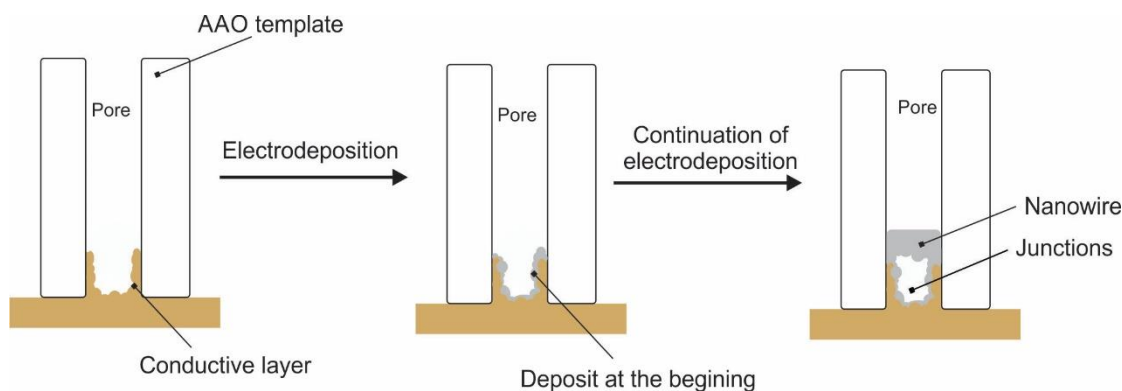


Figure 1.11: Schematic illustration of electrodeposition on the conductive layer of penetrating nanoparticles, and further formation of junctions.

- c) At relative negative potentials in aqueous electrolytes, the hydrogen bubbles can be produced due to the water electrolysis reaction on the cathode. The hydrogen might have a significant influence on the final electrodeposition of nanowires/nanotubes, as it can block the pores and metal ions cannot arrive at the reaction spot. This situation leads to the formation of cracks, pinholes, etc. (Figure 1.12, A) because the transport of the bubbles out of the pores is hindered, while the transport of the H^+ to the interface is relatively fast. This effect can be reduced by using the pulse plating deposition (Figure 1.12, B). The main principle of this technique is that the metal is deposited during t_{on} at E_{on} , while at t_{off} at E_{off} the gas bubbles are removed from the reaction spot and pores. The t_{off} is also called relaxation time.

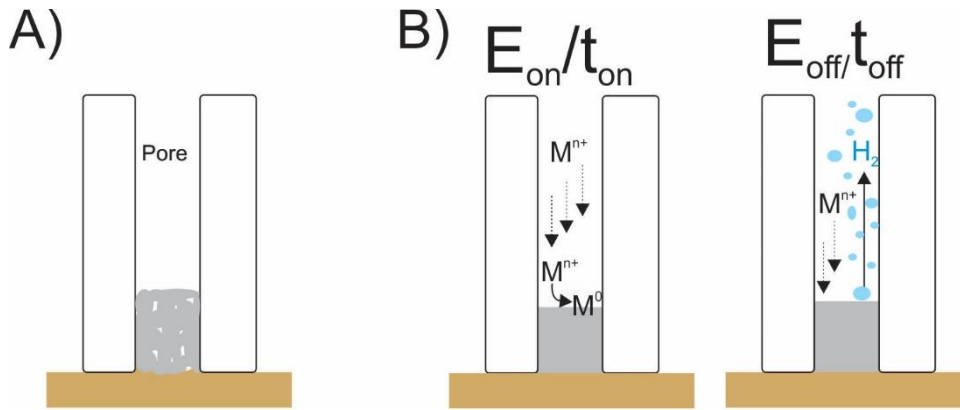


Figure 1.12: Schematic illustration of A) electrodeposition of nanowires under strong hydrogen evolution reaction conditions; B) pulse deposition at E_{on} where reduction of metal occurs, and at E_{off} where hydrogen bubbles are removed from the pores.

- d) The pore length influences the mass transport which is limited by the diffusion; the diffusion limiting current is proportional to the reciprocal value of the length of pores ($i_{lim} \propto 1/L$) [9]. When the actual current is smaller than i_{lim} (Figure 1.13, A), the compact nanowires are deposited. In contrast, if the external current is larger than i_{lim} (Figure 1.13, B), the limiting current is forced through the electrode, and the double layer is further charged. Due to this, the potential of the electrode will change until some electrochemical process other than reduction will occur [9]. The pulse plating deposition can be used to reduce this effect, as it enables similar concentration gradients at the beginning of each pulse (t_{on} , E_{on}) and thus recovers the concentration of ions at the surface of the electrode at relaxation time (t_{off} , E_{off}).

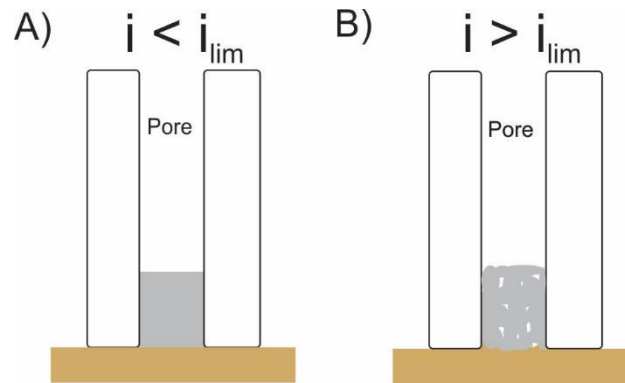


Figure 1.13: Schematic illustration of electrodeposited nanowires when A) $i < i_{lim}$ and B) $i > i_{lim}$.

All of these above-mentioned facts should be taken into account when electro-depositing nanostructures into templates, either PC or AAO.

In order to understand the interrelationship between structure and properties, the characterisation of nanostructured electrodeposited material should be provided. The structural features include the grain size, distribution and morphology, composition profiles across interfaces, their thickness, and identification of defects or residual species trapped during electrodeposition. Many characterization techniques can be used to yield structural information of deposits. These include microscopic techniques (SEM, TEM, etc.) and spectroscopic techniques (FT-IR, Raman, etc.).

As electrochemical techniques are surface dependent, electrodeposited nanowires can bring new features in the sensing field, different from bulk material [2]. Nanowires from different materials (e.g. metals and their alloys, metal oxides, hybrid materials or polymers) have been employed in a wide variety of applications, ranging from platforms for

immobilization of biomaterials to surface-enhanced electrodes which have a number of key features, including high sensitivity, fast response, exquisite selectivity, fast recovery, and potential for integration of addressable arrays on a massive scale. Their outstanding characteristics relate to their size, so their large surface-to-volume ratio makes nanowires excellent candidates to lead a new generation of sensors including biological, gas, optical, pH, orientation, electrochemical sensors [2, 17].

1.3 Sensors

Sensors act as the interfaces that receive and translate information across biological, chemical or physical domains. They are devices that detect, record, and indicate physical or chemical properties, such as measuring the quantities of molecules at a small scale, e.g. low concentrations of gas molecules, ions or proteins, existence of toxic molecules, or genetic information from cells; each with a high stability, selectivity, and sensitivity at a molecular scale [17, 18]. The sensors can be broken down into three elements [18]:

- Capture and recognition** (Figure 1.14, A) refer to a reaction between a receptor element (sensor component) and a target molecule. The desired characteristics for this stage are observation of the sensing effect with only the target molecule (selectivity), obtaining a large sensing effect with a small number of target molecules (sensitivity), and also the sensing effect should not be saturated with a large number of a target or other molecules (dynamic range);
- Transduction** (Figure 1.14, B) refers to the conversion of the detection event into a measurable signal and can be divided into three main types based on the phenomena utilized signal conversion: electrical (electrochemical sensors and semiconductors), optical (optical molecular sensor), and mechanical transducers (cantilevers, acoustic wave sensors and thermal sensors). High sensitivity and wide dynamic range are desirable characteristics for transducers.
- Measurement and analysis** (Figure 1.14, C); the signal from the transducer is measured, recorded, and interpreted as the number of molecular activities.

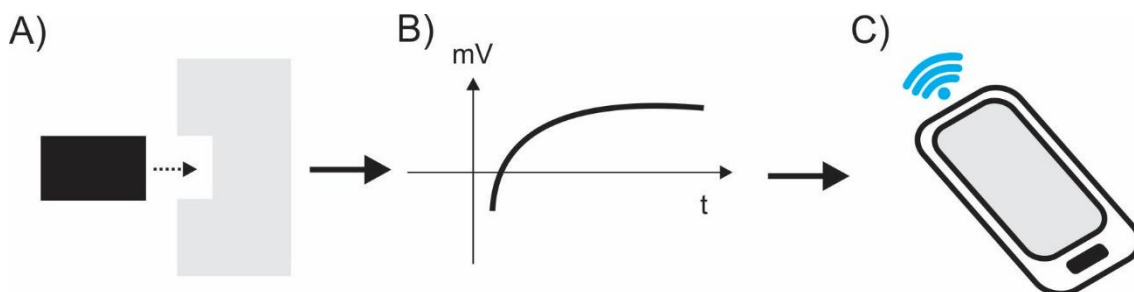


Figure 1.14: Three main steps of a sensor.

In this thesis, we focus on the description of fundamental principles of electrical transduction designed sensors, i.e. electrochemical sensors.

1.3.1 Electrochemical sensors

Based on the nature of the signal, the electrochemical sensors fall into three major categories:

- Potentiometric**; where the potential difference between the working electrode and the reference electrode is measured. The electrostatic potentials are measured in Volts [V] and practically no current is involved in the measurements. The measured potential is proportional to the relative concentration or activity of the target molecule. One of the most commonly used potentiometric sensors are pH meters; by definition [18].
- Conductometric**; where the resistance change is measured between two sensing electrodes. In principle, the sensing material that is specific to the analyte is sandwiched between two contact electrodes and the resistance of the entire device

is measured. These sensors are mostly based on conductive or semiconductive material. One of the main advantages is its low manufacturing cost [18, 19].

- c) Voltammetric or amperometric; where the electric current between the working and reference is measured. In the voltammetric sensors, the current is measured as a function of an applied potential which is varied either step by step or continuously. Amperometric sensors measure the current response to detect the concentration of an analyte at a fixed applied potential.

The latest ones are based on transfer electron between oxidant (molecules that are capable of removing electrons from another substance) and reductants/reducers (molecules that are capable of transferring electrons to other substances). The oxidation and reduction are the main reactions for electrochemical measurements and quantifications. In principle, at least two electrodes are needed. However, the use of three electrodes allows more accurate applications of potential and currents. A three-electrode system can be constructed in the way of the electrolytic cell (Figure 1.8) or in the way of screen-printed electrodes (SPE), as it is presented in Figure 1.15 [20-23]. Compared to the basic electrolytic cell, screen-printed electrodes enable site-of-interest and rapid *in-situ* analyses of target molecules, since they are transferable. They are highly reproducible and inexpensive because they are fabricated by printing different inks on plastic or ceramic substrates and can be modified with highly sensitive material, such as polymers, enzymes or metallic nanomaterials (Bi, Au, Ag, Ni, etc.).

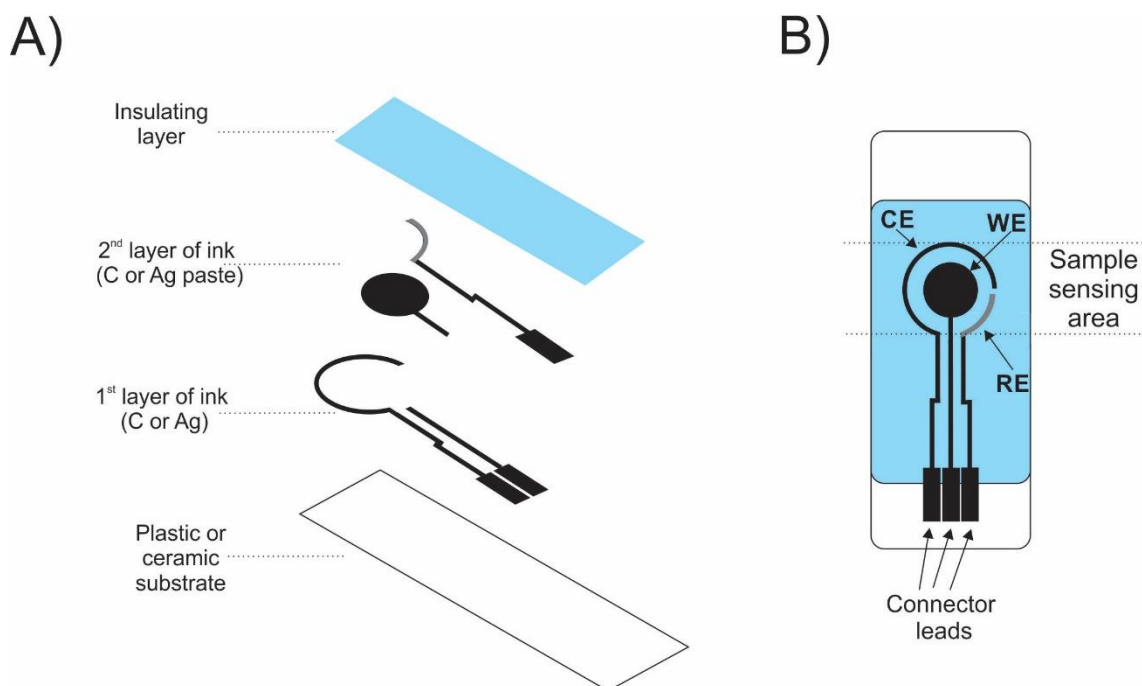


Figure 1.15: A) Scheme of preparation steps in preparation of screen-printed electrodes; and B) final look of the screen-printed electrode.

At this point, a question may arise: "What makes each electrochemical sensor unique? What is the key electrochemical sensing component or the design that enables the detection of a specific target molecule?" By all means, the working electrode that is usually modified or constructed by specific nanostructured material, i.e. electroactive material, dictates the durability and quality of the electrochemical sensors. It represents a place where electrochemical recognition and discrimination processes occur [24]. Many kinds of electrodeposited nanostructured receptor elements based on metals, metal oxides, their alloys, etc., have been widely used as a working electrode. They might be (electro)chemically synthesised and then transferred to a working electrode, or they can be directly electrodeposited on a substrate [18].

These materials play important roles in electrochemical sensing systems based on their unique chemical, electric, magnetic and physical properties and can be mainly classified as

a catalysis of electrochemical reactions [25]. Among their characteristics their enhanced conductivity and large specific surface areas stand out. The advantages derived from the use of such materials are usually expressed by [2]:

- a) Lower detection potentials: the larger surface area of nanomaterial leads to lower detection potentials or “overpotentials” and results in more efficient electrocatalysis. Many nanostructured materials, especially metal-based, have excellent catalytic properties. Consequently, the overall selectivity of the analysis can be improved.
- b) Higher currents: greater surface areas of nanomaterial enable larger redox scale conversions resulting in enhanced output signals and consequently in the increased analytical sensitivity.
- c) Higher stability and resistance to passivation: due to the larger surface areas, nanomaterials can imply better reproducibility because the resulting signal is less prone to fouling.

Of all electrochemical sensor research, noble or non-noble metals-based nanomaterials that exploit the unique properties (nanoporous electrodes, nanoparticles, nanowires, etc.) are the most rapidly expanding area and continue to be a mainstay of analytical chemistry as demands for increasingly sensitive and selective detection systems grow [26]. Especially metal or metal oxides nanowires have been used as the electrochemical transducers in an effort to increase the surface area of the electrode with the final objectives of improving sensitivities and lowering detection limits. In contrast to conventionally spectroscopic and chromatographic methods that suffer from several shortcomings (time-consuming, lab-based, costly in devices or consumables), electrochemical sensors are simple and adaptable to demanding environments where miniaturised and robust analytical techniques are required [26-29].

1.3.2 Nickel as the electrode material for electrochemical sensors

Nickel is particularly attractive as a receptor element due to its low price, and excellent catalytic performance that is based on the electron transfer between an active $\text{Ni(OH)}_2/\text{NiOOH}$ redox couple and target molecules (e.g. methanol [30, 31], formaldehyde [32-37], glucose [28, 38-40], hydrogen peroxide [41], water splitting [42-46]). Compared to other metals, Ni with high natural abundance is economically attractive which makes this metal suitable for numerous applications, including fuel cells, energy storage, organic synthesis, rechargeable batteries, supercapacitors, wastewater treatment, and electrochemical sensors for pharmaceutical, environmental, medical and food analysis [47, 48].

1.3.2.1 Synthesis of Ni and its oxides/hydroxides

Nickel-based receptor elements can be prepared or synthesised by several different methods, such as [48, 49]:

- Chemical methods, i.e. chemical precipitation and ageing,
- Physical methods, or
- Electrochemical methods, i.e. electrochemical deposition/growth on conductive substrates.

1.3.2.1.1 Chemical methods

Chemical approaches can be used to synthesise Ni, Ni_xO_y , or Ni(OH)_2 . The structure, shape, crystallinity, etc., might be controlled by numerous parameters, such as solvent (organic, water, etc.), the temperature of preparation, the use of surfactants, concentration of the reactants and others [48, 49].

1.3.2.1.2 Physical methods

Ni or Ni_xO_y can be prepared by using a variety of physical methods, such as sputtering, chemical vapour or pulsed laser deposition, electron beam evaporation, spray pyrolysis, or electrospinning [48].

1.3.2.1.3 Electrochemical methods

Electrochemical approaches are employed to deposit Ni, Ni(OH)₂, or NiOOH on a conductive substrate.

- 1.) **Electrochemical deposition of metallic Ni:** it can be cathodically electrodeposited from Ni²⁺ containing the solution, according to reaction 1.21 [48, 49]:



- 1.) **Electrochemical deposition of Ni(OH)₂:** it can be synthesised directly from Ni²⁺ acidic solution; achieved by applying a negative potential to elicit a cathodic current from the reduction of water (1.22). Due to the presence of Ni²⁺ ions in the solution, chemical precipitation immediately occurs at the electrode surface (1.23) [48, 49].



It is also possible to form a mixture of metallic Ni and Ni(OH)₂ if both reactions occur simultaneously (1.21, 1.23).

Furthermore, Ni(OH)₂ can be synthesised indirectly by placing a Ni or NiO conductive substrate in an alkaline electrolyte containing OH⁻ ions. This can be yielded by potential cycling at positive potentials (described in detail in Chapter 1.3.2.2).

- 2.) **Electrochemical deposition/preparation of NiOOH:** it can be yielded if Ni, NiO or Ni(OH)₂ are fully oxidised by potential cycling in alkaline solutions [48] (described in detail in Chapter 1.3.2.2).

However, the composition and structure of Ni (electro)deposits are dependent on the nature of Ni(II) salt, temperature and pH of the solution, concentration Ni²⁺ ions in solution, and employed cathodic potential [1, 49-51]. The effect of these parameters on the form in which Ni in a given oxidation state exists can be summarized with predominance diagram such as Pourbaix diagram, known as the potential-pH diagrams. In general, it maps out possible stable, i.e. equilibrium, phases of an aqueous electrochemical system at different temperatures [50]. An example of a Pourbaix diagram for Ni deposition at 25°C is shown in Figure 1.16. The vertical axis is labelled E for the potential with respect to the standard hydrogen electrode (SHE) as calculated by the Nernst equation (1.3). Low E values represent a reducing environment, while high E values represent an oxidising environment. The horizontal axis is labelled as a pH which is -log function of the H⁺ ion activity (*a*_{H⁺}). The areas on the diagram give the thermodynamically most stable form of the Ni for that E and pH. More stable species tend to occupy larger areas. The areas in the Pourbaix diagram are separated with the lines that represent redox and acid-base reactions and mark places where two Ni species exist in equilibrium.

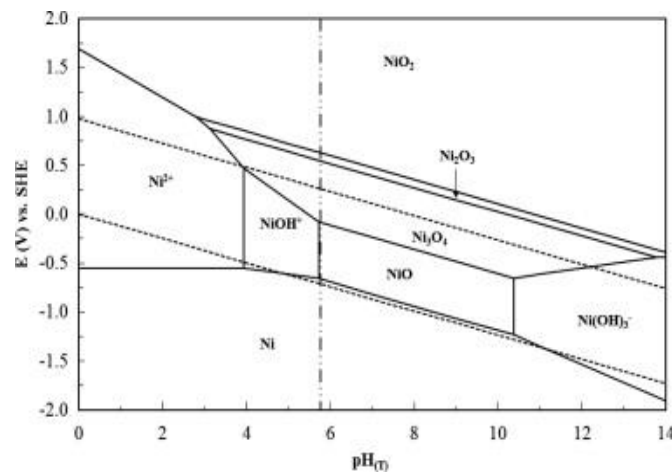


Figure 1.16: Pourbaix diagram for Ni at 25°C [51]. (Reprinted by permission from Elsevier (2020), License Number: 4753480492226)

1.3.2.2 The behaviour of the synthesised Ni, Ni oxides/hydroxides in the air, water or alkaline solutions

Ni (in oxidation state 0) is very sensitive to air or water molecules, and the surface of Ni⁰ might remain un-oxidised only under conditions of ultrahigh vacuum. Once it is exposed to the air or aqueous solutions, its surface becomes easily passivated. Thus, a several-atomic-layers-thick passive film forms on the Ni surface immediately [48, 52, 53]. Figure 1.17 represents the composition of the passive layer of Ni surface that consists of the two layers [48, 52]:

- “inter” layer of Ni oxide (NiO); it is formed between the metallic Ni and the outer, hydroxide layer, and
- “outer” layer of Ni hydroxide (Ni(OH)₂); it is formed at the solution/air and Ni oxide interface.

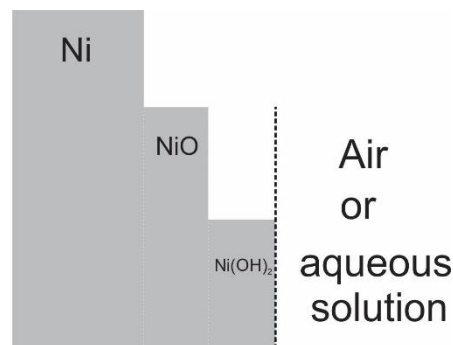
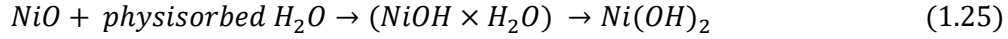
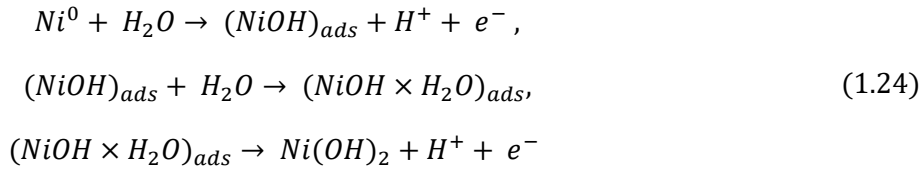


Figure 1.17: The schematic representation of the Ni-containing surface layers under exposure to air or aqueous solutions.

The “inter” NiO layer is formed by the reaction of oxygen on a Ni surface. This reaction is divided to here-defined reaction regions: the dissociative chemisorption of oxygen on Ni⁰, and later nucleation and lateral growth that results in the formation of ~ 2-atomic-thick layer of NiO that becomes thicker with time [52, 54]. It was proven that air-formed NiO is crystalline with a (1 1 1) texture on a Ni (1 1 1) single crystal electrode [52, 53]. The “outer” Ni-hydroxide layer is formed by strong adsorption of water molecules onto Ni (1.24) or NiO (1.25), where air-formed NiO accepts the proton from water molecule which is followed by the formation of hydrogen bond and leading to the conversion of NiO to the Ni(OH)₂ [48, 52, 53]. The formation of “outer” Ni(OH)₂ can be expressed as follows [48]:

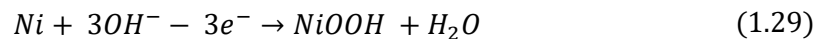
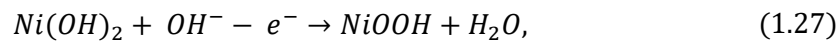


The amount of spontaneously formed $\text{Ni}(\text{OH})_2$ (1.24 and 1.25), i.e. thickness of “outer” layer, is limited and uncontrolled due to the interaction of water and hydroxyl ions in the bulk solution [55]. However, the thickness of $\text{Ni}(\text{OH})_2$ might be controlled and accelerated by potential cycling over the $\text{Ni}(\text{OH})_2/\text{NiOOH}$ redox peaks, at relatively high positive potentials, i.e. oxyhydroxide region, in alkaline electrolytes (KOH or NaOH). As it was presented by Rahim et al. [30] (Figure 1.19.), the potential cycling of Ni electrode in KOH induces significant changes in the nickel-based oxidised layers in terms of chemical changes and crystallographic structures. In the anodic region, two different crystal structures of $\text{Ni}(\text{OH})_2$ can be formed, denoted as α or β (1.26):

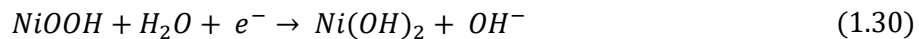


An α - $\text{Ni}(\text{OH})_2$ is formed at the less positive potentials in the 1st cycle (presented in Figure 1.19, as anodic peak current of a_1). Along the potential range from $E(a_1)$ to $E(a_2)$ the transformation of α - to β - $\text{Ni}(\text{OH})_2$ takes place. Once the β -phase of $\text{Ni}(\text{OH})_2$ is formed, it cannot be electrochemically reduced back to α - $\text{Ni}(\text{OH})_2$ or metallic Ni due to its high electrochemical stability [36]. This is the reason why anodic peak a_1 disappears during multiple potential cycling, e.g. up to 50 cycles (see Figure 1.19, right).

Continuous potential cycling to more positive potentials comprising an anodic peak a_2 and cathodic peak c_1 in the 1st cycle (Figure 1.19, left) that corresponds to the oxidation of $\text{Ni}(\text{OH})_2$ to NiOOH and reduction of NiOOH to $\text{Ni}(\text{OH})_2$, respectively. Increasing the number of cycles from 2nd to 50th (Figure 1.19, right) results in a progressive increase of the current density values of the anodic peak a_2 , because of the entry of OH^- ions into the $\text{Ni}(\text{OH})_2/\text{NiO}/\text{Ni}$ layers, which leads to the progressive formation of a thicker NiOOH layer (1.27–1.29) [47, 48, 53, 54, 56, 57]:



The NiOOH that is formed in a forward scan is reduced back to the $\text{Ni}(\text{OH})_2$ in the reverse scan (cathodic current peak c_1) according to the reaction (1.30):



The schematic representations of the Ni-based surface layers transformation during potential cycling up to 50 cycles in alkaline solution is presented in Figure 1.18.

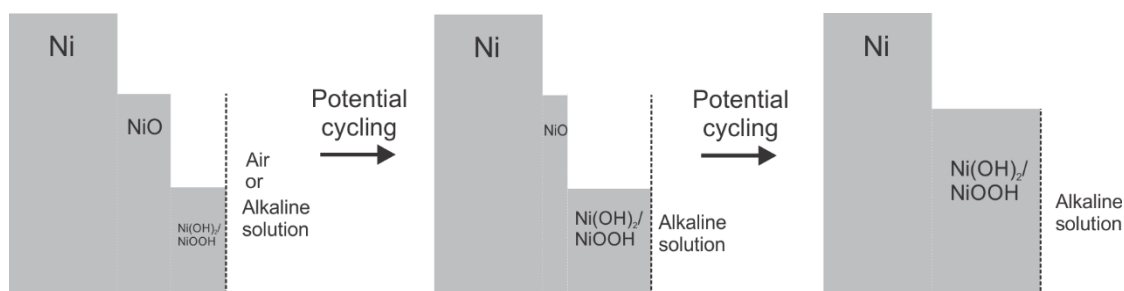


Figure 1.18: The schematic representation of the Ni-containing surface layers transformation during potential cycling in alkaline solution.

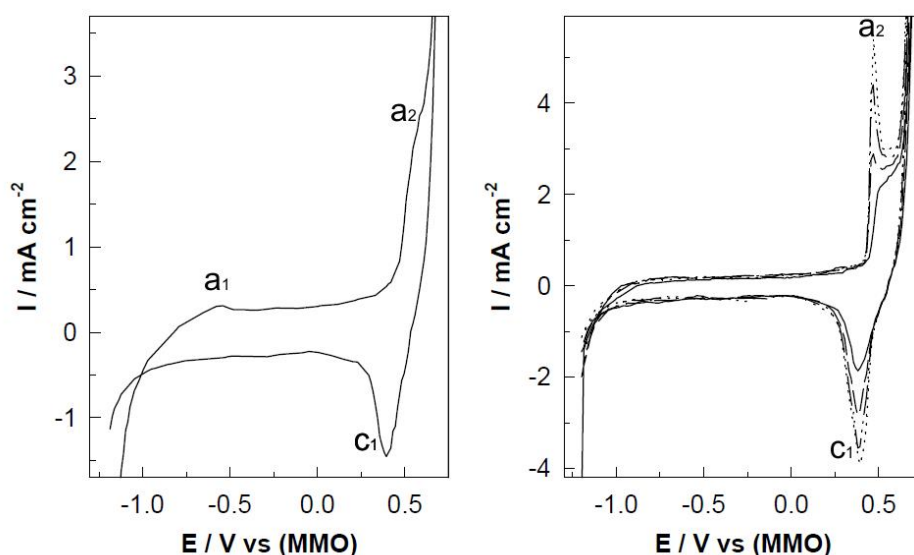


Figure 1.19: Voltammetric behaviour of the Ni electrode [30] in 1 mol L⁻¹ KOH solution after continuous potential cycling at a scan rate of 50 mV s⁻¹: left – 1st cycle; right – 2nd cycle (solid curve), 10th and 30th cycle (dash curves) and 50th cycle (dot curve). (Reprinted by permission from Elsevier (2020), License Number: 4753470988843)

Regarding the crystallographic structure, the formed Ni(OH)₂/NiOOH layers can exist in an amorphous structure or various crystal structures [47, 56, 57]. According to Bode's diagram [58, 59] (Figure 1.20), Ni(OH)₂ can exist in two crystal structures, in the literature denoted as “poorly-crystallised” α -phase or “well-crystallised” β -phase [49, 58]. The structure of “well-crystallised” β -Ni(OH)₂ is described as a hexagonal close-packed layered structure of hydroxyl ions with Ni occupying octahedral interstices. The structure of “hydrated” α -Ni(OH)₂ is still considered as a Ni(II) hydroxide but contains variable excess of intersheet water [49, 58]. A principal difference between the α - and β -phases arises in the stacking of the planes along the c-axis [45]. In addition to these two fundamental phases, several possible types of structural and crystal disorder can exist, including stacking faults, incorporation of foreign ions, or variable hydration [49, 60, 61]. Depending on the experimental method and experimental conditions either “well-” or “poorly-” crystallised hydroxides can be prepared. Usually, α -Ni(OH)₂ is isolated as a primary product, from which β -Ni(OH)₂ might be obtained by potential cycling in alkaline solution [58].

As it is seen from Figure 1.20, α -Ni(OH)₂ and β -Ni(OH)₂ might be transformed into γ -/ β -NiOOH if chemical or electrochemical oxidation (e.g. potential cycling in alkaline solution)

is introduced. β -NiOOH is a relatively well-defined material that crystallised in the hexagonal system and can be regarded as being derived from β -Ni(OH)₂. On the other hand, γ -NiOOH represents a whole family of compounds exhibiting a large intersheet distance. γ -NiOOH crystallised in the rhombohedral system and can be regarded as deriving from α -Ni(OH)₂ or β -NiOOH once overcharge happens [48, 58]. Such a redox transition between Ni(OH)₂ and NiOOH has been used to describe the electrochemical catalytic reactions towards small inorganic and organic compounds in alkaline electrolyte [62].

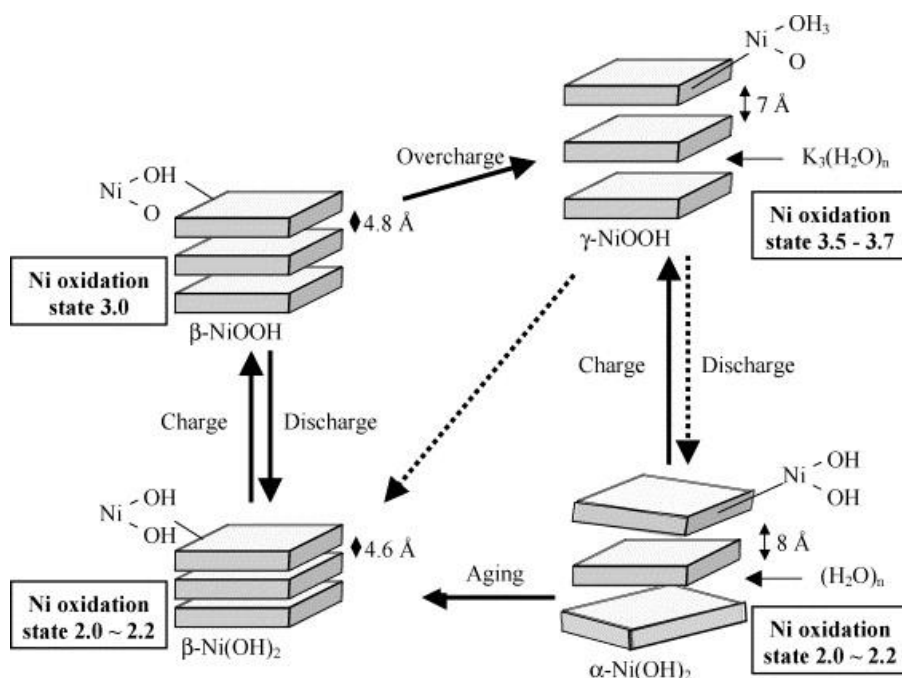


Figure 1.20: The general reaction scheme initially proposed by Bode [59]. (Reprinted by permission from Elsevier (2020), License Number: 4753490623513)

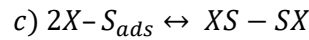
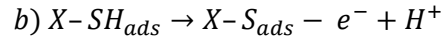
1.3.2.3 Electrochemical catalysis on “nanostructured” Ni-based electrodes

Efficient catalysts for electrochemical oxidation reactions are a key source for many applications in electro-analysis, electro-synthesis, fuel cells, water-splitting, etc. “Good” catalysts require a low over-potential and good durability to promote the reaction kinetics, i.e. high current densities [46]. The noble metals are known to exhibit the best overall performances, but they are scarce and expensive to satisfy the industrial market. Due to these facts, the research has been focused on seeking new non-precious electrocatalysts. The Ni-based electrodes, those with an adjusted electronic structure of the electrochemical active phase, are efficient and comparable to noble metal-based catalysts.

In the literature, the electro-catalytic mechanisms for oxidation of small organic compounds are proposed from the three following aspects [48]:

- Direct electro-catalysis of Ni(OH)₂ occurs with the organic compounds containing a sulfur atom, e.g. cysteine, hydrogen sulphide, etc. The mechanisms can be ascribed by three steps (1.31): a) at first, the molecule is adsorbed onto Ni(OH)₂ surface through hydrogen bond, then, b) the electron transfer happens from adsorbed molecule to Ni-based electrode which results in the formation of the sulfhydryl radical, and finally, c) the formed radical dimerizes [48, 63-65].





The voltammetric behaviour, where the direct electro-catalysis of $Ni(OH)_2$ in alkaline solution occurs, is presented in Figure 1.21. It was explained that in the absence of S-containing molecules, only in an alkaline electrolyte, a single oxidative wave (at +0.4 V) is observed which is attributed to the oxidation of $Ni(OH)_2$ to $NiOOH$. Upon the introduction of sulphide into alkaline electrolyte a pre-oxidative oxidation peak (at +0.25 V) emerges and continues to grow with the increased concentration of hydrogen sulphide. The pre-oxidation peak was attributed to the direct oxidation of sulphide with the Ni hydroxide [65].

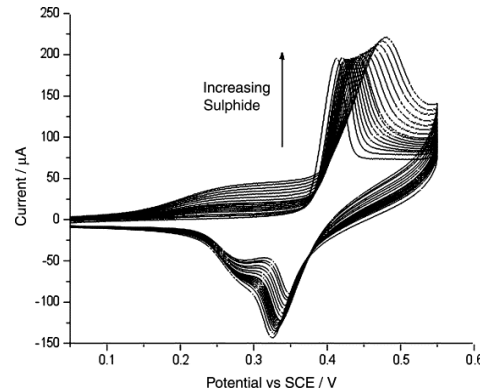


Figure 1.21: CV behaviour of the $Ni(OH)_2$ electrode after the addition of various concentrations of S-containing molecule in NaOH solution [65]. (Reprinted by permission from Elsevier (2020), License Number: 4753491151606)

- Direct electro-catalysis of $NiOOH$ can be considered to arise from the unpaired d-electrons or empty d-orbitals of ammonium, alcohols, urea, etc., associated with $NiOOH$. These are available for bond formation with adsorbed species or redox intermediates. The mechanism of direct electro-catalysis of Ni-based electrode towards ammonia was presented by Kapalka et al. [66]. As seen in CV (Figure 1.22), the oxidation peak A_1 is attributed to the formation of $NiOOH$ from $Ni(OH)_2$ and oxidation peak A_2 to the direct catalysis of $NiOOH$ towards ammonia. The oxidation peak A_2 continues to grow with the increased concentration of ammonia.

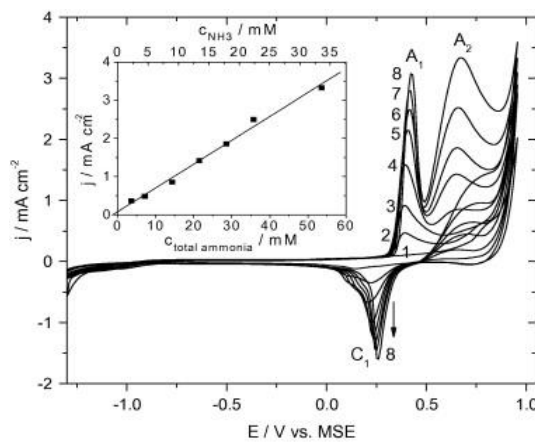
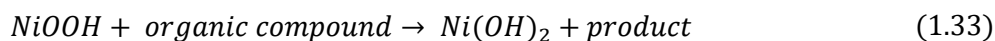
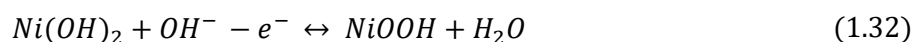


Figure 1.22: CV behaviour of the $Ni(OH)_2$ electrode after the addition of various concentrations of ammonia [66]. (Reprinted by permission from Elsevier (2020), License Number: 4753500423322)

- **Ni(OH)₂/NiOOH mediated electrolysis** is most often present in the electro-catalytic reactions of various organic compounds and can be ascribed as (1.32, 1.33):



The mechanism of mediated electrolysis was presented by Touny et al. [67]. They studied the electro-oxidation of formaldehyde on nanoporous nickel phosphate modified (nano-NiPh) electrode. As shown in CV (Figure 1.23), in the absence of organic molecule (blue curve), a well-defined anodic and cathodic current peak of Ni(OH)₂/NiOOH (1.32) is observed. Upon the addition of organic compound (red curve) into the alkaline electrolyte, the anodic current peak dramatically increases due to the production of Ni(OH)₂ (1.33) through the reaction of NiOOH and organic compound [48].

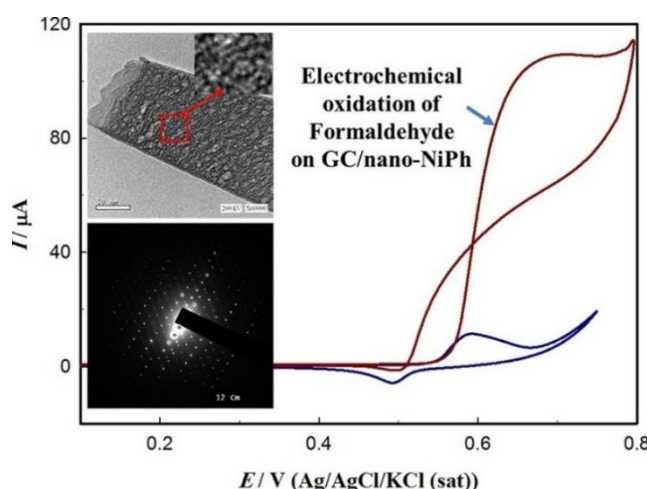


Figure 1.23: CV behaviour of the nanoporous Ni(OH)₂-phosphate (nano-NiPh) electrode in the absence (blue) and the presence (red) of HCHO in alkaline media [67]. (Reprinted by permission from Elsevier (2020), License Number: 4753540911064)

If the electro-catalytic oxidation occurs via mediated mechanisms, the following two parameters should be considered to fabricate a highly efficient electro-catalyst for electrochemical oxidation of target molecules:

- The work function of catalytically-active Ni(OH)₂/NiOOH, and
- Crystal structure of catalytically-active Ni(OH)₂/NiOOH.

1.3.2.3.1 The work function of catalytically-active Ni(OH)₂/NiOOH species

In the Ni(OH)₂/NiOOH mediated electro-catalytic oxidation of organic or inorganic compounds, the NiOOH is considered as the active phase during the charging and discharging process. However, this active phase suffers from a relatively high onset over-potential and low current density. This can be ascribed to a high work function of bulk NiOOH ($w_f = 5.96$ eV), to match the potential of oxidation reactions [46, 68], for example, oxygen evolution reaction ($w_f = 4.84$ eV). From this point of view, metallic Ni ($w_f = 4.6$ eV) would be a more suitable candidate for electro-catalytic oxidation if its surface could remain un-oxidised in the air/aqueous solutions. However, once the surface is oxidized, the w_f increases and becomes too high to meet the potential of the oxidation reaction. Consequently, the over-potential of oxidation reaction increases, and the current density decreases.

Wang et al. [46] proposed a strategy based on electron injection to manipulate the work function and to shift the Fermi surface of Ni/NiOOH composed electro-catalysts in order to obtain an outstanding electrochemical catalytic performance beyond noble metal catalysts. As it is schematically represented in Figure 1.24, the w_f of Ni is lower than that of NiOOH,

Targeting a low onset-over potential and high current density, Wang et al. [46] validated this theory by designing the Ni/NiOOH catalysts with a different thickness of NiOOH layer. The experimental results were also confirmed by the density function theory (DFT) calculation. They showed that the corresponding w_f of Ni/NiOOH increases with the thickness of NiOOH layer, the onset-overpotential of Ni/NiOOH tends to increase, and the current density decreases.

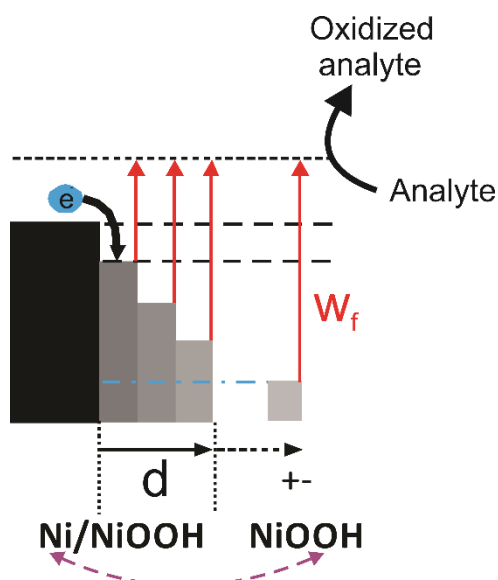


Figure 1.24: Schematic presentation of NiOOH-Ni catalyst, where w_f represents the work function and d the thickness of the NiOOH layer [46].

1.3.2.3.2 Crystal structure of Ni(OH)₂/NiOOH layer

The high catalytic activity of the $\text{Ni}(\text{OH})_2/\text{NiOOH}$ -based electrodes is also known to differ depending on the crystallinity of the phases. The Bode's diagram [69] (see Chapter 1.3.2.2, Figure 1.20) shows that during the charging and discharging process in alkaline electrolytes (1.32), various redox transformations can occur between $\text{Ni}(\text{OH})_2$ and NiOOH : in between disorder materials, $\beta \leftrightarrow \beta$, or $\alpha \leftrightarrow \gamma$ transformations. The oxidation state of Ni in disordered- $\text{Ni}(\text{OH})_2$, disordered- NiOOH , $\beta\text{-Ni}(\text{OH})_2$ and $\beta\text{-NiOOH}$ are +2, +2, +3, respectively. The transformation between these phases involves a one-electron transfer. It has been reported [70-72] that $\alpha \leftrightarrow \gamma$ transformation requires more than one electron (up to 1.6–1.67 electrons) for oxidation, suggesting that $\gamma\text{-NiOOH}$ might include Ni^{+4} ions. Consistent with this view, the $\gamma\text{-NiOOH}$ phase is generally considered as the less active, while it is generally believed that $\beta\text{-NiOOH}$ phase is the most active [73, 74]. However, the crystalline active phases (β or γ) possess some intrinsic disadvantages, including low stability during the long electrochemical reactions [46, 52, 75]. Recently, disordered/amorphous NiOOH -based materials [53, 76, 77] have attracted much interest because of their electrochemical and mechanical stability, as well as a complicated structure (lattice distortion, abundant surface defects, etc.) that results in the remarkable performances in electrochemical oxidation

reactions. It remains unclear whether this is attributed to increased proton vacancies [78] or increased stacking fault disorder [49] of $\text{Ni}(\text{OH})_2$ electrodes.

1.3.3 The determination of the electrochemically active surface area of nanostructured nickel electrodes

Surface catalysis, in general, is assumed to occur at active sites, meaning that only a small percentage of the accessible surface or surface atoms are involved in catalytic reactions. An understanding of the behaviour of surface atoms is crucial for the interpretation of the catalysis, including electrochemical catalysis [79, 80]. To be able to compare electrocatalytic reactions or electrochemical catalysts, normalised activities (current densities) have to be determined rather than simply comparing polarisation curves [81]. The normalisation of the output current can be based either on mass or specific activity. For determination of the mass activity, the complete use of the catalysts is mandatory, and the electrochemically active area (A_{ecsa}) has to be linearly dependent on the loading [81]. While for the determination of specific activity, the A_{ecsa} has to be evaluated by applying a proper method. The study of the behaviour and properties of A_{ecsa} for Ni catalysts is a very challenging area due to the quick passivation of metallic Ni and formation of native surface oxides that cannot be removed electrochemically. Several methods have been used formerly to estimate the A_{ecsa} of Ni catalysts, for example:

- **The voltammetric formation of a surface oxide/hydroxide layer** [47, 82]; Machado and Avaca [82] determined an electrochemical surface area of the Ni electrodes based on the cyclic voltammetric studies. Charge for the $\alpha\text{-Ni}(\text{OH})_2$ formation and reduction was conveniently analysed from polarisation curves, the corresponding real electrochemical surface area of Ni electrodes was determined. However, the authors did not take into account that also the non-stoichiometric NiO_x forms in the potential region where $\alpha\text{-Ni}(\text{OH})_2$ is formed. Therefore, this method yields only an approximate surface area due to the fact that the voltammetric behaviour depends on the formation of Ni hydroxides and Ni oxides of which the exact thickness has not been known or determined.
- **Measurements of the faradaic desorption** of surface intermediates [45]; this method involves the measurements of the charge of adsorbed hydroxide species formed in the Ni(III) potential region. Therefore, the method is imprecise between measurements of different Ni electrodes because the peak potential for the formation of Ni(III) species overlaps with the oxygen evolution reaction. Furthermore, this method is unsuitable for metallic electrodes since it does not involve the removal of the native surface Ni oxides/hydroxides prior to the measurements.
- **The measurements of electrochemical double-layer capacitance (C_{dl})** [83, 84]; Lasia and Rami [84] presented the AC electrochemical impedance measurements for the determination of the electrochemical surface area of Ni electrodes. Along with AC measurements, the double-layer capacitance was measured. However, the accuracy of determination is questionable, since the values of electrochemical areas in AC experiments depend only on the surface roughness factor.
- **Oxalate method** which involves the electrochemical measurements of a charge of the surface-limited process with highly unusual voltammetric characteristics [75, 85]. However, in comparison to the above-mentioned methods, this one is the only method that does not involve initial assumptions or estimations that may limit the confidence of the calculated A_{ecsa} of Ni-based electrocatalysts [75]. For this reason, an oxalate method is described in detail in the following chapter.

1.3.3.1 An oxalate method for measuring the electrochemically active surface area of Ni electrodes

The oxalate method presented by Hall et al. [75] and Drunen et al. [85] enables the determination of A_{ecsa} of Ni electrodes by controlling the formation of an oxalate layer that stabilises the surface nickel hydroxide, $\text{Ni}(\text{OH})_2$.

This method is based on the addition of oxalic acid to the alkaline electrolyte (OH^- ions) forming an oxalate anion, i.e. chelating ligand, that forms solid dehydrate chains with several metals (Mg, Mn, Fe, Zn, Ni, etc.) or adsorbs on a wide variety of metal hydroxide and oxyhydroxide surfaces. For example, it can adsorb onto the $\text{Ni}(\text{OH})_2$ or NiOOH surface by

substituting the surface hydroxide groups and forming a five-membered ring [75, 86], as presented in Figure 1.25.

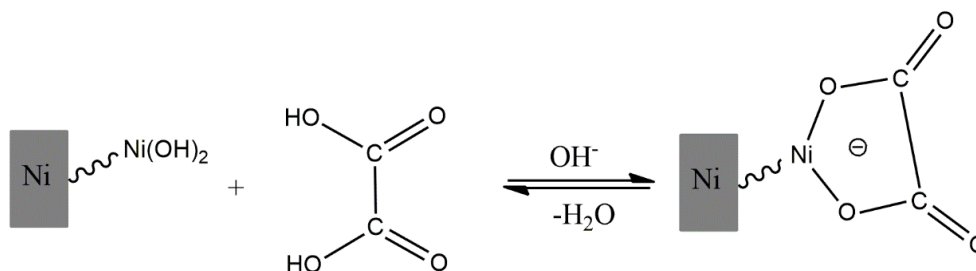


Figure 1.25: The formation of oxalate-stabilised Ni surface species.

The electrochemical formation of oxalate-stabilised $\text{Ni}(\text{OH})_2$ and NiOOH surface species was studied via cyclic voltammetry by Hall et al. [75] and Drunen et al. [85]. As a standard electrode, a surface oxide-free Ni substrate was used; the surface was cleaned in the strong mixture of acids prior to measurements in order to remove all the native oxides/hydroxides [75]. Also, by the standard electrode, it is meant that the electrode, according to the electrode's geometry, should be as smooth as possible [87].

According to Hall et al. [75], the cyclic voltammogram, presented in Figure 1.26, shows the behaviour of standard Ni electrode in the absence and the presence of oxalic acid in an alkaline solution. It can be assessed that the oxalate has a minor effect on the anodic scans up to 1.3 V. It means that an oxalate does not affect the formation of $\text{Ni}(\text{II})$; i.e. formation of $\alpha\text{-Ni}(\text{OH})_2$ at $E = 0.3$ V and $\beta\text{-Ni}(\text{OH})_2$ at the potential range from 0.3 V-1.0 V. Above 1.3 V, the effect of oxalate on the voltammetric behaviour is marked. The anodic peak at $E \approx 1.4$ V (red curve) and $E \approx 1.5$ V (black curve), which corresponds to the oxidation of stabilised or non-stabilized $\text{Ni}(\text{OH})_2$ to NiOOH , respectively, is shifted to the less positive potentials. Also, the width of the current peaks decreases and the current density drastically increases once the Ni surface species are stabilised by oxalate. Continuing in the positive potential direction, the increase in the current density was observed for the oxalate-free and oxalate-containing electrolytes that were ascribed to the oxygen evolution reaction. In the cathodic potential region, the cathodic current peak for the reduction of NiOOH to $\text{Ni}(\text{OH})_2$ is shifted to the less positive potential, the peak width is reduced, and the current density increases. Below this potential, there are no further effects of oxalate on voltammetric behaviour of Ni. Throughout this study, it was shown how oxalate affects voltammetric measurements. It was demonstrated that the amount of NiOOH formed and reduced in the presence of oxalate is significantly higher due to the increased current densities of NiOOH anodic and cathodic peak currents. Furthermore, the sharpness of these two current peaks in the presence of oxalate was attributed to the layered structure of Ni hydroxides, and the *in-situ* infrared spectroscopy with cyclic voltammetric measurements confirmed that the solution oxalate does not participate in the electrochemical reaction, but rather it chemically adsorbs on the surface Ni hydroxide, as it is proposed by mechanisms in Figure 1.25.

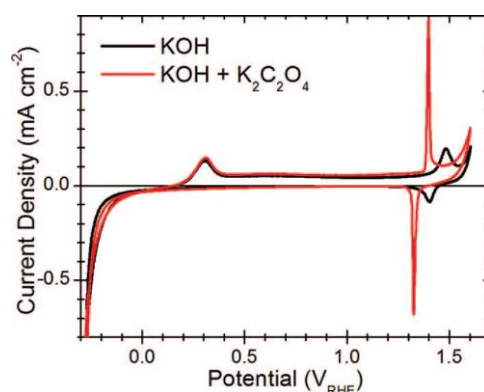


Figure 1.26: Cyclic voltammograms recorded on oxide-free surface Ni electrode in KOH solution (black curve) and KOH+oxalate solution (red curve) at a scan rate 20 mV s^{-1} [75].

The measurements of the number of electrons liberated during the formation of NiOOH or accepted during the reduction of NiOOH give the amount of active Ni species on the electrode's surface. This defines the electrochemically active surface area of electrodes. However, to determine the real electrochemically active surface areas of Ni electrodes (different from standard) from the voltammetric curves, the NiOOH reduction peak should be analysed. As it was shown on the standard Ni electrode, it does not overlap with other electrochemical processes (e.g. oxygen/hydrogen evolution reaction, etc.) and the capacitive current is zero. The total charge corresponding to the NiOOH reduction can be related to the integral of the voltammetric curve.

Furthermore, the degree to which an oxalate affects the charge values for NiOOH reduction is dependent on several parameters, including the temperature, the concentration of KOH, and the scan number. For this purpose, Hall et al. [75] and Drunen et al. [85] considered these parameters in order to achieve repeatability of the voltammetric measurements:

- **The effect of the temperature;** Figure 1.27 represents the charge density values as a function of scan number for different temperatures from 0°C to 20°C . The charge densities, as well as the slopes, decrease with decreasing temperature indicating the rapid formation of a thicker $\text{Ni}(\text{OH})_2$ layer at higher temperatures. However, Drunen et al. [85] explained that the temperature does not affect the charge values for NiOOH reduction significantly.

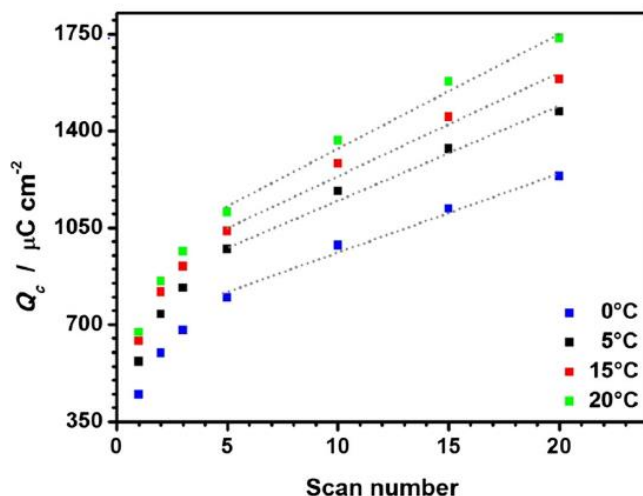


Figure 1.27: Charge density values calculated from the NiOOH reduction peak as a function of CV scan number at scan rates of 200 mV s^{-1} and temperatures: 0°C (blue), 5°C (black), 15°C (red) and 20°C (green). The squares correspond to the $0.1 \text{ mol L}^{-1} \text{ KOH} + 0.08 \text{ mol L}^{-1}$ electrolyte [85]. (Reprinted by permission from Springer Nature (2020), License Number: 4753501466186)

- **The effect of the KOH concentration** demonstrates the charge density values as a function of scan number for two different electrolyte concentrations: 0.1 mol L^{-1} (black) and 0.5 mol L^{-1} (red), each with 0.08 mol L^{-1} oxalic acid. The charge density values are higher in the $0.5 \text{ mol L}^{-1} \text{ KOH}$ due to the higher ionic strength of the electrolyte. However, the ionic strength is more severe in the first five cycles, after which the relationship between charge densities and cycles number is very similar.

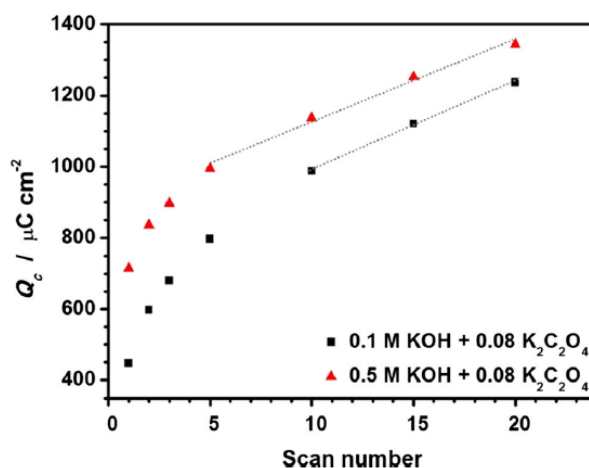


Figure 1.28: Charge density values calculated from the NiOOH reduction peak as a function of CV scan number in $0.1 \text{ mol L}^{-1} \text{ KOH} + 0.08 \text{ mol L}^{-1}$ (black) and $0.5 \text{ mol L}^{-1} \text{ KOH} + 0.08 \text{ mol L}^{-1}$ (red) electrolytes at scan rates of 200 mV s^{-1} [85]. (Reprinted by permission from Springer Nature (2020), License Number: 4753501466186)

- **The effect of a scan rate;** Figure 1.26 represents the charge density values as a function of scan number for three different scan rates: 20 mV s^{-1} (black), 150 mV s^{-1} (red) and 200 mV s^{-1} (blue), each observed in 0.1 mol L^{-1} with 0.08 mol L^{-1} oxalic acid. In all three situations, a non-linear growth of the charge densities is is

observed in the first five cycles, after which the charge density values increase approximately linearly with increasing cycle number. However, the charge densities are higher at a slower scan rate. Hall et al. [75] demonstrate that the largest Coulombic charges calculated at a slower scan rate ($v > 100 \text{ mV s}^{-1}$) appear due to the formation of a thicker surface layer. When cyclic voltammetry is applied at a sufficient high scan rate ($> 150 \text{ mV s}^{-1}$), the formation of adsorbed species is limited to one monolayer in the first cycle. With the limited thickness, the oxidation and reduction current peak of the stabilised Ni(OH)_2 and NiOOH surface layer can be measured.

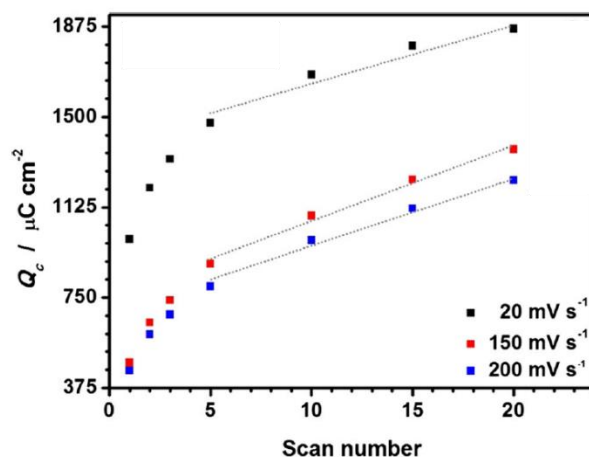


Figure 1.29: Charge density values calculated from the NiOOH reduction peak as a function of CV scan number at scan rates of 20 mV s^{-1} , 150 mV s^{-1} and 200 mV s^{-1} . The squares correspond to the $0.1 \text{ mol L}^{-1} \text{ KOH} + 0.08 \text{ mol L}^{-1}$ electrolyte [85]. (Reprinted by permission from Springer Nature (2020), License Number: 4753501466186)

The experimental error of the oxalate method was estimated to be less than 10 %. Thus, the oxalate-method presented by Hall et al. [75] and Drunen et al. [85] is extremely valuable because, as of yet, there is not a precise method for determining the A_{ecsa} of Ni electrodes, and that is agreed upon by the majority of research in this field.

1.4 Formaldehyde

Combining the versatility of the electrochemical methods with the implementation of metal-based nanostructured materials to sensing devices results in a development of a low-cost and sensitive sensors for the in-situ analysis of a wide range of organic, inorganic and biological compounds, such as methanol [31], formaldehyde [29, 32-37, 88-97], ascorbic acid [98], hydrazine [99], carbon monoxide, hydrogen peroxide [27, 41], glucose [25, 28, 38], lactate [19], DNA[19], etc. Significant attention, studies and optimizations have been directed towards formaldehyde (HCHO), since it can be considered as a model compound due to its simple structure, and since it is involved as an intermediate in the oxidation of many organic molecules [96], e.g. methanol, which has technological significance in industrial catalytic processes [100]. Besides, the HCHO is widely used in household products and manufacturing of building materials [29]. Upon that it can be found in many products, to which many industrial workers and customers are exposed on a daily basis [93].

Furthermore, the presence of formaldehyde in the aqueous systems is very common due to its high water solubility. Formaldehyde has been found and detected in food, drinking water and in agricultural runoff or wastewater effluents, in the latter case mostly arisen from the oxidation of natural organic matter during the disinfection (ozonation and chlorination) [101, 102]. Currently, several analytical techniques including high-performance liquid chromatography, gas chromatography, spectroscopic and colourimetric methods are applied for detection of HCHO ; which are, however, allocated from the source, time-

consuming and expensive [29, 103, 104]. Therefore, instant on-site monitoring of HCHO is important from the perspective of controlling the industrial process, as well as from protecting humans from being exposed to this toxic chemical. The addition of formaldehyde to consumable items may be the main reason for a growth disorder, blindness and respiratory diseases [93, 101].

1.4.1 Electrochemical detection of formaldehyde in aqueous solutions

Formaldehyde is commercially available as a 30–50% (by weight) aqueous solution, known as »formalin«. Formaldehyde exists in a dilute aqueous solution in equilibrium with the hydrated, gem-diol form of methylene glycol (Figure 1.30) [100]. In a more concentrated aqueous solution, oligomers and polymers that are mainly polyoxymethylene glycols are formed. Usually, a small amount of stabiliser (e.g. methanol) is added to commercial formaldehyde to prevent polymerisation [100, 101].

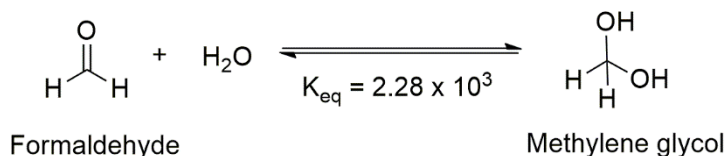


Figure 1.30: Formaldehyde in aqueous solutions.

Electrochemical detection for the system presented in Figure 1.30 is complicated due to the existence of a hydration equilibrium involving HCHO and methylene glycol (gem-diol form), which is the main species in aqueous solutions [96, 105]. This reaction plays an important role in the studies of electrochemical oxidation reactions in alkaline or acidic solutions on noble-metal [95, 106, 107], or transition-metal [33–36] based receptor elements.

However, the researchers tend to fabricate the receptor elements for HCHO detection that are showing enhanced electron transfer properties. Those ensure reduced oxidation over-potentials (low input energy), high and rapid current density responses (high catalytic rates) which are the sensors' most required and desired characteristics. These characteristics imply improved sensitivity that is defined as a ratio of the calibration curve slope of analytical signal at a given HCHO (i.e. analyte) concentration (Figure 1.31) by 1.34 [10]:

$$m = \frac{\Delta j}{\Delta c} \quad (1.34)$$

Where m is a sensitivity, j is a current density, and c is a concentration of HCHO.

Furthermore, the fabrication of new receptor elements with improved catalytic properties is a promising approach for further improvement of the analytical features, such as a limit of detection (LOD), linear range and reproducibility in order to meet the necessary requirements for implementation in routine analysis of HCHO. The LOD (Figure 1.31) is defined in a practical sense by Equation 1.35 as the lowest HCHO concentration in alkaline solution (i.e. blank) that produces the response equal to k times the standard deviation of the blank s_b . The k -factor is usually 2 or 3, which means that 2 corresponds to a 92.1 % confidence level, while 3 corresponds to a confidence level of 98.3 % [10]:

$$LOD = \frac{k s_b}{m} \quad (1.35)$$

Where k is a confidence factor ($k = 3$), s_b is a standard deviation of blank and m is a calibration sensitivity (the slope of the calibration curves). The linear range (Figure 1.31) refers to the HCHO concentration range over which the HCHO can be determined using a linear calibration curve (grey curve).

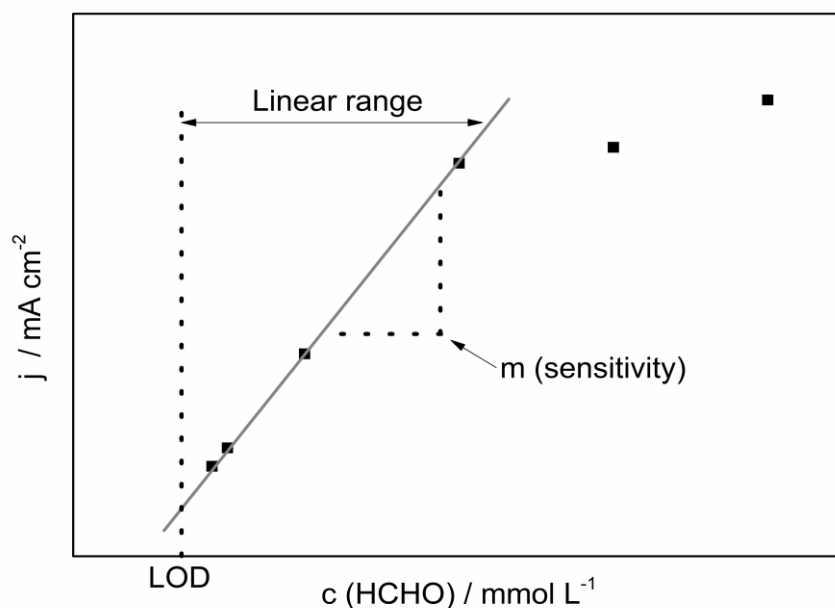


Figure 1.31: The graph of figures of merit that are commonly used and discuss the reporting of analytical results.

High catalytic activity (i.e. low detection potentials and high catalytic rates), as well as high sensitivity, low detection limit, wide linear range and good reproducibility are desirable characteristics for receptor elements that are used in HCHO electrochemical detection.

Noble metal-based receptor elements (Pt, Pd, Au, Ag, etc. [29, 94-97, 100, 103, 107-109]) can provide an excellent way to accelerate the electron transfer processes, decrease the over-potentials and increase the intensity of the corresponding voltammetric responses which results in high sensitivities and low detection limits. On the other hand, the limiting factor in using the noble metals is that they get readily deactivated and poisoned by adsorbed intermediates [29], which leads to the reduced linear range and poor repeatability. Literature states that the oxidation of HCHO to CO_2 at nanostructured noble metal-based electrodes can occur via two competitive pathways (Figure 1.32) where several reaction intermediates can be formed during oxidation reaction [29].

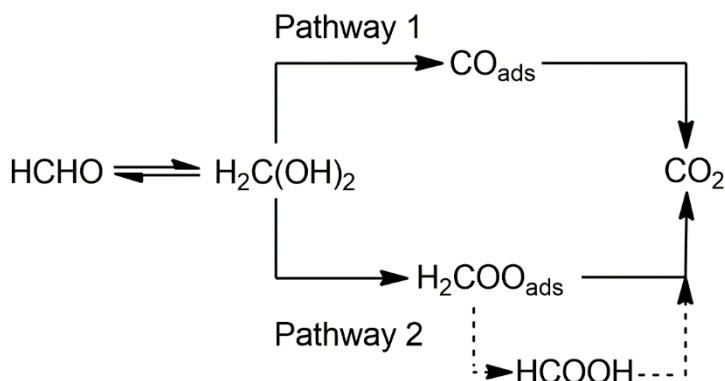


Figure 1.32: Schematic presentation of HCHO electrochemical oxidation on noble metal-based receptor elements.

When the oxidation is indirect (Pathway 1), a chemisorbed carbon monoxide (CO_{ads}) is formed. Whereas pathway 2 represents the direct electrochemical oxidation via the formation of active adsorbed intermediate ($\text{H}_2\text{COO}_{\text{ads}}$) and it is formed as long as the surface is not blocked with CO_{ads} . It was reported that on Pt (100) and Pt (110) the CO_{ads} is formed immediately, in contrast to the Pt (111) electrode, where CO_{ads} is formed after some time [100]. If CO_{ads} is formed, the reaction of oxidation to CO_2 stops due to a blocking effect of CO_{ads} [29, 103]. Further oxidation of CO_{ads} to the final product occurs only when the activation of water or hydroxyl group occurs, which requires the application of higher potentials [100]. Besides deactivation with adsorbed carbon monoxide that in overall limits their practical application [29, 43, 103], the cost price, and limited supply constitute a major barrier to the development of noble-metals-based receptor elements for HCHO detection.

In the realm of non-noble metal materials, many efforts have been focused on developing new electrodes for the HCHO electrochemical detection to address the cost and stability issues of the receptor elements. Those are based on more abundant metals, but still nonetheless active and include first-row transition metals (Ni, Co, Fe and their alloys). However, Ni, Co and Fe electrodes suffer from a relatively poor electrocatalytic activity in comparison to the noble metal-based electrodes due to the formation of a passive surface layer under exposure to air or aqueous solutions [48]. On the other hand, their surface hydroxides have been recognised as promising electro-catalysts for HCHO electro-oxidation (Figure 1.33) due to their excellent stability in alkaline media [53].

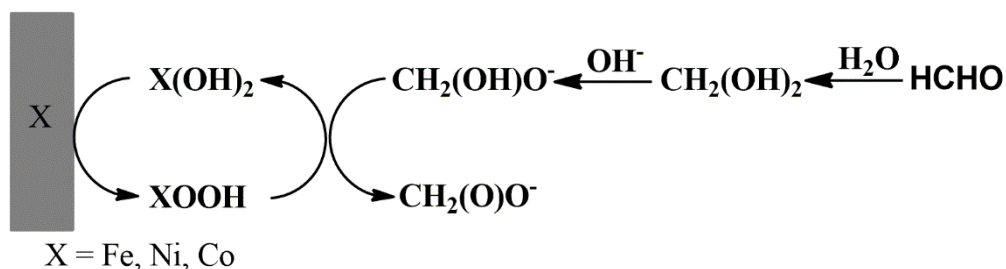


Figure 1.33: Schematic presentation of HCHO electrochemical oxidation on transition metal (Fe, Ni, or Co) based receptor elements.

By manipulation of the work function of these metals and their hydroxides (as already explained in Chapter 1.3.2.3.1) [46, 110], they can exhibit the comparable electrocatalytic activity to noble-metals-based electrodes. Furthermore, they demonstrate an improvement in terms of sensory functions over noble metals that are readily poisoned or blocked by

intermediate carbon monoxide that leads to the reduced linear range, poor reproducibility and repeatability and worsened catalytic utility, as already mentioned before [29].

Recently, the use of Ni receptor elements for the electrochemical detection of HCHO in alkaline media has been investigated and reported. Several modified Ni-nanoparticles-based electrodes (chitosan-modified carbon paste-Ni [32], poly (o-toluidine)-Triton X-100-Ni [34], poly(N-methylaniline)-Ni [33] and poly(1,5-diaminonaphthalene-carbon paste-Ni [36]) or ionic liquid-carbon paste-Ni [35]) have shown great enhancement in terms of the electro-oxidation of HCHO, but there was no information about the detection limits. Azizi et al. [37] reported a new receptor element based on a Ni/P nanozeolite-modified electrode, which showed the relatively good sensory properties, including a broad linearity range and a low detection limit ($5.8 \mu\text{mol L}^{-1}$), and good catalytic rate for HCHO oxidation [53].

Chapter 2

Aims and Hypothesis

2.1 Aims

The purpose of this dissertation was to develop active, stable and cost-efficient electrodes, i.e. receptor elements based on Ni nanostructures, with a high electro-catalytic affinity towards formaldehyde (HCHO) oxidation, which can be used for sensing applications. The electrodes were based on Ni thin films (2D) and Ni nanowires (1D) that were produced by electrochemical deposition. The deposited Ni-electrodes were further KOH-modified in alkaline solutions (i.e. potential cycling) using different scan rates in order to transform the Ni surface to electro-active redox pair of $\text{Ni}(\text{OH})_2/\text{NiOOH}$. A further intention was to manipulate its formation and its physical properties in order to enhance its electrocatalytic activity towards HCHO oxidation. Such prepared nanostructured $\text{Ni}(\text{OH})_2/\text{NiOOH}$ -Ni electrodes were expected to enable real-time detection of HCHO in alkaline media with high sensitivity and low limits of detection.

Main goals of the dissertation:

1. Preparation of nanostructured Ni-based electrodes (nanowires, thin films) via electrochemical deposition.
2. Determination of electrochemically active surface areas of as-deposited Ni electrodes via oxalate method.
3. Controlled formation of the passivation resistant and stable catalytically-active $\text{Ni}(\text{OH})_2/\text{NiOOH}$ redox couple on as-deposited Ni electrodes by the modification process in KOH electrolyte using cyclic voltammetry.
4. Electrochemical testing and detection of formaldehyde in alkaline media on KOH-modified Ni-based electrodes via cyclic voltammetry and chronoamperometry.
5. Evaluation of the catalytic activity of electrodeposited KOH-modified Ni electrodes by combined experimental electrochemical studies and analysis of the surface morphology and crystallinity of Ni-based electrodes (XRD, FEG-SEM, TEM).
6. Determination of HCHO sensor characteristics by calculating detection limits, sensitivities, reproducibility, repeatability and selectivity of KOH-modified Ni-based electrodes.

2.2 Hypothesis

2.2.1 Hypothesis 1

We hypothesise that the surface morphology and the crystal structure of the Ni thin films, prepared via electrochemical cathodic reaction: $\text{Ni}^{2+} + 2\text{e}^- \rightarrow \text{Ni}^0$, is influenced by the pH of the electrolyte. In order to investigate the morphology of the Ni films, two samples under different pH (2.5 and 5.5) are electrodeposited on the Au substrate.

If the pH of the electrolyte is low (2.5), the hydrogen evolution (at $E = -1.0$ V) is sufficiently effective and leads to the massive production of the hydroxide anion. As a consequence, immediate chemical precipitation of $\text{Ni}(\text{OH})_2$ occurs at the electrode surface

due to its low solubility. The morphology of the Ni film prepared at low pH is most probably composed of the nanosized crystallites (max. 100 nm) due to the massive hydrogen evolution that increases the micro-stirring, which also suppresses the continuous Ni deposition on the substrate.

If the pH of the electrolyte is higher, i.e. 5.5, the surface of the Ni film is expected to be different from that deposited at lower pH. Due to the less efficient hydrogen evolution reaction (at $E = -1.0$ V), the deposit would most probably result in larger crystallites (100-300 nm).

The pH of the electrolyte and the Au substrate (1 1 1)-orientation also influence the crystal structure of Ni deposits. For both used pHs the fcc Ni is expected with the reflection (1 1 1) that is the most pronounced, and additional (2 2 0) and (2 2 2) reflections. For lower pH = 2.5, additional diffraction peaks of precipitated Ni(OH)_2 are expected.

We hypothesise that high surface/volume ratio Ni-based electrodes (e.g. 1D nanowires) can be prepared via template-assisted electrochemical deposition from Ni^{2+} -based electrolyte into aluminium oxide membranes (AAO). The crystal structure of the as-deposited Ni-nanowires is expected to be polycrystalline and isotropic due to their sizes and diameters in μm ranges, and due to the fact that the Au substrate is isotropic as well. However, the surface morphology of Ni nanowires electrode is influenced by post-electrodeposition treatment: exposure to air and to a strong alkaline solution (during the etching of AAO template) that leads to the formation of air/water-formed Ni oxide and non-controllable growth of solution-formed Ni(OH)_2 layer.

2.2.2 Hypothesis 2

We hypothesise that the amount of electrochemically active surface Ni species is crucial to the interpretation of electrochemical output signal, i.e. currents. In order to be able to compare Ni-based electrocatalysts for formaldehyde electro-oxidation with those already explained in the literature (which involves different compositions, shapes, sizes and dimensionalities), normalised activities (normalised currents) need to be done rather than simply comparing polarisation curves. However, it is very important to determine the accurate Ni active surface area since it can deviate from geometrically determined (> 20%) and lead to inaccurate and non-representative results when defining catalysts. In order to determine the amount of electrochemically active surface Ni species and related electrocatalytic activity on certain electrodes, the electrochemically active surface areas have to be determined by applying an appropriate method, which is oxalate method for Ni electrodes. Furthermore, we postulate that Ni nanowires would have a higher electrochemically active surface area compared to the Ni films due to the high surface/volume ratio.

2.2.3 Hypothesis 3

The electrochemical approach was employed to deposit Ni electrodes (thin films and nanowires) from a nickel salt-containing solution. However, after deposition, the electrodes get exposed to water or air in order to clean and dry samples after the deposition. Ni nanowires were also exposed to the alkaline solution in order to release the deposited nanowires from the anodized alumina (AAO) templates. These processes are unavoidable and result in a several-atomic-layers thick Ni-passive film on the surfaces of electrodes that is most probably composed of a Ni hydroxide layer (at the solution-oxide interface) and a Ni oxide layer (between the metal surface and the outer hydroxide layer). Due to passivation, Ni electrodes suffer from a relatively high onset over-potential and a low catalytic activity, the promotion of which is the focus of many research studies that are focused on seeking new, Ni-based electrocatalysts with a low over-potential to reduce the input energy costs [46]. The $\text{Ni(OH)}_2/\text{NiOOH}$ redox couple has been reported to be an efficient, non-precious, metal-based electro-catalyst that lowers the over-potential of certain electro-oxidation reactions. Upon that we postulate that the CV modification of Ni electrode surfaces in the alkaline electrolyte (KOH) is necessary in order to transform the inactive surface Ni oxides to active surface Ni species of $\text{Ni(OH)}_2/\text{NiOOH}$.

We postulate that KOH-modification does not cause any significant changes of surface composition of Ni film that is prepared from a strong acidic electrolyte (pH=2.5) since the surface is already occupied by precipitated Ni(OH)_2 . Once the KOH-modification is introduced to the Ni film electrodeposited at pH=5.5, the surface metallic Ni is transformed

to the $\text{Ni}(\text{OH})_2$ according to the reaction: $\text{Ni}^{2+} + 2\text{OH}^- \rightarrow \text{Ni}(\text{OH})_2$. We hypothesise that the $\alpha\text{-Ni}(\text{OH})_2$ should grow on the surface of both Ni films (electrodeposited at pH = 2.5 and 5.5) whose crystallinity is going to depend on the texture of the underlying Ni film. We also postulate that KOH-modification can induce significant changes on the surface of Ni nanowires that are composed of air/water-formed NiO.

2.2.4 Hypothesis 4

We hypothesise that the crystallinity of active $\text{Ni}(\text{OH})_2/\text{NiOOH}$ layer can influence the electro-catalytic activity of HCHO oxidation. According to Bode's diagram, the better catalytic properties (increased current densities and lower onset-overpotential) are expected at amorphous- $\text{Ni}(\text{OH})_2/\text{NiOOH}$ and $\beta\text{-Ni}(\text{OH})_2/\beta\text{-NiOOH}$ surface species, since these transformations require the transfer of one-electron during the charging and discharging process in alkaline electrolytes. On the other hand, poorer catalytic properties are expected from $\alpha\text{-Ni}(\text{OH})_2/\gamma\text{-NiOOH}$ transformation which requires more than one electron (~ 1.67 electrons) for HCHO oxidation since $\gamma\text{-NiOOH}$ includes Ni^{+4} ions. All the deposited Ni-based electrodes and CV KOH-modified electrodes are assessed towards the HCHO oxidation upon these criteria.

2.2.5 Hypothesis 5

We hypothesise that the thickness of active $\text{Ni}(\text{OH})_2/\text{NiOOH}$ layer can influence the electro-catalytic activity of HCHO oxidation by manipulation of the Ni and NiOOH work function (w_f) [46]. In the electro-catalytic oxidation of many organic and inorganic compounds, the NiOOH is considered as the active phase. However, NiOOH (as a bulk catalyst) suffers from a relatively poor catalytic activity due to a high work function [46]. With regards to the strategy based on electron injection, we are able to reduce the work function of active NiOOH by constructing a thin layer of active NiOOH on the surface of Ni electrodes. Due to the fact that the work function of Ni is lower than NiOOH, the electrons from Ni can be transferred to surface NiOOH species and build up an internal electric field in their interface. The formed internal electric field reduces the work function of NiOOH catalysts and accelerates the electron transfer between active NiOOH catalyst and HCHO. Additionally, the thickness of the active NiOOH active layer should be as thin as possible, since the internal electric field becomes weaker once the thickness of NiOOH layer increases. Thus, we postulate that the better catalytic activity (lower onset potential and higher current density) will be achieved by the formation of a thin NiOOH layer since the corresponding w_f of active NiOOH will decrease due to the formation of the strong electric field at the interface of Ni and NiOOH.

Furthermore, we assume that the transformation of the inactive interlayer of NiO to active $\text{Ni}(\text{OH})_2/\text{NiOOH}$ is necessary to achieve the above-mentioned strategy based on the internal electric field. Once the contact between NiOOH and Ni is interrupted with the NiO, the strength of the internal electric field is weaker, and the corresponding work function of NiOOH remains high, i.e. the value of work function is comparable to the value of bulk NiOOH. Consequently, the electron transfer for HCHO oxidation is decelerated, and the onset-overpotential of Ni/NiOOH tends to increase, while the current density decreases.

We hypothesise that the scan rate in the KOH-modification process influences the thickness and the chemical composition of active surface species ($\text{Ni}(\text{OH})_2/\text{NiOOH}$) on as-deposited Ni electrodes. We postulate that at slow scan rates ($<150 \text{ mV s}^{-1}$) the thickness of outer $\text{Ni}(\text{OH})_2$ and inner NiO layer increases due to the dispersion of OH^- into Ni/NiO/ $\text{Ni}(\text{OH})_2$ layers and due to the penetration of molecular oxygen (formed in oxygen evolution reaction by application of higher potentials) into the Ni-Ni layer, respectively. Furthermore, we postulate that at higher scan rates ($<200 \text{ mV s}^{-1}$) only the thickness of outer $\text{Ni}(\text{OH})_2$ increases, since the penetration of OH^- into Ni layers is faster than penetration of molecular oxygen due to the fast potential scanning. These morphological changes of active surface Ni species would result in a different electrocatalytic activity towards HCHO by accelerating or hindering electron transfer.

2.2.6 Hypothesis 6

We postulate that the outstanding catalytic properties of KOH-modified Ni-based electrodes (related to the crystallinity and thickness of $\text{Ni(OH)}_2/\text{NiOOH}$) should lead to the preparation of a new generation of electrochemical sensors with the following sensory advantages: lower HCHO detection concentrations, improved overall selectivity, increased analytical sensitivity, and higher stability and resistance to passivation that implies better reproducibility [22].

Chapter 3

Materials and Methods

3.1 Materials

For the electrochemical deposition of Ni films, nickel sulphate hexahydrate ($\text{NiSO}_4 \cdot 6\text{H}_2\text{O}$, > 98%, Acros Organics), sulphuric acid (H_2SO_4 , > 99.9%, Sigma-Aldrich), and borofloat 33 glass (1.1 mm thick, PI-KEM Ltd.) were used.

For the electrochemical deposition of Ni nanowires nickel sulphate hexahydrate ($\text{NiSO}_4 \cdot 6\text{H}_2\text{O}$, > 98%, Acros Organics), boric acid (H_3BO_3 , Sigma-Aldrich), sulphuric acid (H_2SO_4 , > 99.9%, Sigma-Aldrich) and aluminium(III) oxide templates (AAO, Whatman Anopore, pore diameter 200 ± 50 nm) were used.

For the measurements of electrochemically active surface areas of Ni electrodes, the following reagents were used: potassium hydroxide (KOH pellets, >85 %, Acros Organics Sigma-Aldrich), oxalic acid dehydrate ($\text{C}_2\text{H}_2\text{O}_4 \cdot 2\text{H}_2\text{O}$, 97%, Fisher chemical) and nickel foil (1.0 mm thick, 99.9945 %, Alfa Aesar).

For the formation of $\text{Ni}(\text{OH})_2$ layer on the surface of Ni electrodes (i.e. KOH-modification) the potassium hydroxide (KOH pellets, >85 %, Acros Organics Sigma-Aldrich) was used.

For the electrochemical testing of $\text{Ni}(\text{OH})_2/\text{NiOOH}$ -Ni electrodes in terms of formaldehyde electro-oxidation the formaldehyde solution (aq. HCHO , 37 % w/w, Carlo Erba Reagents), sodium hydroxide (NaOH pellets, anhydrous, >98%, Sigma-Aldrich) were used. For the measurements of selectivity of Ni-based electrodes, the following reagents were used: absolute ethanol (EtOH , anhydrous, >99.9%, Carlo Erba Reagents), 1- Propanol (anhydrous, >99.7%, Sigma Aldrich), hydrogen peroxide solution (aq. H_2O_2 , 30 % w/w, Sigma Aldrich), acetaldehyde (CH_3CHO , >99.5 %, Sigma Aldrich).

3.2 Electrochemical Deposition of Ni Electrodes

The electrochemical depositions of Ni films and Ni nanowires were performed in a Teflon electrolytic cell, on a potentiostat/galvanostat Gamry Reference 600 equipped PHE 200 software at room temperature. A standard three-electrode system was used during the experiment (Figure 3.1):

- a reference electrode was an $\text{Ag}/\text{AgCl}/3.5$ M KCl (HANA Instruments GmbH-type HI5311),
- a counter electrode was a platinum mesh, and
- a working electrode was a flat SiO_2/Au substrate for the electrodeposition of Ni films; and the Au-AAO template for the electrodeposition of Ni nanowires.

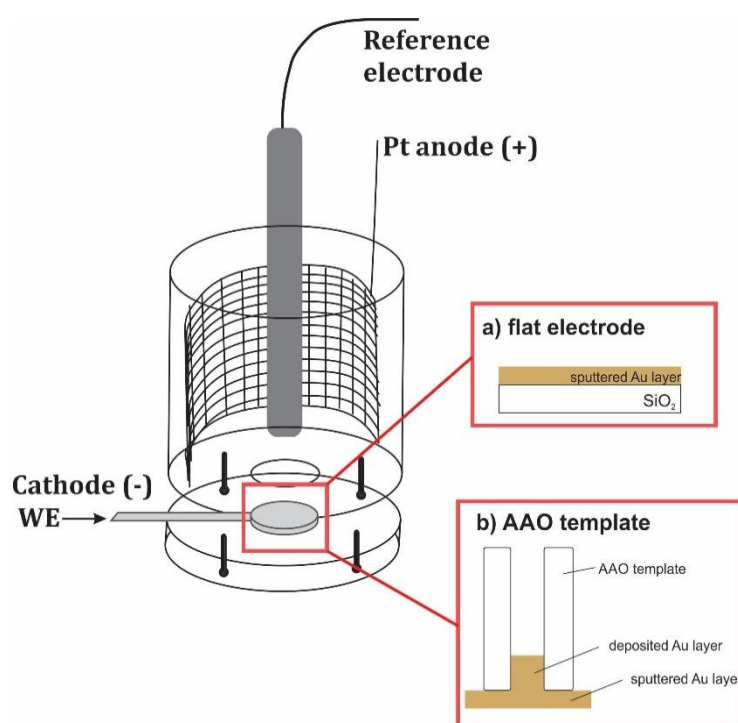


Figure 3.1: Scheme of the Teflon electrolytic cell for the electrodeposition of a) Ni films and b) Ni nanowires.

3.2.1 Electrochemical deposition of Ni films

Ni films were electrodeposited on the surface of conductive SiO₂/Au substrate which was prepared by Physical Vapour Deposition (PVD) of the Au (600 nm-thick-layer) on the glass. Before the PVD of Au, a 30 nm-thick layer of Cr was sputtered for better adhesion of Au. Electrodeposition of Ni films (fine- and coarse-grained) was carried out potentiostatically by applying the constant potential of -1.0 V for 300s. The electrolyte was composed of 1 mol L⁻¹ NiSO₄ × 6H₂O. The pH was adjusted in the range of 2.5–5.5 by addition of H₂SO₄. Fine-grained Ni film was electrodeposited from electrolyte with a pH of 2.5, and a coarse-grained Ni film was electrodeposited from electrolyte with a pH of 5.5.

3.2.2 Electrochemical deposition of Ni nanowires

Ni nanowires were electrodeposited into commercially available anodised aluminium oxide (AAO) templates (Whatman Anodics Filter Membranes), with a pore diameter of 200 ± 50 nm, a pore density of 1×10^9 cm⁻², and narrow pore size distribution (Figure 3.2) [111].

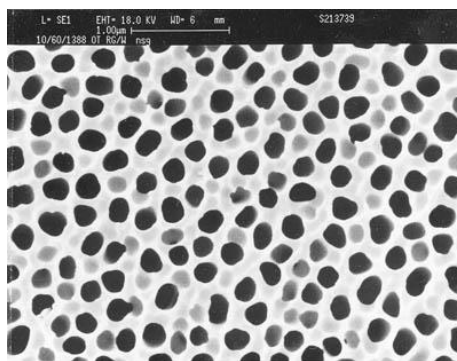


Figure 3.2: Top-view FEG-SEM image of AAO template provided by Whatman Anodics Filter Membranes [111].

In order to achieve the conductivity of AAO template for further electrodeposition of Ni nanowires, the bottom side of the membrane was covered with Au via two processing steps (Figure 3.3):

- **Au sputtering**; the bottom part of the AAO template was sputter with a 600 nm thick layer of Au by using PVD machine. Before the PVD of Au, a thin layer of Cr (≈ 30 nm) was sputtered to achieve better adhesion of Au, and
- **Subsequent electrodeposition of Au**; the bottom branched parts [9] of the AAO template pores were filled with Au nanowires (approx. length 1 μm) using a pulse potentiostatic mode: $E_{\text{on}} = -0.8$ V / $t_{\text{on}} = 1$ s and $E_{\text{off}} = \text{OCP}$ / $t_{\text{off}} = 10$ s for 80 cycles. The electrodeposition of Au nanowires was performed from the top of the AAO template using commercially available Au electrolyte (Ecolyt SG100, Gramm).

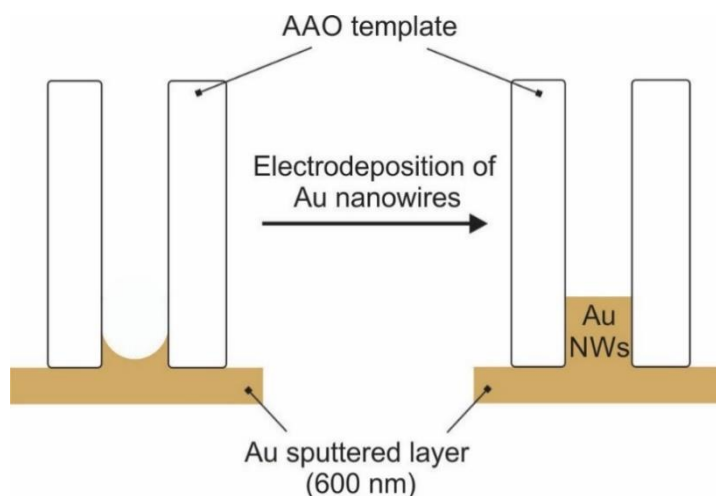


Figure 3.3: Schematic illustration of the preparation of conductive bottom Au layer; left: after sputtering of Au, and right: after electrochemical deposition of Au nanowires.

Prior to the electrodeposition of Ni nanowires (Figure 3.4, a), the template was wetted for 1 h in water and 30 min in Ni-based electrolyte. The Ni salt solution was composed of 0.2 mol L⁻¹ NiSO₄·6H₂O, and 0.1 mol L⁻¹ H₃BO₃ and the pH of 2.0 was adjusted by the addition of H₂SO₄. The Ni nanowires were prepared from the top side of the AAO template (Figure 3.4, b) potentiostatically by applying a constant potential of -1.0 V for 1200 s. The as-deposited Ni nanowires were finally dipped in a 10 mol L⁻¹ NaOH solution for 2 h to completely remove the AAO template (Figure 3.4,c). Further, the free-standing nanowires were washed with distilled water and ethanol several times and finally dried in the air.

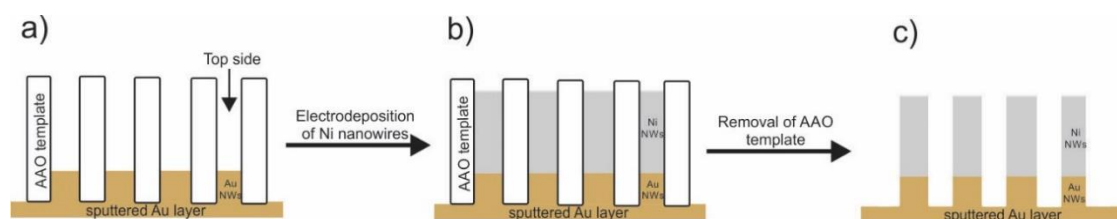


Figure 3.4: Schematic illustration of a) AAO-Au substrate, b) Ni nanowires after electrodeposition and c) free-standing Ni nanowires after AAO were etched away in a strongly alkaline solution.

3.3 Characterisation and KOH-Modification of As-Prepared Ni-Based Electrodes

The electrochemically active surface area, the KOH-modification and the HCHO electrochemical testing/detection of as-prepared Ni electrodes (fine-grained and coarse-grained Ni film and Ni nanowires) were investigated using cyclic voltammetry (CV) and chronoamperometry (CA). The measurements were carried out in Teflon cell with a standard three-electrode system (Ag/AgCl/3.5 M KCl – reference electrode, Pt mesh – counter electrode and as-prepared Ni electrodes – working electrodes) as it is shown in Figure 3.1. The experiments were performed using a Gamry potentiostat/galvanostat, Reference 600 equipped PHE 200 software at room temperatures.

3.3.1 Electrochemical determination of the electroactive surface areas of as-prepared Ni electrodes

The electrochemically active surface area (A_{ecsa}) of the Ni-based receptor electrodes was determined with the oxalate-based method using cyclic voltammetry. Prior to the measurements, the as-prepared Ni electrodes (fine-grained film, coarse-grained film and nanowires) and the Ni foil (standard electrode with known surface area, 0.785 cm^2) were etched for 2 minutes in the following mixture of acids: 15 mL of conc. HNO_3 , 5 mL of conc. H_2SO_4 , 5 mL of conc. H_3PO_4 and 25 mL of CH_3COOH . This experimental pre-step ensured the oxide-free Ni surfaces. The electrolytes were composed of $0\text{--}0.5 \text{ mol L}^{-1}$ KOH and the 0.08 mol L^{-1} oxalic acid dihydrate. The CV scans were initiated from $E = 0 \text{ V}$ to $+0.9 \text{ V}$. For each CV experiment, 20 cycles were collected at a scan rate of 200 mV s^{-1} .

3.3.2 KOH-modification of as-prepared Ni electrodes

The cyclic voltammetry (CV) was applied in a KOH-modification process. The measurements were performed in 0.5 mol L^{-1} KOH electrolyte, de-aerated with Ar gas (for $\sim 15 \text{ min}$) before its use. The CV experiments were carried out in a potential range from -1.0 V to $+0.7 \text{ V}$ for at least 50 cycles with a scanning rate of $10\text{--}200 \text{ mV s}^{-1}$.

3.3.3 Electrochemical oxidation and detection of formaldehyde

The cyclic voltammetry (CV) and chronoamperometry (CA) measurements were performed on KOH-modified Ni films (fine- and coarse-grained) and KOH-modified free-standing Ni nanowires in the solutions with the HCHO concentrations ranging from $0.1 \mu\text{mol L}^{-1}$ – 0.02 mol L^{-1} . The pH of 13.7 was adjusted with the addition of NaOH pellets (0.1 mol L^{-1}) into HCHO solutions. Electrolytes were prepared freshly for every set of CV and CA experiments using double-distilled water. Before each experiment, the HCHO-NaOH solutions were deoxygenated with pure nitrogen for approximately 15 min and used immediately.

The cyclic voltammograms were recorded in a potential range from 0 V to $+1.0 \text{ V}$ at a scan rate of 100 mV s^{-1} .

The CA measurements were performed to investigate the sensitivity, reproducibility and detection limits, where the Ni-based electrodes were exposed to the potentials from +0.7 V to +1.0 V for 10 s.

The CV measurements of selectivity of as-prepared Ni electrodes were performed from the following solutions: 1 mmol L⁻¹ 1-PrOH and 0.1 mol L⁻¹ NaOH, 1 mmol L⁻¹ EtOH and 0.1 mol L⁻¹ NaOH, 1 mmol L⁻¹ MeCHO and 1 mmol L⁻¹ H₂O₂ and 0.1 mol L⁻¹ NaOH solutions. The measurements were carried out from potentials 0 V to +1.0 V at a scan rate of 100 mV s⁻¹. Each CV experiment was performed at a fresh, KOH-modified Ni electrode. The CA measurements of selectivity were carried out under a constant applied potential of 0.8 V for 60 s. The current response was observed after successive addition (after every 10 s) of 1 mmol L⁻¹ 1-PrOH, 1 mmol L⁻¹ EtOH, 1 mmol L⁻¹ MeCHO and 1 mmol L⁻¹ H₂O₂ into the 0.1 mol L⁻¹ NaOH solution.

3.4 Material Characterisation

3.4.1 Scanning electron microscopy

The morphology, porosity, composition and size of as-deposited fine-grained Ni film and coarse-grained Ni film, as well as the as-deposited and free-standing Ni nanowires were determined using a field-emission-gun scanning electron microscope (FEG-SEM) JEOL JSM-7600F equipped with an energy-dispersive X-ray spectroscopy (EDXS) system INCA (Oxford Instruments, United Kingdom) with a 20-mm² silicon drift detector (SDD). The chemical composition of Ni-based electrodes was examined by quantitative EDXS analyses. A FEG-SEM accelerating voltage of 10 kV and spectrum-acquisition time of 60 s was sufficient to detect Ni and Au.

3.4.2 Transmission electron microscopy

For the TEM studies, the KOH-modified free-standing Ni nanowires were immersed in an EtOH solution and moved to the ultrasonic bath for approximately 15 min. This experimental procedure enabled a separation of Ni nanowires from Au sputtered layer. The morphology, crystal structure, and thickness of the Ni(OH)₂/NiOOH layer formed on the surface of free-standing Ni nanowires were investigated using the TEM, Jeol JEM-2010F equipped with energy-dispersive X-ray spectroscopy (EDXS).

3.4.3 X-ray diffraction analysis

The crystal structure of as-deposited and KOH-modified Ni films (fine- and coarse-grained), and as-deposited and differently KOH-modified free-standing Ni nanowires were examined by powder X-ray diffractograms (XRD) using a Siemens D5000 diffractometer with a Cu-K α source ($\lambda = 1.5406 \text{ \AA}$). The XRD patterns were collected at 2-theta range from 10–90°.

3.4.4 Fourier-transform infrared spectroscopy

Fourier-transform infrared spectroscopy (FTIR) was performed in order to evaluate the presence of –O–H, Ni–O– and Ni–O–H chemical bonds on the surface of the KOH-modified Ni nanowires electrode. The spectra were recorded on a dried as-deposited and KOH-modified Ni films and Ni nanowires in the wavenumber range from 400 to 4000 cm⁻¹ on a Spectrum 100 spectrometer (Perkin Elmer, USA).

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Chapter 4

Results and Discussion

4.1 Electrodeposition of Ni Electrodes

Nanostructured electrodeposited Ni electrodes have many potential applications in the field of electrochemical sensors that arise from their shape, size and dimensionality, which can be easily controlled. In this chapter, the electrodeposition of differently structured Ni electrode is described. The electrodes were fabricated on flat and into porous working electrodes, aiming at their application as the receptor elements or catalysts for HCHO electro-oxidation. 2-D Ni films were electrodeposited on the flat Au working electrode (Figure 4.1, a), and their morphology was controlled by electrolyte composition (concentration of Ni^{2+} , pH, etc.). 1-D Ni nanowires were prepared into a porous working electrode, i.e. porous anodised aluminium oxide (AAO) template (Figure 4.1, b). The effect of experimental parameters on the Ni electrodeposition was studied using cyclic voltammetry (CV) and chronoamperometry (CA).

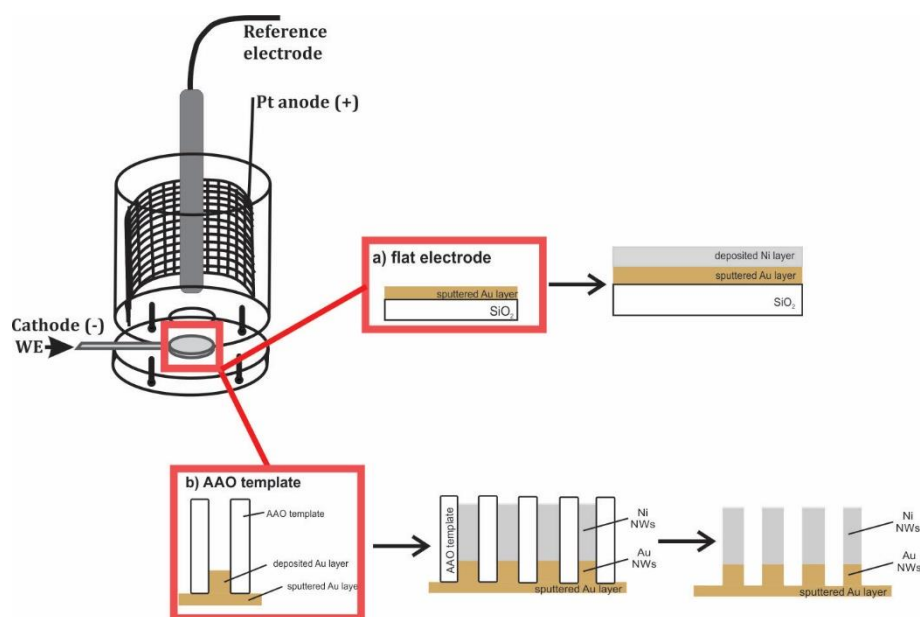


Figure 4.1: Schematic presentation of electrodeposition of a) 2-D Ni films and b) 1-D Ni nanowires.

4.1.1 Electrodeposition of Ni films

Ni films were potentiostatically electrodeposited on a flat Au substrate using three-electrode configuration, as presented in Figure 4.1, a. In order to achieve a different

morphology and porosity, electrodepositions were performed from two acidic electrolytes with different pH, using a hydrogen bubble formation as a dynamic environment.

4.1.1.1 Electrochemical study of Ni films deposition process

Figure 4.2 shows CV profiles of Au flat substrate in A) 1 mol L⁻¹ NiSO₄ solution, pH = 2.5 was adjusted with H₂SO₄ (green), and B) 1 mol L⁻¹ NiSO₄ solution, pH = 5.5 (blue). The CVs were observed at a scan rate 50 mV s⁻¹ in the potential window from the open-circuit-potential (OCP, ~ 0 V) to the -1.2 V, then the scans were reversed to the +0.4 V and back to the 0 V. In the forward scan, the CV profiles (A and B) were characterized by cathodic peak (c_{Ni}) which indicates the reduction of nickel according to the overall reaction: $Ni^{2+} + 2e^- \rightarrow Ni^0$, and hydrogen evolution region (c_H) at $E > -0.8$ V: $2H_2O + 2e^- \rightarrow H_2 + 2OH^-$. From graphs, A and B, it is evident that electrolyte pH influences the onset potentials for the reduction of Ni²⁺. The shift of the onset potential to a more negative potential is observed as pH increases (from -0.45 V – green to -0.7 V – blue). The shift of the onset potential for Ni deposition to less negative potentials is strongly influenced by protons in the case of lower pH (2.5). Also, the current density is strongly influenced by pH. When electrolyte pH decreases (from 5.5 to 2.5), the current density increases. As it was explained by Boubatra et al. [112], during the electrodeposition of Ni, some of the current is consumed by hydrogen formation. This “side reaction” reduces the current efficiency, thus affects the pH at the vicinity of the cathode surface and the kinetics of metal reduction. Also in our case, the current density at $E > -0.8$ V is ~2 times higher at lower pH (green) than at higher pH (blue) because more current is consumed by hydrogen evolution reaction. Significant hydrogen evolution at lower pH (2.5) leads to the massive production of the hydroxide anions, and consequently to the immediate chemical precipitation of Ni(OH)₂ at the electrode surface due to its low solubility [49].

In the reverse scan, the anodic current peak a_H at $E = -0.015$ V was observed on graph A and B (Figure 4.2). This peak is attributed to the oxidation of the adsorbed hydrogen that is formed during the forward scan. However, the anodic peak a_{Ni} at $E = +0.15$ V that corresponds to the oxidation of Ni according to the reaction $Ni^0 + 2OH^- \rightarrow Ni(OH)_2 + 2e^-$, is only observed on the CV presented in Figure 4.2, B. The anodic peak (a_{Ni}) cannot be seen from CV curve observed at lower pH (Figure 4.2, A) due to the chemical reactions between Ni and hydroxide ions in the forward scan at highly negative potentials, which leads to the direct precipitation of Ni(OH)₂ at the electrode surface (as described above).

From CV profiles we assumed that a different composition and morphology of the Ni films could be achieved by varying the deposition parameters (i.e. potential). Therefore, the different mechanisms on the surface of Au substrate are expected due to the intensified hydrogen evolution that is followed by immediate Ni(OH)₂ precipitation in the case of lower electrolytic pH. According to these observations, the Ni films were electrodeposited under applying a constant potential of -1.0 V.

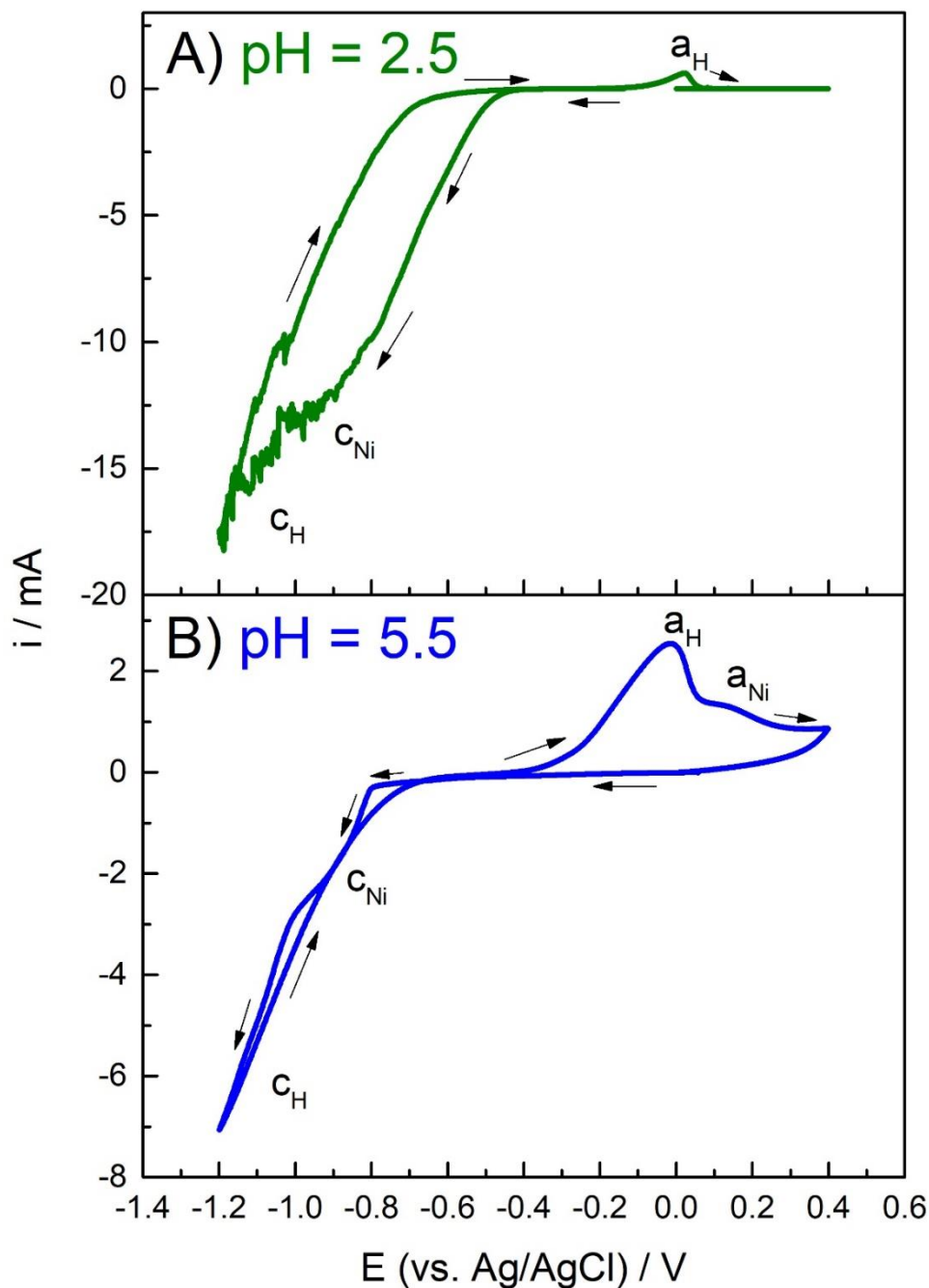


Figure 4.2: CV profiles of Au substrate in 1 mol L⁻¹ NiSO₄ solution at two different pH: 5.5 – blue curve and 2.5 – green curve. The scan rate was 50 mV s⁻¹.

4.1.1.2 Influence of the pH on the morphology of Ni films

The typical morphology of Ni film obtained by electrodeposition from electrolyte with a pH of 2.5, i.e. “fine-grained” Ni film, is presented in Figure 4.3. This film was electrodeposited under applying a constant potential of -1.0 V for 300 s. At these conditions, the Au substrate

could not be entirely covered by Ni due to the extensive hydrogen formation (Figure 4.3, A). However, the resulting film is composed of small crystalline nanoparticles (50-70 nm). The lines that are seen in image B are present due to the topography of underlying Au substrate (with however a smooth surface, a root-mean-square roughness = 1.6 nm [113]). The crystal structure and the chemical composition of electrodeposited Ni were examined by XRD (explained in Chapter 4.3.1.1.) and EDS by which the main detected element was Ni (91-95 at. %). Also, the residual amounts of oxygen (1-5 at. %) and gold (1-5 at. %) from the underlying substrate were detected which implies that the film is thin ($< 1 \mu\text{m}$), as the interaction volume with using accelerating voltage of 10 keV is below $1 \mu\text{m}^3$.

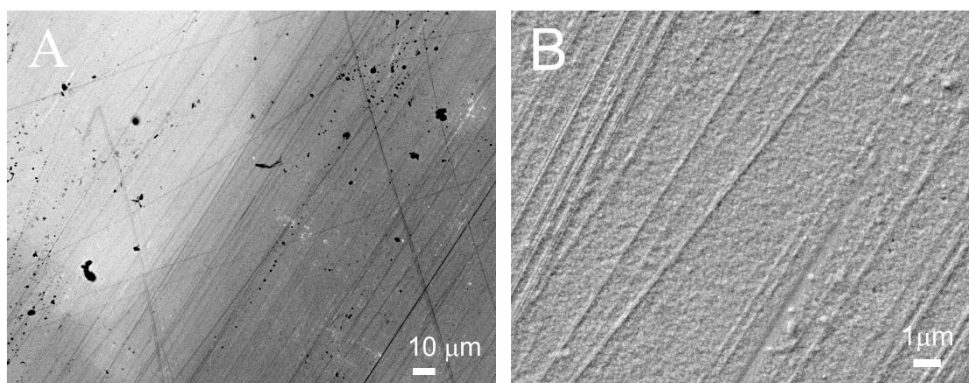


Figure 4.3: FEG-SEM images of fine-grained Ni film, prepared from Ni^{2+} electrolyte with pH = 2.5; A) Backscattered electrons (BE) image with bright Au phase (from substrate) and darker electrodeposited Ni; B) Secondary electron (SE) image of electrodeposited Ni, composed of small nanoparticles ($\sim 100 \text{ nm}$).

The typical morphology of Ni film obtained by electrodeposition from electrolyte with the pH of 5.5, i.e. “coarse-grained” Ni film, is presented in Figure 4.4. The coarse-grained Ni film is more homogeneously covering the Au substrate than the fine-grained Ni film (Figure 4.4, A) and is composed of larger crystallites expanded in the size of 100–300 nm (B). The chemical composition of electrodeposited Ni was determined by XRD (explained in Chapter 4.3.1.1.) and EDS by which the main detected element was Ni (97-99 at. %). This film does not show the presence of Au due to the larger thickness of the film. However, the residual amount of oxygen was detected (1-3 at. %).

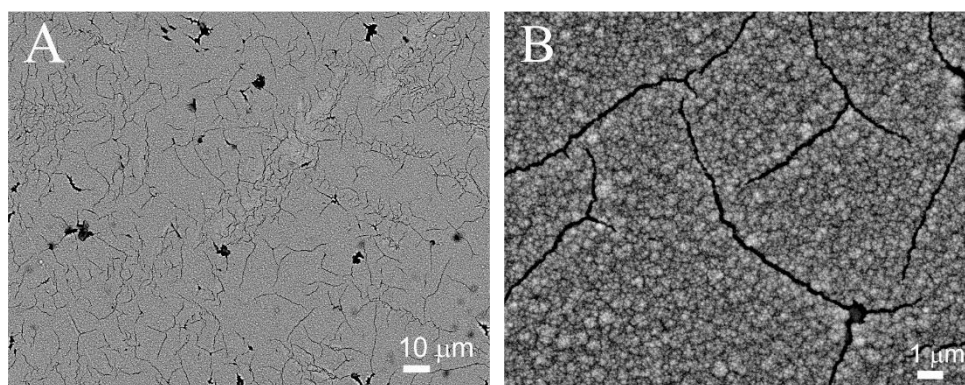


Figure 4.4: A) BSE-SEM image of coarse-grained Ni film (prepared from Ni^{2+} electrolyte with pH = 5.5; B) SE-SEM image of coarse-grained Ni, composed of larger nanoparticles (100-300 nm).

From CV measurements and FEG-SEM analysis, it can be concluded that the reduction of Ni^{2+} to Ni^0 from electrolytes with a different pH proceeds differently on the flat Au electrode. The intensive hydrogen evolution (favoured at lower pH) influences the electrochemical conditions at the vicinity of the cathode and reduces the diffusion layer thickness, and changes the growth and nucleation process. Due to the changed kinetics and deposition

mechanism, the final size distribution of crystallites is different, and consequently, the final thickness of films differ. Our results are in agreement with the already published literature about Ni electrodeposition from acidic-based electrolytes [112, 114, 115]. As it was explained by Boubatra et al. [112] and Pangarov et al. [116], a lower pH decreased the grain size of the deposit by increasing the nucleation rate, while a higher pH increased the grain size of deposit by reducing the nucleation rate.

All of these observations are also important from practical reasons, especially if we are targeting the preparation of material for electro-analysis, where the choice of nanostructured electrode material is greatly influenced by the morphological aspects of its surface.

4.1.2 Electrodeposition of Ni nanowires

Ni nanowires were electrodeposited in the porous anodic aluminium oxide (AAO) template, as presented in Figure 4.1, b. The template-assisted electrodeposition is more complex than deposition on a flat substrate, because of several additional experimental steps: preparation of the conductive substrate and wetting of the template. Introduction of these experimental steps provides a stable system and repeatability of the Ni nanowires electrodeposition.

4.1.2.1 Preparation of conductive substrate

One side of the AAO template was sputtered with the Au using physical vapour deposition (PVD) due to the AAO non-conductivity. Figure 4.5, A, represents the completely covered bottom part of an AAO template with the ~ 600 nm thick Au layer. Based on this image (A) we also confirmed the presence of Au particles on the walls of the pores which penetrate (~ 1 μm in-depth) during PVD. Despite the fact that template conductivity is achieved by the PVD technique, the subsequent electrodeposition of Au nanowires was necessary for two main reasons:

- During the sputtering, Au particles penetrate the AAO pores and are deposited on the walls of the pores. This would lead to the formation of non-homogeneous nanowires due to the preferential electrodeposition of Ni on the Au particles [9];
- From Figure 4.5, B, it can be seen that bottom part pores are branched (c) due to the AAO template preparation. Therefore, the electrodeposition of Ni would start at the Au sputter layer and deposited Ni nanowires would not be homogeneous and completely cylindrical [9].

In order to obtain completely cylindrical and homogeneous Ni nanowires, subsequent electrodeposition of Au nanowires was implemented from the top of the AAO template using a pulse plating technique. The method and electrodeposition conditions were chosen according to the preliminary research of Pečko et al. [9]: E_{on} of -0.8 V for t_{on} of 80 s and the E_{off} of OCP for t_{off} 10 s with 80 repetitions. Figure 4.5 B represents the FEG-SEM image after sputtering and electrodeposition of Au. It can be seen that the length of Au nanowires is ~ 1 μm and the diameter is 200 ± 50 nm.

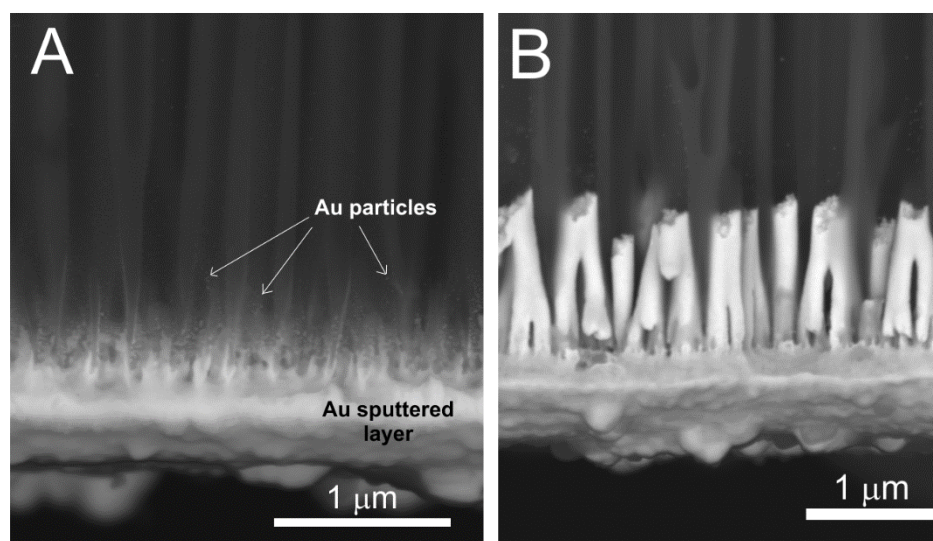


Figure 4.5: A: Backscattered electron (BE) image of AAO template after Au sputtering, and B) Secondary electron (SE) image of AAO template after electrochemical deposition of Au on Au sputter layer.

After a successful preparation of the Au substrate, the template was wetted for 1 h in water and 0.5 h in Ni^{2+} electrolyte. This step was introduced in order to enable the formation of homogeneous nanowires and thus to avoid the formation of annual nanowires bottom, as presented by Pečko et al. [9].

4.1.2.2 Electrochemical study of Ni nanowires deposition process and morphology of deposits

In order to determine the optimal plating conditions for the Ni nanowires synthesis, several approaches have been used and examined. Figure 4.6, A and B, represents the first experiments of Ni nanowires deposition, where $1 \text{ mol L}^{-1} \text{ NiSO}_4$ was used as a source of Ni^{2+} ions. The pH of the electrolyte was adjusted to 2.5 by the addition of H_2SO_4 . Ni nanowires were deposited under A) potentiostatic regime ($E = -1.0 \text{ V}$, $t = 300\text{s}$) and B) pulse electrodeposition (E_{on} of -1.0 V for t_{on} of 2 s and the E_{off} of OCP for t_{off} 10 s with 450 pulse repetitions). As seen from Figure 4.6, A we were not able to deposit uniform Ni nanowires when using the potentiostatic regime. The inhomogeneity of deposited nanowires is most probably the result of pronounced hydrogen evolution reaction, which blocks the pores and metal ions cannot arrive at the reaction spot. In order to reduce the effect of hydrogen bubbles and thus remove them from the reaction spots and pores, the pulse technique was performed (as it is explained in Introduction, Section 1.2.1.1.). As shown in Figure 4.6, B the pulse electrodeposition method is suitable for the deposition of homogeneous nanowires. However, the length of the electrodeposited nanowires varied from $0.5\text{--}1.5 \text{ }\mu\text{m}$ and nanowires were unexpectedly short after long (1.5 h) deposition.

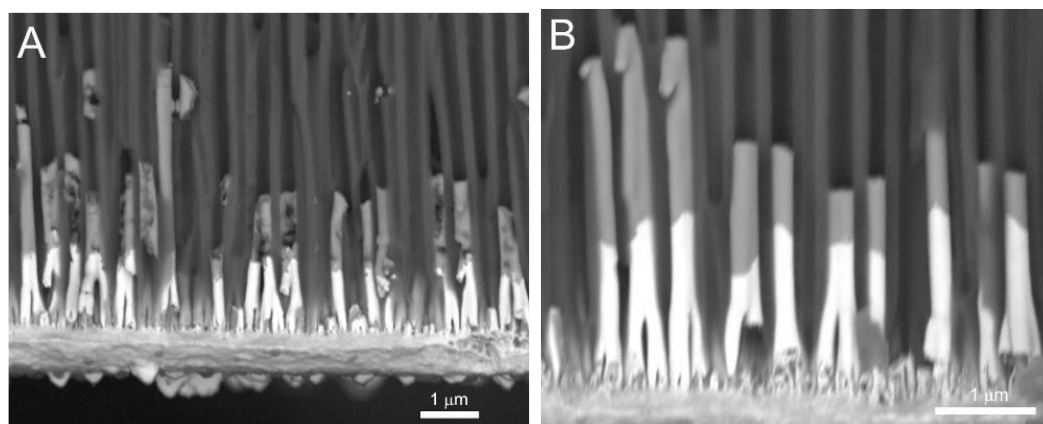


Figure 4.6: FEG-SEM cross-section view images of electrodeposited Ni nanowires in the AAO template under A) potentiostatic regime and B) pulse technique.

Based on these results, we have decided to limit the effect of hydrogen evolution by the addition of buffer, i.e. boric acid. According to the literature, boric acid is a buffer which has a function to limit the effect of the pH resulting from the discharge of hydrogen ions, thereby simplifying pH control. The mechanism by which boric acid operates is complex, but it is generally understood that it exists in a solution as a mixture of borate ions and non-ionized boric acid. When hydrogen is discharged, some boric acid will ionise to replace the hydrogen [117].

Figure 4.7 shows the CV profiles of the conductive Au-AAO template observed in a $0.2 \text{ mol L}^{-1} \text{ NiSO}_4$, $0.1 \text{ mol L}^{-1} \text{ H}_3\text{BO}_3$ electrolyte, where pH of 2.2 was adjusted with the addition of H_2SO_4 (the concentrations of solution species were selected from the literature [118]). The CV was obtained in a potential range from 0 V to -1.5 V, and then the scan was reversed to the +0.3 V and back to the 0 V. The first increase in the cathodic current (c_{Ni}) was observed from -0.7 V to -1.2 V and indicated the reduction of Ni^{2+} to Ni^0 . The following increase in the cathodic current (c_{H}) from $E = -1.2 \text{ V}$ to -1.5 V corresponds to the hydrogen evolution reaction. In the reverse scan, the anodic peak a_{H} at $E = 0.015 \text{ V}$ is attributed to the oxidation of the adsorbed hydrogen that is formed during the cathodic scan and the anodic peak a_{Ni} at $E = +0.2 \text{ V}$ to the oxidation of Ni according to the reaction $\text{Ni}^0 + 2\text{OH}^- \rightarrow \text{Ni}(\text{OH})_2 + 2e^-$.

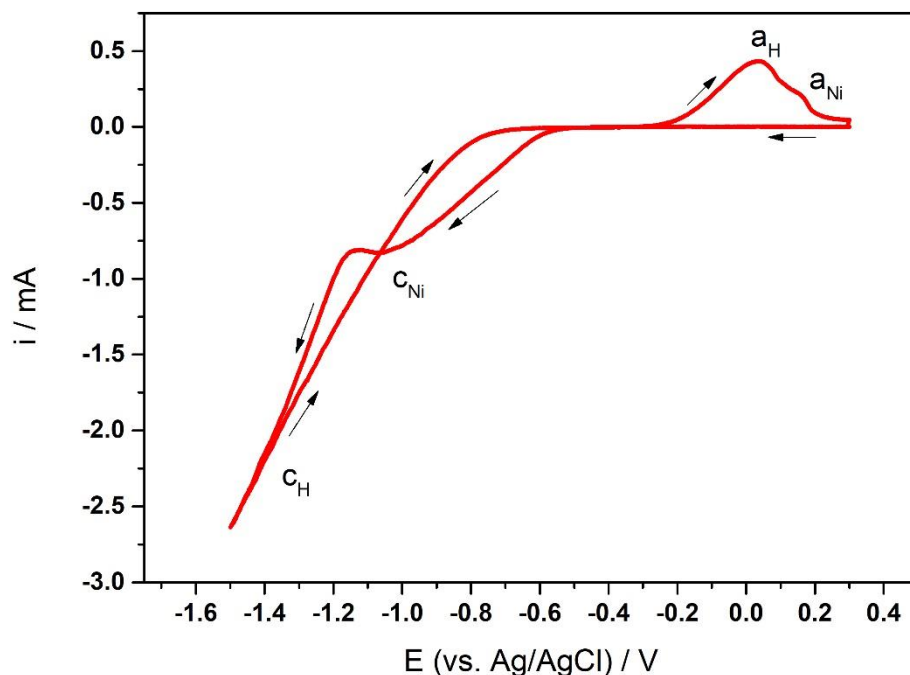


Figure 4.7: Cyclic voltammograms for $0.2 \text{ mol L}^{-1} \text{ NiSO}_4$ and $0.1 \text{ mol L}^{-1} \text{ H}_3\text{BO}_3$ (pH of 2 was adjusted with H_2SO_4), observed on the AAO-sputtered Au-Au nanowires substrate at a scan rate 50 mV s^{-1} .

Morphologically uniform Ni nanowires (length of $2\text{--}2.5 \mu\text{m}$, the diameter of $200 \pm 50 \text{ nm}$) were deposited by applying a constant potential of -1.0 V for 900s (Figure 4.8). The potentiostatic regime for the Ni nanowires deposition in this system worked due to the following reasons: first, concentration of Ni^{2+} ions is high enough to enable fast transport of the ions to the bottom part of the pores, and second, the present boric acid controls the electrolyte pH and liberates the blocking effect of hydrogen bubbles.

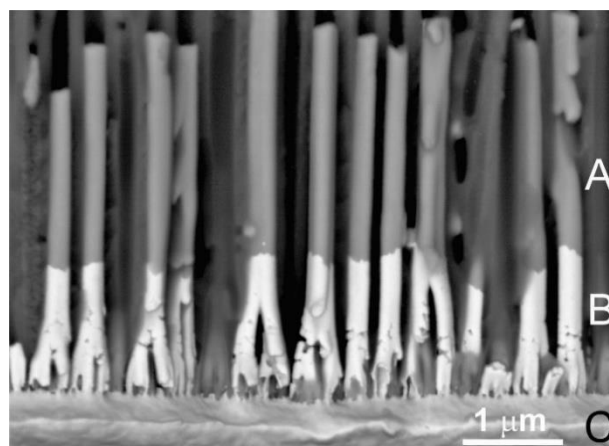


Figure 4.8: SEM-BSE image of Ni nanowires (A) in the AAO template with the conductive Au sputtered layer (C) and Au nanowires (B); deposited at -1.0 V for 900s.

In order to use Ni nanowires as an electrode for electro-catalytic oxidation of formaldehyde, the removal of the AAO template was required for the Ni nanowires ($2\text{--}3 \mu\text{m}$). This step was

introduced in order to produce a space in between pores to provide a maximum exposed area of Ni nanowires. Figure 4.9 shows free-standing Ni nanowires after the AAO template was etched away in a strongly alkaline solution of 10 mol L⁻¹ NaOH for 2 hours. From side view SEM-SE image (Figure 4.9, A) it is seen that the AAO template is completely dissolved/removed after 2h. From the top-view SEM-SE image (Figure 4.9, B), it is seen that most of the nanowires are separated; however, some of them are fused. We assumed that this might happen during the SEM sample preparation (the sample was dried) or inside SEM in a vacuum.

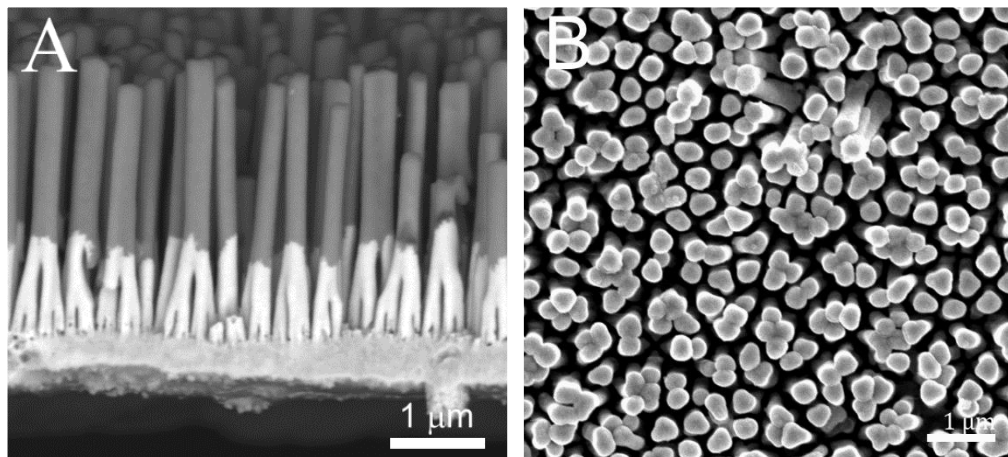


Figure 4.9: A) A top view and B) a side view SEM-SE images of free-standing Ni nanowires after AAO template was removed in 10 mol L⁻¹ solution of NaOH.

4.1.2.3 Determination of the geometric surface areas of Ni electrodes

Firstly, the surface of the Ni electrodes was investigated using FEG-SEM, based on which the geometrical models were proposed.

The exposed geometrical surface area of fine-grained Ni film and coarse-grained Ni film is 0.2 cm². To determine the actual active surface area of these two electrodes, the roughness should be known. However, it is not possible to determine the roughness precisely due to the inhomogeneous coverage of Au substrate with the Ni in the case of fine-grained Ni film, and due to the variable size of Ni crystallites throughout the area in the case of coarse-grained Ni film. Therefore, the electrochemical method (Chapter 4.2) was used to test the divergence of the geometrical model.

The cross-section (Figure 4.8 and Figure 4.9, A) and top view (Figure 4.9, B) FEG-SEM images were utilised for the determination of geometric surface area (A_{geom}) of Ni nanowires via the following calculations. The actual pore diameter (d_p) was found to be 200 ± 50 nm. A pore density is (n_p) of 1×10^9 cm⁻² and it is in agreement with other reports [113]. The diameter of the circular opening, where Ni nanowires were exposed to the electrolyte is $r = 0.5$ cm and the calculated corresponding area ($A_1 = \pi r^2$) is 0.196 cm². The total number of pores (N_p) in this area was calculated from the equation: $N_p = n_p \times A_1$ and it is 196×10^6 . For the determination of A_{geom} , the cross-sectional area of one pore (S_1) was calculated by the equation: $S_1 = \pi r_p^2 + 2\pi r_p L$ (where r_p is the radius of the pores equal to ~ 0.1 μm and L is the length of the nanowires). By multiplying N_p and S_1 the A_{geom} was calculated as 2.9 cm². Secondly, the electrochemical method (described in the next section) was used to confirm or reject the correctness of the above-described Ni nanowires geometrical model.

4.2 Determination of the Electrochemically Active Surface Area of As-Prepared Ni Electrodes

To be able to evaluate and compare sensor characteristics (e.g. sensitivities) of as-prepared Ni electrodes or the electro-catalysts activities (output current densities) of as-prepared Ni electrodes in terms of HCHO electro-oxidation (explained in the following chapters), the electrochemically active surface areas (A_{eCSA}) were determined.

Oxalate method [75, 85] has been selected for the determination of A_{eCSA} of as-prepared Ni electrodes (fine- and coarse-grained Ni films and Ni nanowires). Having established oxalate as a candidate for the adsorption onto Ni electrode surfaces, the electrochemical formation of surface oxalate-stabilised-Ni(OH)₂/NiOOH was investigated via CV. The CV studies were done on a standard Ni electrode (Ni foil) with a known surface area of 0.785 cm², and under well-controlled experimental conditions that include: a) the effect of the KOH concentration on the oxalate formation, c) the effect of oxalic acid in KOH solution, c) the effect of scan rates and d) the effect of the scan number. The experimental conditions proven to be the most relevant in the case of Ni foil were later introduced to the as-deposited Ni electrodes. The A_{eCSA} was evaluated with respect to calculations based on the charge of Ni(OH)₂ formation. It is necessary to emphasise that the several-atomic-layers thick passive film of native Ni oxide was removed from the surface of Ni electrodes prior to the CV measurements. For this purpose, a strong mixture of acids (conc. HNO₃, conc. H₂SO₄, conc. H₃PO₄ and CH₃COOH) was used.

4.2.1 Effect of the KOH concentration on the oxalate formation

In order to form the oxalate-stabilised- Ni(OH)₂/NiOOH surface species, it is necessary to find the right ratio of the oxalic acid and KOH concentrations. For this purpose, the effect of the KOH concentrations in the 0.08 mol L⁻¹ oxalic acid solution was studied via CV.

Figure 4.10 presents CV curves of Ni foil recorded in 0.08 mol L⁻¹ oxalic acid solution with 0 (inset graph), 0.25 (burgundy curve) and 0.5 (grey curve) mol L⁻¹ KOH at a scan rate of 200 mV s⁻¹. The CV scans were recorded in the potential window from the -1.0 V to the +0.7 V. From curves it is evident that the addition of KOH into oxalic acid solution changes the anodic and cathodic peak potentials of oxalate-stabilised-Ni species and the onset potential for hydrogen evolution.

Firstly, to clarify the effect of the KOH addition, the first CV was observed only in 0.08 mol L⁻¹ oxalic acid solution (pH = 0.4) without the addition of KOH (Figure 4.10, inset graph). In the forward scan, the anodic peak a_{H} at $E = +0.05$ V is attributed to the oxidation of the adsorbed hydrogen that is embedded in a Ni layer in a potential window from -1.0 V to approx. -0.6V. This oxidation peak is followed by a plateau (a_{Ni}) that indicates the oxidation of Ni to α -Ni(OH)₂. In the reverse scan, one cathodic peak (c_{Ni}) was observed at $E = -0.3$ V which indicates the reduction of α -Ni(OH)₂ to Ni and is followed by the hydrogen evolution region (c_{H}) at approximately $E = -0.6$ V. Once the 0.25 mol L⁻¹ KOH (Figure 4.10, burgundy) or 0.5 mol L⁻¹ KOH (Figure 4.10, grey) is added into 0.08 mol L⁻¹ oxalic acid solution the pH of electrolyte increases due to the formation of oxalate and further adsorption of oxalate to the surface hydroxides, as shown in Figure 1.25. Consequently, the CV profiles of Ni foil (burgundy and grey) are completely different from the one observed only in oxalic acid: the additional anodic and cathodic current peaks appeared, and the onset potential for hydrogen evolution is shifted to a more negative potential and cannot be observed in this potential range. In the forward scan, the first increase in the anodic current was observed at a_1 , $E = -0.6$ (burgundy) or $E = -0.65$ (grey). This peak (a_1) corresponds to the oxidation of Ni according to the reaction $\text{Ni}^0 + 2\text{OH}^- \rightarrow \text{Ni(OH)}_2 + 2\text{e}^-$. The next increase in the current density was observed from -0.4 V to 0.2 V (grey and burgundy) where α -Ni(OH)₂ is transformed to β -Ni(OH)₂. In the positive potential region, anodic current peaks of a_3 were observed at $E = 0.5$ V (burgundy curve) or $E = 0.45$ V (grey curve); a_3 represents the oxidation of β -Ni(OH)₂ to β -NiOOH. Next, the cathodic current peaks of c_1 for reduction of β -NiOOH to β -Ni(OH)₂ were observed at $E = 0.35$ V. Also, at approx. $E > +0.55$ V (a_4) an increase in the anodic current densities was observed due to the oxygen evolution reaction ($4\text{OH}^- \rightarrow \text{O}_2 + \text{H}_2\text{O} + 4\text{e}^-$).

From these observations it was concluded that the concentration of 0.25 mol L⁻¹ KOH is high enough to form the oxalate stabilized Ni surface species, however, 0.5 mol L⁻¹ KOH is more suitable for the following two reasons: the amount of oxalate-stabilized-

$\text{Ni}(\text{OH})_2/\text{NiOOH}$ species is significantly higher (higher current density – grey curve), and oxidation and reduction current peaks c_1 , a_3 and a_4 are well-separated.

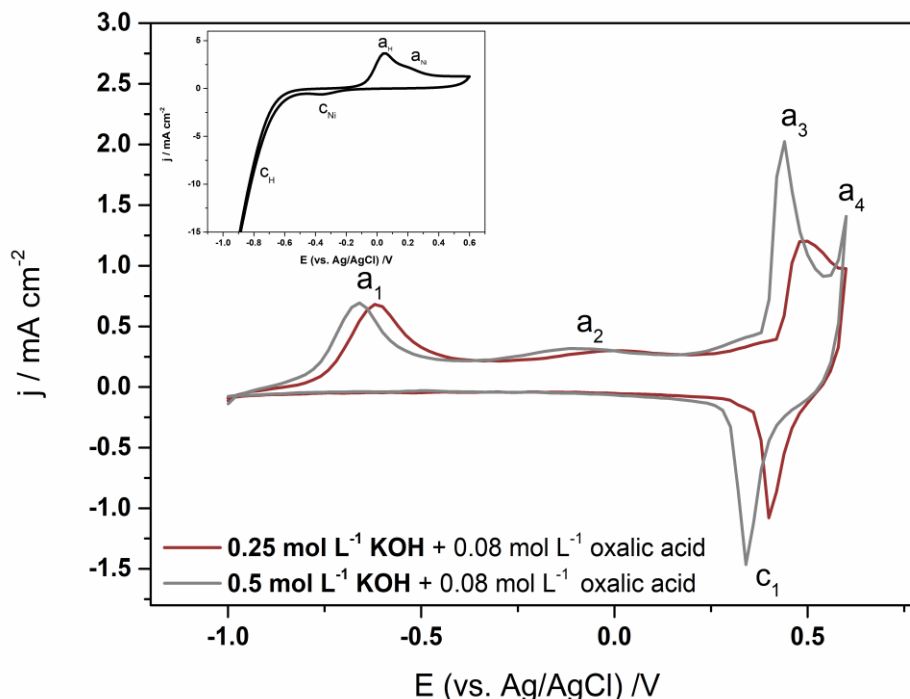


Figure 4.10: CV profiles for Ni foil in 0.25 mol L⁻¹ (burgundy) and 0.5 mol L⁻¹ (grey) in 0.08 mol L⁻¹ oxalic acid solution; inset demonstrates a CV profile of Ni foil in 0.08 mol L⁻¹ oxalic acid solution. Each curve was observed in the potential window from -1.0 V to +0.7 V at a scan rate of 200 mV s⁻¹.

4.2.2 Effect of oxalic acid in KOH solution

In order to answer the question “*why it is necessary to stabilise the surface $\text{Ni}(\text{OH})_2/\text{NiOOH}$ with an oxalate?*”, the cyclic voltammetry was performed in 0.5 mol L⁻¹ KOH, i.e. oxalate-free electrolyte, and 0.5 mol L⁻¹ KOH with 0.08 mol L⁻¹ oxalic acid, i.e. oxalate-containing electrolyte. Figure 4.11 shows the CV profiles of Ni foil observed in “oxalate-free” (pink curve) and “oxalate-containing” (grey curve) electrolytes. The CVs were recorded in the potential range from the -1.0 V to the +0.7 V and back to the -1.0 V at a scan rate 200 mV s⁻¹. From CV curves it can be seen that the addition of the oxalic acid to the KOH solution does not cause any changes to the current densities at the potential $E = -0.7$ V, where $\alpha\text{-Ni}(\text{OH})_2$ is formed (a_1 , $j \approx 0.7$ mA cm⁻²) and $E = -0.1$ V, where $\alpha\text{-Ni}(\text{OH})_2$ is transformed to $\beta\text{-Ni}(\text{OH})_2$ (a_2 , $j \approx 0.3$ mA cm⁻²). From these observations, we concluded that oxalate does not affect the formation of $\text{Ni}(\text{OH})_2/\text{NiOOH}$ surface species in this potential range; its role is probably a subtle one [75]. Above +0.2 V, the effect of solution oxalate is significant. In the positive potential region, two oxidation peaks (a_3 – formation of NiOOH and a_4 – oxygen evolution) and one reduction peak (c_1 – formation of $\text{Ni}(\text{OH})_2$) were observed, see Chapter 4.2.1. Continuing potential cycling in the anodic region to the direction of the negative potentials (from +0.2 V to -1.0 V) did not show any differences in the observed current density.

From these observations, it was concluded that the presence of oxalic acid in KOH (grey) demonstrates the pronounced differences in the current densities of a_3 and c_1 compared to the CVs recorded only in the KOH (pink). As it is seen from Figure 4.11, after the addition of oxalic acid to the KOH solution the oxidation peaks a_3 and c_1 reached higher current densities (for ~ 0.7 mA) due to the stabilisation of the $\text{Ni}(\text{OH})_2$ and NiOOH species on the electrode surface. Results demonstrate that the amount of formed $\beta\text{-Ni}(\text{OH})_2$ and $\beta\text{-NiOOH}$

species in the presence of oxalate is significantly higher (30–40%) in comparison to the one observed in the “oxalate-free” electrolyte. Furthermore, the position of the $\text{Ni}(\text{OH})_2/\text{NiOOH}$ anodic and cathodic peaks is not shifted after oxalate formation meaning that oxalate is not involved in the electrochemical reaction and is just adsorbed on the electrode surface.

According to these results and findings, the answer for the above question is that the addition of oxalate has a significant effect on the determination of the right amount of active surface Ni species. We concluded that the amount of active Ni species is more accurately and precisely determined in oxalate-containing than in oxalate-free electrolyte. These results are in accordance with the findings presented by Hall et al. [75] and Drunen et al. [85].

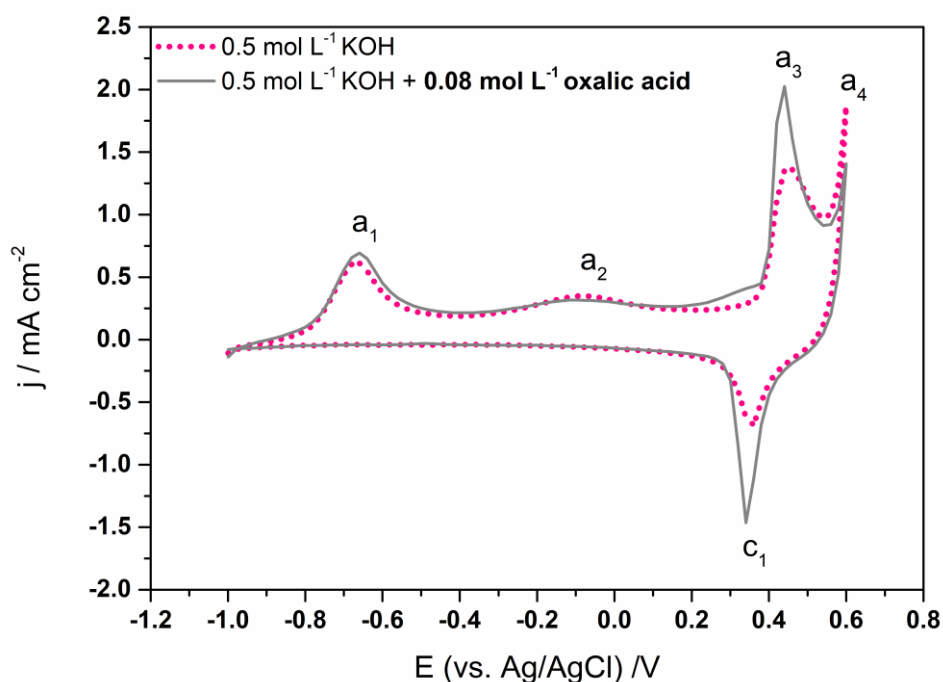


Figure 4.11: CV profiles for Ni foil in “oxalate-free” ($0.5 \text{ mol L}^{-1} \text{ KOH}$) electrolyte (pink curve) and “oxalate-containing” ($0.5 \text{ mol L}^{-1} \text{ KOH} + 0.08 \text{ mol L}^{-1} \text{ oxalic acid}$) electrolyte (grey curve) observed in the potential window from -1.0 V to $+0.7 \text{ V}$ at a scan rate of 200 mV s^{-1} .

4.2.3 Effect of number of scans

In the next set of experiments, we studied how potential cycling in oxalate-containing electrolyte influences the shape and the values of current densities for the oxidation and reduction peaks. Figure 4.12 shows the CV curves of Ni foil observed in $0.5 \text{ mol L}^{-1} \text{ KOH}$ and $0.08 \text{ mol L}^{-1} \text{ oxalic acid}$ electrolyte at a scan rate 200 mV s^{-1} . The CV scans were initiated directly from $E = -1.0 \text{ V}$ to $+0.7 \text{ V}$ in the anodic region, and then the scans were reversed back to -1.0 V in the cathodic region. The 1st and 20th cycle are included to demonstrate the evolution of the CV profiles with increasing the cycle number. In the negative potential region, two oxidation peaks were observed in the 1st cycle (grey curve): a_1 at $E = -0.6$ that corresponds to the oxidation of Ni to $\alpha\text{-Ni}(\text{OH})_2$ and a_2 at $E = -0.1$ where $\alpha\text{-Ni}(\text{OH})_2$ is transformed into $\beta\text{-Ni}(\text{OH})_2$. Once the β -phase is formed, it cannot be electrochemically reduced back to metallic Ni, because of its high stability. For this reason, the oxidation peaks (a_1 and a_2) are not discernible in the 20th cycle (orange curve). Following a potential excursion to more positive potentials, the next anodic current increase (a_3) was observed at $+0.5 \text{ V}$ and cathodic current increase (c_1) at 0.35 V and corresponds to the reversible

reaction of $\text{Ni}(\text{OH})_2 + \text{OH}^- \leftrightarrow \text{NiOOH} + \text{e}^-$. If we compare the 1st and 20th cycle, the increase in the current density ($> 1 \text{ mA cm}^{-2}$) is observed with increasing numbers of cycles. These results imply progressive enrichment of active $\text{Ni}(\text{OH})_2/\text{NiOOH}$ species at the surface due to the entry of OH^- into the Ni foil, indicating the thickening of $\text{Ni}(\text{OH})_2/\text{NiOOH}$ layer [75].

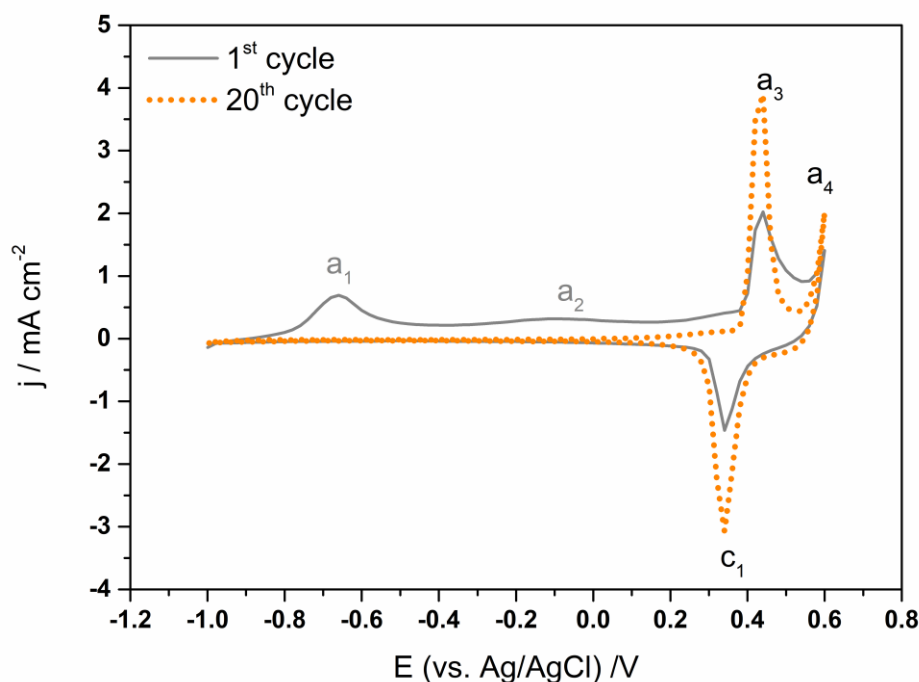


Figure 4.12: CV profiles for Ni foil in $0.5 \text{ mol L}^{-1} \text{ KOH} + 0.08 \text{ mol L}^{-1} \text{ oxalic acid}$ electrolyte observed in the potential window from -1.0 V to $+0.7 \text{ V}$ in the 1st cycle (grey) and 20th cycle (orange) at a scan rate of 200 mV s^{-1} .

4.2.4 Effect of scan rate

Next, the effect of the potential scan rate on the position of the anodic and cathodic peaks was explored in the potential window from the -1.0 V to the 0.7 V . Figure 4.13 shows the CV profiles of Ni foil tested in $0.08 \text{ mol L}^{-1} \text{ oxalic acid}$ and $0.5 \text{ mol L}^{-1} \text{ KOH}$ electrolyte in the 1st cycle at two different scan rates: 50 (violet) and 200 (grey) mV s^{-1} . With the increase in the scan rate, the anodic peak potential for a_1 , a_2 , and a_3 oxidation peaks shifts to more positive potentials ($\sim 30 \text{ mV}$). Furthermore, the oxidation peak a_3 overlaps with the oxygen evolution reaction (oxidation peak a_4) at a higher scan rate, while the cathodic peak (c_1) position does not shift with increasing scan rate, and is well-separated from other electrochemical processes. Based on these observations, we concluded that reduction peak c_1 should be selected for the determination of the A_{ecsa} by calculating the absolute charge (explained below).

It was demonstrated by Hall et al. [75] and Drunen et al. [85] that the composition of surface hydroxides is the reason for the peak shift (a_1 , a_2 and a_3) in the anodic region when increasing the scan rate. They explained that at higher scan rates ($>150 \text{ mV s}^{-1}$), surface hydroxides are composed of ordered $\beta\text{-Ni}(\text{OH})_2$ and a monolayer of stabilised- $\text{Ni}(\text{OH})_2/\text{NiOOH}$ is formed in the 1st cycle. On the other hand, at slower scan rates (50 mV s^{-1}), OH^- ions and molecular O_2 (formed at a_4) penetrate into the inner Ni layer, leading to the formation of thicker hydroxide layer (in the 1st cycle) composed of $\alpha/\beta\text{-Ni}(\text{OH})_2$ or oxalate-intercalated $\alpha\text{-Ni}(\text{OH})_2$ or NiO_x . Therefore, the electric charge (Q) measurements at higher scan rates ($>150 \text{ mV s}^{-1}$) can be reliably attributed to the formation of surface ordered $\beta\text{-}$

Ni(OH)_2 . On the other hand, the electric charge (Q) measurements at lower scan rates ($\sim 50 \text{ mV s}^{-1}$) refer to the formation of α/β - Ni(OH)_2 or NiO_x , leading to incorrect Q measurements. The observations presented by Hall et al. [75] and our results brought us to the conclusion that a scan rate of 200 mV s^{-1} should be used to measure the A_{ecsa} .

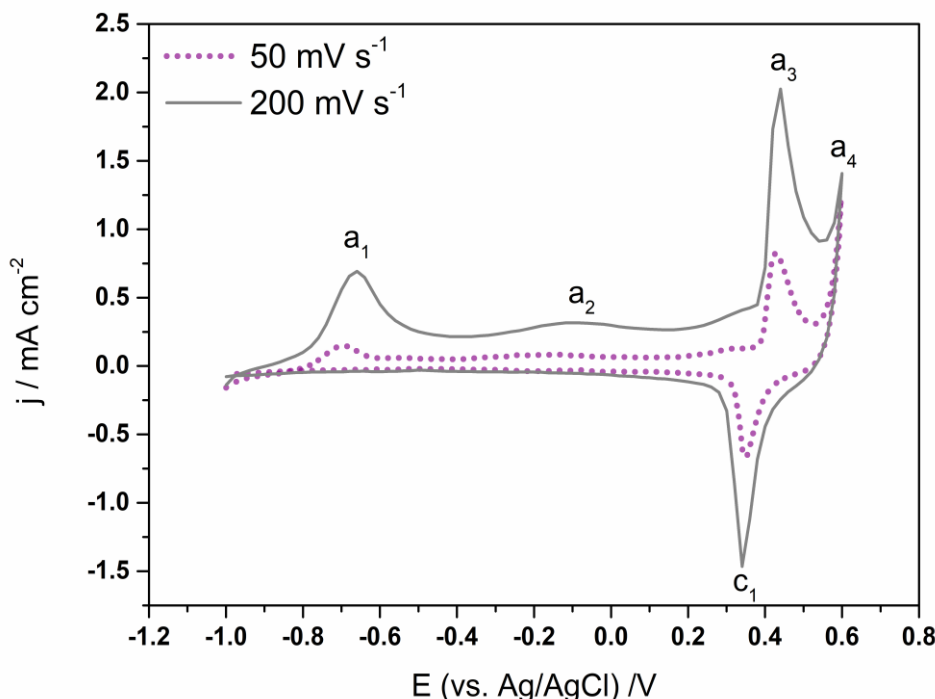


Figure 4.13: CV profiles for Ni foil in $0.5 \text{ mol L}^{-1} \text{ KOH} + 0.08 \text{ mol L}^{-1} \text{ oxalic acid}$ solution observed in the potential range from -1.0 V to $+0.7 \text{ V}$ at a scan rate of 50 (violet) and 200 mV s^{-1} .

The oxalate method studies were applied to different Ni-based electrodes that were as-electrodeposited: fine-grained Ni film, coarse-grained Ni film and Ni nanowires. From above-explained studies (Chapter 4.2.1 – 4.2.5.) the following experimental conditions were chosen: $c(\text{KOH}) = 0.5 \text{ mol L}^{-1}$, $c(\text{oxalic acid}) = 0.08 \text{ mol L}^{-1}$, scan rate of 200 mV s^{-1} and the number of cycles of 20.

4.2.5 Electrochemical study of as-prepared Ni-based electrodes in an oxalate-containing electrolyte

In order to determine the electrochemically active surface area of as-prepared Ni electrodes with high accuracy, the CV studies were performed on a fine-grained Ni film, a coarse-grained Ni film and Ni nanowires in $0.08 \text{ mol L}^{-1} \text{ oxalic acid}$ and $0.5 \text{ mol L}^{-1} \text{ KOH}$ electrolyte. Figure 4.14 presents CV profiles of A) Ni foil (grey), B) fine-grained Ni film (green), C) coarse-grained Ni film (blue) and D) Ni NWs (red); each observed in a potential range from -1.0 V to $+0.7 \text{ V}$ in anodic region and from $+0.7 \text{ V}$ to -1.0 V in cathodic region at a scan rate 200 mV s^{-1} . Cycles 1 (inset graphs), 2, 10 and 20 are shown to demonstrate the evolution of the CV profile with increasing cycle number. In order to produce the comparable results between Ni foil (i.e. standard electrode), the surfaces of as-prepared Ni electrodes were cleaned in a strong mixture of acids to remove all the native surface oxides. The features present in the CV profiles of b) fine-grained Ni film, c) coarse-grained Ni film, and d) Ni nanowires are similar to those displayed for the a) Ni foil:

- In the negative potential region two oxidation peaks: a_1 for the formation of α - Ni(OH)_2 and a_2 for the dehydration of α - Ni(OH)_2 to β - Ni(OH)_2 in the 1st cycle,

- In the 2nd – 20th cycles a_1 and a_2 disappear due to the formation of highly stable β -Ni(OH)₂ in the 1st cycle,
- In the positive potential region oxidation and reduction peak: a_3 and c_1 from the formation and reduction of β -NiOOH,
- The current densities of a_3 and c_1 increase from the 2nd to the 20th cycle due to the thickening of the Ni(OH)₂/NiOOH layer on the surface,
- In the positive potential region oxidation peak for the formation of O₂ from H₂O at $E > 0.5$ V.

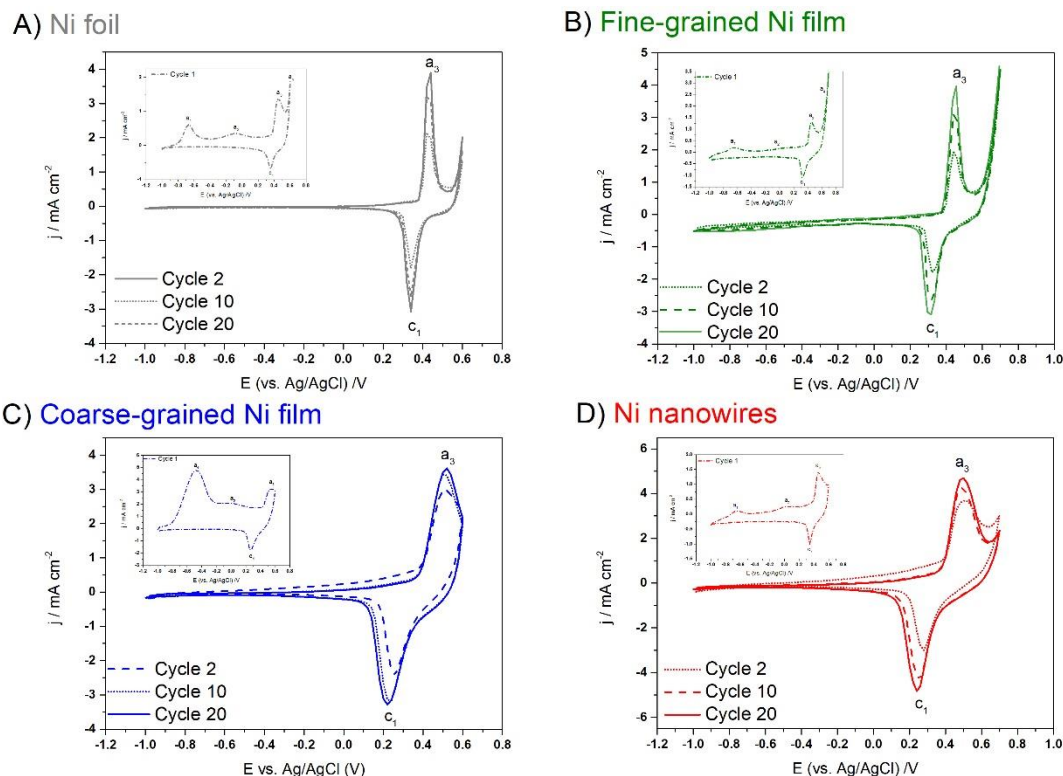


Figure 4.14: The CV profiles of A) Ni film (grey), B) fine-grained Ni film (green), C) coarse-grained Ni film (blue) and D) Ni nanowires (red) in 0.5 mol L⁻¹ KOH + 0.08 mol L⁻¹ oxalic acid solution; each observed in the potential window from -1.0 V to +0.7 V from the 1st cycle (insets) to the 20th cycle at a scan rate of 200 mV s⁻¹.

From the comparison of the CV curves, it was observed that the current densities for anodic peak current a_3 and cathodic peak current c_1 ($j(a_3 \text{ and } c_1)$) vary between the individual electrodes. The lowest peak current densities are achieved at the Ni foil electrode; then the current densities increase in the following sequence: $j(a_3 \text{ and } c_1)$ of fine-grained Ni film < $j(a_3 \text{ and } c_1)$ of coarse-grained Ni film < $j(a_3 \text{ and } c_1)$ of Ni nanowires. According to these observations, it was assumed that the Ni foil contains less active surface Ni species, while the amount of these active Ni sites is much higher in the case of Ni nanowires electrode. However, to determine the area of active surface Ni species (i.e. electrochemically active surface area), the electric charge (Q) should be calculated, since it can be directly associated with the thickness of the active surface sites. For the calculations of Q, the reduction peak (c_1) was chosen because it does not overlap with any other electrochemical processes. This means that in the cathodic region (from +0.7 V to -1.0 V) no other electrochemical reaction occurs ($i \approx 0$ mA), except the reduction of oxalate-stabilized-NiOOH to oxalate-stabilized-Ni(OH)₂ (c_1). On the other hand, the oxidation peak (a_3) in the anodic scan from -1.0 V to +0.7 V (Figure 4.14) overlaps with the oxygen-evolution reaction (a_4) that starts at the potential $E \geq 0.5$ V.

4.2.6 Determination of the A_{ecsa} of Ni-based electrodes by measuring the absolute charges

Figure 4.15 presents the measured absolute charge (Q) values as a function of the scan number for the Ni foil (black curve), fine-grained Ni film (green curve), coarse-grained Ni film (blue curve) and Ni nanowires (red curve) electrodes. The Q values were calculated for the NiOOH reduction peak (c_1) (Figure 4.14) according to equation (4.1):

$$Q = \int i d\tau = \frac{1}{v} \int i dE \quad (4.1)$$

Where Q is the charge, v is the scan rate, i is the peak current, and dE is the potential difference.

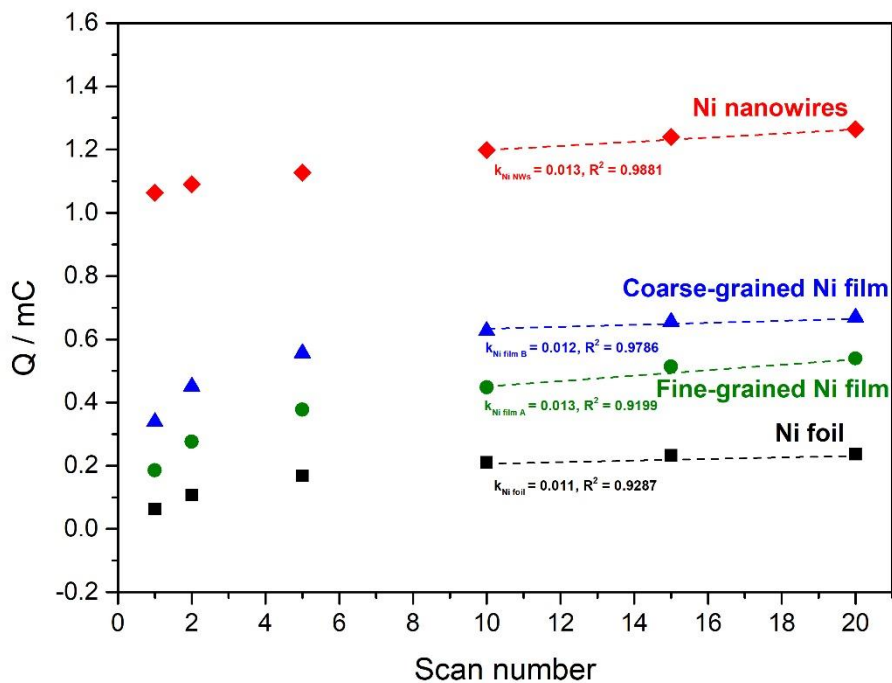


Figure 4.15: Charge values (Q) for the Ni foil, fine-grained Ni film, coarse-grained Ni film and Ni nanowires-based electrodes as a function of CV scan number.

As seen from Figure 4.15, in the first five CV scans (scan number) a non-linear response of the Q values is observed for fine-grained Ni film, coarse-grained Ni film, Ni nanowires and Ni foil electrodes, after which Q increases approximately linearly with the increasing cycle number (the slopes of $k_{\text{fine-grained Ni film}} \approx k_{\text{coarse-grained Ni film}} \approx k_{\text{Ni NWs}} \approx k_{\text{Ni foil}}$ from the 10th to the 20th cycle). These results are a consequence of the non-linear growth of the stabilized-Ni(OH)₂/NiOOH layer on the surface of Ni electrodes in the first ten scans [85]. Using the calculated charge values and the theoretical value of the Ni foil's surface area, the A_{ecsa} 's of the as-prepared "oxide-free" Ni electrodes (fine-grained and coarse-grained Ni films, and Ni nanowires) were calculated for cycles 10, 15 and 20 according to Equation 4.2:

$$A_{\text{ecsa}}(\text{smooth Ni film}) = A_{\text{ecsa}}(\text{porous Ni film}) = A_{\text{ecsa}}(\text{Ni nanowires}) = \frac{A_{\text{Ni foil}} \times Q_x}{Q_{\text{Ni foil}}}, \quad (4.2)$$

Where $A_{Ni\ foil}$ is a known geometrically determined area of Ni foil (0.785 cm²) and Q_x is the charge value for fine-grained Ni film, coarse-grained Ni film and Ni nanowires, and $Q_{Ni\ foil}$ is a charge value for Ni foil. The average electrochemically active surface areas of Ni films and nanowires were calculated by Equation 4.3:

$$\overline{A_{ecsa}} = \sum_{n=10,15,20} \frac{A_{ecsa}}{3} \quad (4.3)$$

and the resulting values are:

- A_{ecsa} (fine-grained Ni film) = 1.7175 ± 0.0503 cm²,
- A_{ecsa} (coarse-grained Ni film) = 2.1862 ± 0.0154 cm², and
- A_{ecsa} (Ni nanowires) = 4.2066 ± 0.0472 cm².

The calculated values for Ni electrodes are as expected; fine-grained Ni film exhibits the smallest electrochemically active surface area due to the smoothest and less porous surface, as well as incomplete coverage of the Au substrate after electrochemical deposition of Ni. Once the roughness increases (coarse-grained Ni film), the A_{ecsa} increases. The highest A_{ecsa} exhibited Ni nanowires, due to the highest surface to volume ratio and the highest number of the active Ni sites on the surface. Based on these results, all obtained output currents in further electrochemical measurements presented in this thesis were normalised, giving current densities 4.4:

$$\frac{i\ (\text{output current})}{A_{ecsa}} = j\ (\text{current density}) \quad (4.4)$$

In conclusion, the results presented in Chapter 4.2. support the findings presented by Hall et al. [75] and Drunen et al. [85] and extend the understanding of this method in different experimental conditions. In comparison to their investigations that were mostly done at $T \leq 0$ °C, we proved that similar behaviour and repeatability could also be achieved for experiments performed at room temperature.

In addition, the determined A_{ecsa} of as-prepared Ni electrodes was also compared with the geometrically determined surface areas (A_{geom} , see Chapter 4.1.2.3) of these electrodes, and it was ~40% for fine-grained, ~50% for coarse-grained Ni film and ~30 % for Ni nanowires in favour of the electrochemically active surface area. This comparison illustrates the importance of using the method to accurately determine the “amount” of active Ni surface species, especially if we wanted to expand the application of the electrochemically active surface area determination beyond Ni foil (standard electrode) to interesting and relevant electrochemical catalytic/sensor materials, such as fine-/ coarse-grained Ni films or Ni nanowires.

4.3 Electrochemical Oxidation of Formaldehyde

Electrochemically fabricated Ni electrodes (fine-grained Ni film, coarse-grained Ni film and free-standing Ni nanowires) were further tested as receptor elements for HCHO electrochemical detection by monitoring their oxidation ability in alkaline media. According to the literature [33-37], the electrochemical oxidation of HCHO in alkaline media occurs through a mediated electron transfer mechanism catalysed by Ni(OH)₂/NiOOH surface species.

In this chapter, the study focused on an investigation of Ni electrodes, their transformation from Ni to NiO and Ni(OH)₂/NiOOH or after potential cycling in KOH (i.e. KOH-modification). Furthermore, the Ni electrodes were analysed and subjected to electrochemical testing in alkaline media to clarify the sensory properties of Ni-based receptor elements, as well as the electro-catalysis of the HCHO oxidation. It is necessary to emphasise that the output currents obtained in this chapter were normalised by A_{ecsa} in order to be able to make a direct comparison between fine-grained and coarse-grained Ni film, and Ni nanowires.

4.3.1 Electrochemical oxidation of HCHO on Ni electrodes

The electrochemical oxidation of HCHO in alkaline solution was firstly studied on the as-deposited fine-grained and coarse-grained Ni films, and then on the free-standing Ni nanowires. The XRD or FT-IR investigations have been carried out to identify the composition of the Ni surface species that contributed to HCHO electro-oxidation.

4.3.1.1 XRD of as-deposited fine-grained and coarse-grained Ni films

X-ray analysis was performed to establish the influence of the electrodeposition conditions on the crystal structures of fine-grained and coarse-grained Ni films, and to establish the influence of drying the samples (in the air) after electrodeposition. Figure 4.16 represents the XRD patterns of A) $\text{SiO}_2/\text{Cr}/\text{Au}$ substrate and B) as-deposited fine-grained and C) as-deposited coarse-grained Ni films. The composition and crystal structure of substrate and Ni films were observed in the 2-theta range from 10° – 90° .

The XRD diffraction pattern of $\text{SiO}_2/\text{Cr}/\text{Au}$ substrate is presented in Figure 4.16, A as a background. Indexing of this XRD pattern displays a presence of SiO_2 at $\sim 20^\circ$ – 25° (ICDD 00-033-1161) [119, 120] and indicates the presence of Cr, with the two characteristic peaks at 36.5° and 81.7° that can be ascribed to the (1 1 1) and (2 1 1) planes of cubic Cr (ICDD 00-006-0694) [121]. Also, in the XRD pattern, the peaks of (1 1 1), (3 1 1) and (2 2 2) orientation directions were observed at 38.2° , 77.5° and 81.7° and can be ascribed to the cubic Au that matched with the standard X-ray diffraction powder pattern (ICDD 01-089-3697) [122]. From XRD results of the substrate, we can confirm the presence of Au with a preferential (1 1 1) orientation.

The XRD patterns of Ni films electrodeposited at pH = 2.5 (fine-grained) and pH = 5.5 (coarse-grained) are shown in Figure 4.16. From XRD patterns of fine-grained (B) and coarse-grained (C) Ni films, the diffraction signals of substrate/background were identified for SiO_2 (ICDD 00-033-1161), Cr (ICDD 00-006-0694) and Au (ICDD 01-089-3697) at the same 2-theta values as it was described above. Also, the peaks of (1 1 1) and (2 0 0) orientation directions were observed at 2-theta of 44.5° and 76.5° and can be assigned to the fcc structure of Ni (ICDD 00-001-1258) [112]. These results suggest that Ni planes constitute the preferential crystallographic growth direction. The preferential orientation is related to the growth conditions in electrodeposition processes, i.e. selection of the substrate (retained the preferential orientation of the Au substrate). Furthermore, the intensity of the (1 1 1) is different for Ni films deposited from different pH (it is higher with the increase of pH values) most probably due to different film thicknesses.

Thus, when using the XRD, we were not able to identify the peak at 2-theta of 19° (Figure 4.16, B and C, insets). The peak can be attributed to the rhombohedral NiO_2 (ICDD 04-012-0153) or hexagonal $\beta\text{-Ni}(\text{OH})_2$ (ICDD 04-015-5276). However, the rest of the characteristic peaks for these two components are overlapping with the Au or Ni and could not be identified. Significant differences in the crystal structure of fine- and coarse-grained films were observed at 2-theta of 11.7° , 12.5° , 34.3° and 42.6° . These peaks indicate the presence of hexagonal $\alpha\text{-Ni}(\text{OH})_2$ (ICDD 00-038-0715) on the surface of fine-grained Ni film.

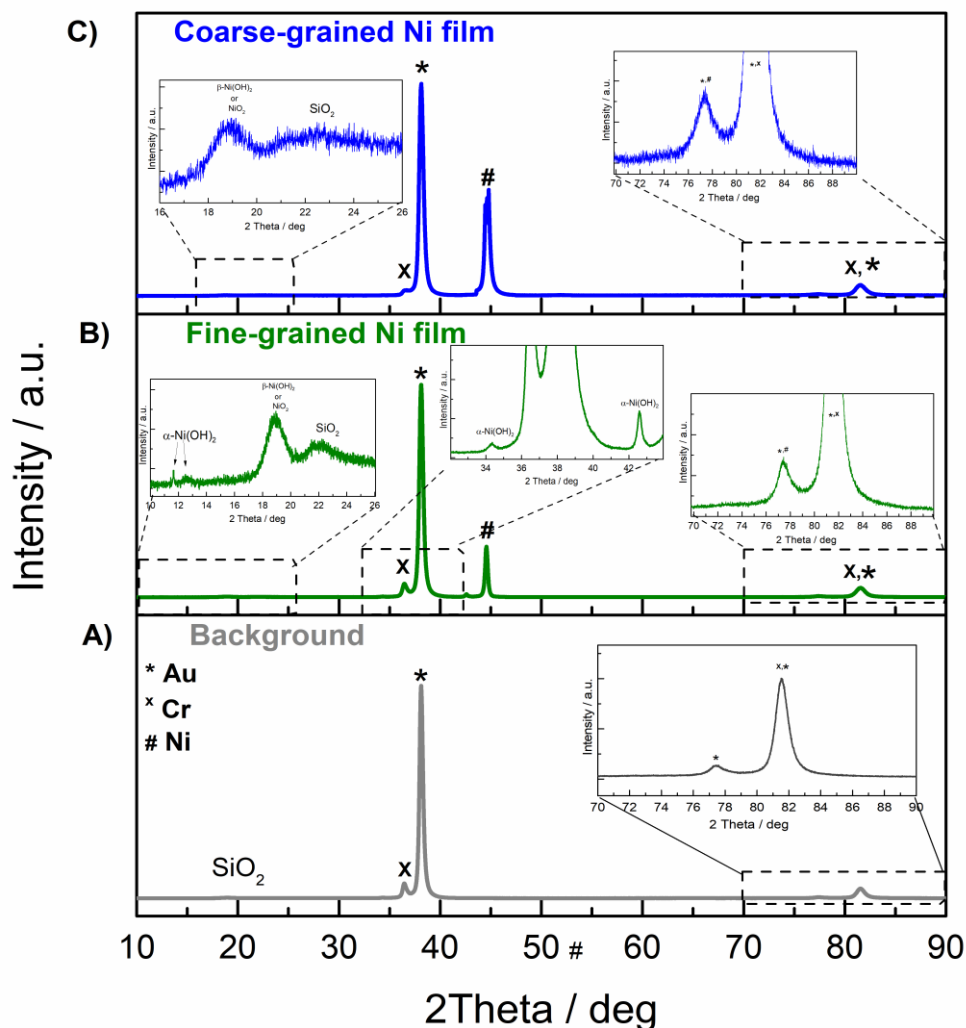


Figure 4.16: XRD spectra of the A) $\text{SiO}_2/\text{Cr}/\text{Au}$ substrate, i.e. background (grey), B) as-deposited fine-grained Ni film (green) and C) as-deposited coarse-grained Ni film, collected at 2 theta of 10–90°.

Since we were not able to confirm the presence of rhombohedral NiO_2 or hexagonal $\beta\text{-Ni}(\text{OH})_2$ on the coarse-grained film using XRD, the FT-IR spectra were recorded. FT-IR technique enables the identification of molecular components and structures, including -O-H , Ni-O-H and Ni-O stretching/bending vibrations by measuring the absorption of infrared radiation. The FT-IR was also performed on the fine-grained Ni film to confirm the presence of -O-H , Ni-O-H and Ni-O stretching/bending vibrations.

Figure 4.17 shows the FT-IR spectra of fine-grained (A) and coarse-grained (B) Ni films that were recorded in the wavelength range of 400–4000 cm^{-1} in order to examine the presence of NiO_2 or $\text{Ni}(\text{OH})_2$. The insets are included to clarify -O-H or Ni-O-H or Ni-O vibrations. From Figure 4.17, A it can be seen that the fine-grained film contains the -O-H stretching vibrations (inset, the broad peak around 3500 cm^{-1}) and the absorption signal for hydroxyl group (peak at around 1720 cm^{-1}). The inset that presents the wavelength region from 400–700 cm^{-1} indicates the presence of Ni-O-H vibration peak at 610 cm^{-1} , and Ni-O bond vibrations at 410 cm^{-1} and 520 cm^{-1} . From Figure 4.17, B the absorption bonds at around 410 cm^{-1} and 520 cm^{-1} (inset) are associated to Ni-O vibration bond and the absorption peak at around 1720 cm^{-1} might be attributed to the Ni-O-H vibrations.

However, the absorption peak that indicated the -O-H stretching vibration at around 3500 cm^{-1} was not observed. Due to the absence of this representative peak, we could not confirm the presence of Ni(OH)_2 on the surface of the coarse-grained film. Thus, it can be concluded that the undefined peak from XRD diffractograms (Figure 4.16, A and B) at 2-theta of 19° can be ascribed to the rhombohedral NiO_2 due to the absence of -O-H stretching vibrations at $3000\text{-}4000\text{ cm}^{-1}$ in the FT-IR spectra of coarse-grained film (Figure 4.17, B). Besides, FT-IR results confirmed the presence of Ni hydroxides on the surface of the fine-grained Ni film.

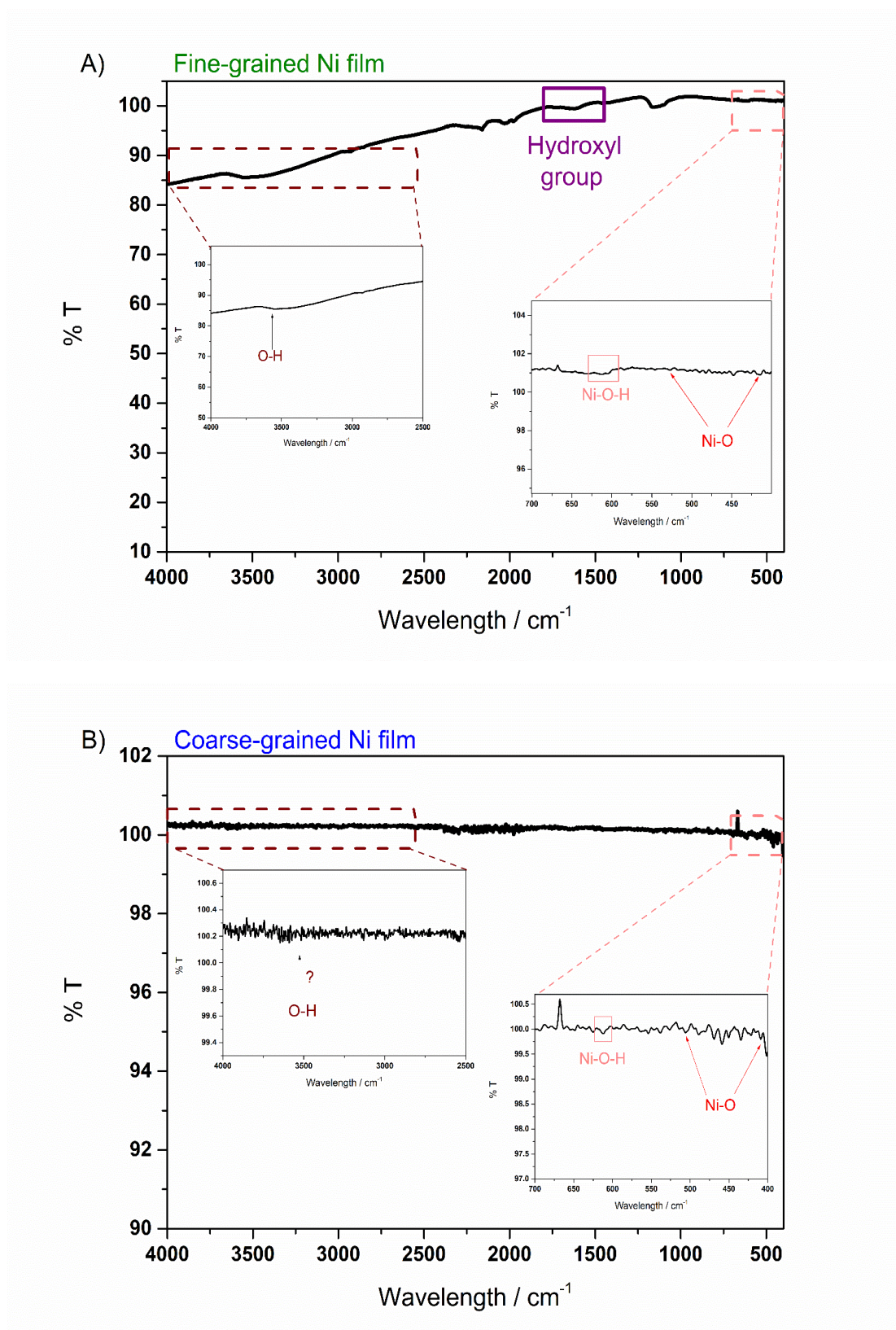


Figure 4.17: FT-IR spectra of the A) as-deposited fine-grained Ni film and the B) as-deposited coarse-grained Ni film observed in the wavelength range from 4000 to 400 cm^{-1} .

4.3.1.2 XRD of free-standing Ni nanowires

The XRD data of Ni nanowires is shown separately from Ni films due to the different sample treatment after the electrodeposition. The Ni nanowires electrode was dried in the air after the electrodeposition and then immersed into a strongly alkaline solution in order to fabricate a free-standing nanowires electrode, and then again dried in the air. Compared to the Ni films, one additional experimental step was introduced. According to the sample treatment and on the basis of the available literature [48, 52], it was assumed that the Ni nanowires surface may contain the Ni oxides (Ni_xO_y) because of drying in the air, and/or the α - or β - $\text{Ni}(\text{OH})_2$ due to the exposure to the alkaline solution.

The XRD pattern of as-deposited Ni nanowires after the AAO template was etched in 10 mol L⁻¹ NaOH is presented in Figure 4.18. The composition and crystal structure of free-standing Ni nanowires were observed in the 2-theta range from 10–90°, with the inset, observed in the 2-theta range from 5–35°. The XRD diffractogram of the wires observed in a wide range consists of isotropic Au (ICDD 01-089-3697), which was used as a conductive underlayer for electrodeposition of Ni nanowires. Five characteristic peaks at 38.0°, 44.4°, 64.5°, 77.6° and 81.7° can be assigned to the (1 1 1), (2 0 0), (2 2 1), (3 1 1) and (2 2 2) crystalline planes of the cubic Au. Also, the XRD pattern in Figure 4.18 indicates the presence of isotropic Ni (ICDD 00-001-1258), with the three characteristic peaks at 44.5°, 51.9° and 76.4° that can be ascribed to the (1 1 1), (2 0 0) and (2 2 0) planes of fcc Ni [123]. However, we were not able to detect the oxidised Ni species (NiO or $\text{Ni}(\text{OH})_2$) on the surface in the 2-theta range from 10–90° due to their poor crystallinity and/or its low thickness compared to the bulk sample. Therefore, the XRD diffractogram of the wires was observed in a narrower 2-theta region (5–35°) for better clarity, see Figure 4.18, inset. Rough indexing of the XRD pattern displays a presence of the cubic (1 1 1)-oriented NiO at 32.5° (ICDD 04-006-6545), while the presence of hexagonal α - $\text{Ni}(\text{OH})_2$ (ICDD 00-038-0715) at 10° and hexagonal β - $\text{Ni}(\text{OH})_2$ (ICDD 04-015-5276) at 19.3° were not observed. The XRD diffractogram, however, revealed the presence of NaOH (ICDD 01-080-578), originating from the precipitation from NaOH solution during the removal of the AAO template and CuO (ICDD 01-073-6237) originating from Cu/CuO tape that was used as a sample fixer for XRD measurements.

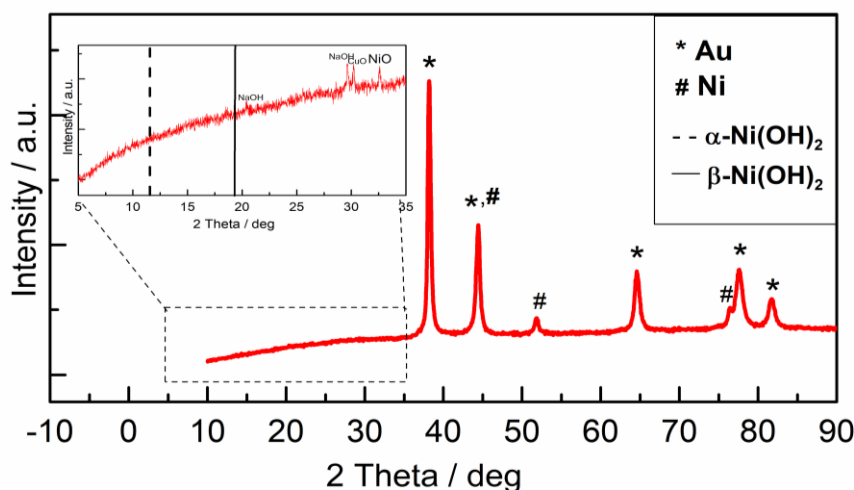


Figure 4.18: XRD spectra of the free-standing Ni nanowires electrode, collected at 2 theta of 10–90° and 5–35° (inset). The inset corresponds to the region where the characteristic peaks for Ni_xO_y and α - or β - $\text{Ni}(\text{OH})_2$ were expected.

To summarise the XRD results of as-deposited Ni-based electrodes:

- 1) In the case of **Ni films** (fine- and coarse-grained), the flat Au substrate exhibits a preferential crystallographic orientation of Au with the (1 1 1) orientation and

consequently, electrodeposited Ni films preferentially orient in the same direction, i.e. (1 1 1).

- 2) In the case of **Ni nanowires**, the substrate (deposited Au wires) and deposited Ni are both isotropic without a pronounced texture.

Based on observations 1) and 2), we concluded that the growth of Ni crystallites is related to the selection and texture of substrate [112].

- 3) The XRD analysis reveals that the surface of **fine-grained Ni film** is composed of hexagonal α -Ni(OH)₂ which chemically precipitates at the surface during electrodeposition (see Section 4.1.1.) and rhombohedral NiO₂ or hexagonal β -Ni(OH)₂. Whether it is NiO₂ or β -Ni(OH)₂ we could not confirm by XRD or FT-IR; however, there is a low probability for β -Ni(OH)₂ to be present. According to the literature and Bode's diagram [69], usually, α -Ni(OH)₂ is isolated as a primary product of electrochemical deposition, from which β -Ni(OH)₂ might be synthesised by KOH-modification process [112].
- 4) In the case of **coarse-grained Ni film**, we confirmed the presence of air/water-formed Ni oxide, since the FT-IR has proved the absence of hydroxides.
- 5) The XRD diffractogram of **Ni nanowires** revealed the presence of fcc NiO on the surface. Even though, we still have not excluded the possibility of any Ni(OH)₂ being present on the surface of nanowires. However, it could be present in such a small amount that is below the detection limit of XRD and FT-IR analysis.

4.3.1.3 Electrochemical oxidation of HCHO on as-deposited Ni electrodes

The as-deposited fine-grained Ni film consisting of α -Ni(OH)₂ and probably NiO₂ surface species, and the as-deposited coarse-grained Ni film consisting of NiO₂ surface species, and the free-standing Ni nanowires consisting of surface NiO were further tested for the HCHO detection (Figure 4.19). By using cyclic voltammetry, it was examined if they are capable of oxidising the HCHO in the potential range from +0.2 V to +1.0 V (scan rate was chosen to be 100 mV s⁻¹).

Figure 4.19, A shows a typical CV profile of as-deposited fine-grained Ni film in 1 mmol L⁻¹ HCHO + 0.1 mol L⁻¹ NaOH solution. The electrochemical behaviour of the as-deposited fine-grained Ni film revealed the presence of the well-defined redox couple for reversible Ni(OH)₂/NiOOH transformation that is essential for HCHO oxidation: an anodic peak (a_{HCHO}) at $E = 0.55$ V and a cathodic peak (c_{HCHO}) at $E = +0.35$ V. This result shows that as-deposited fine-grained Ni film has an ability to oxidize HCHO due to the presence of surface α -Ni(OH)₂ that was confirmed by XRD and FT-IR.

However, the CV response for the as-deposited coarse-grained Ni films (Figure 4.19, B) observed in 1 mmol L⁻¹ HCHO and 0.1 mol L⁻¹ NaOH solution showed a complete electrode's inactivity towards HCHO in the potential range where the oxidation from Ni(OH)₂ to NiOOH should occur. In other words, if the surface of the coarse-grained Ni film would be covered by active Ni species (i.e. Ni(OH)₂), the well-defined anodic peak (a_{HCHO}) should appear at the potential less positive than potential where oxygen evolution reaction (a_{O_2}) occurs, $E < \sim 0.8$ V. Also, Ni nanowires exhibit similar CV behaviour (Figure 4.19, C) as as-deposited coarse-grained Ni film.

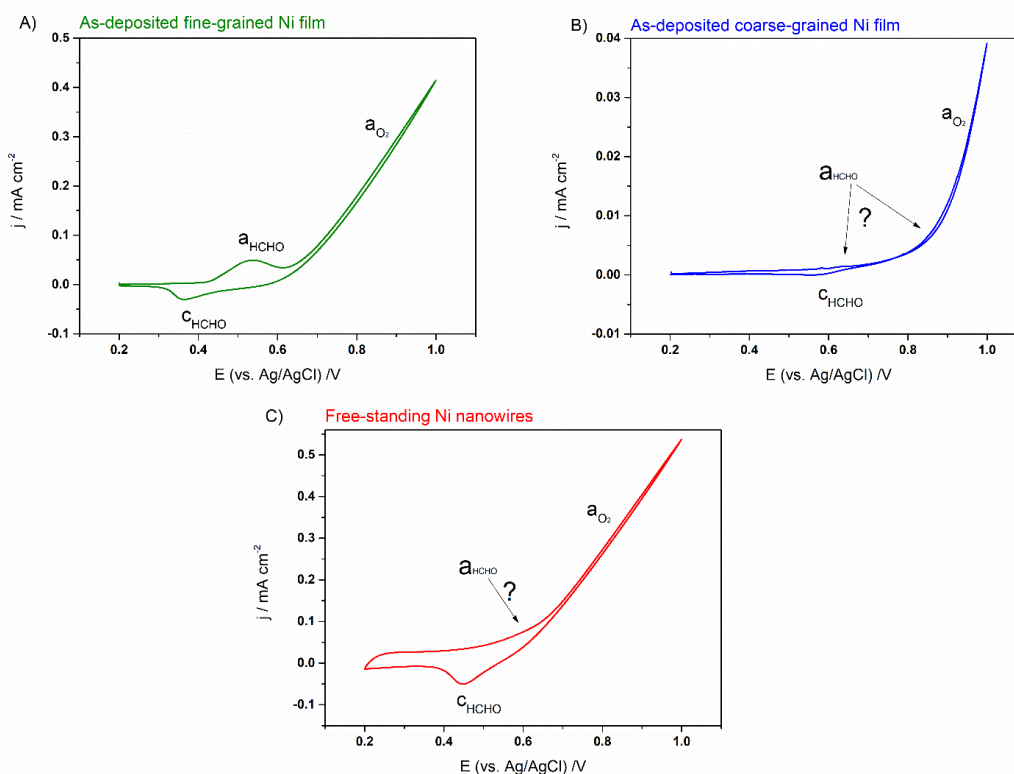


Figure 4.19: The CV profiles of the A) as-deposited fine-grained Ni film (green), B) coarse-grained (blue) Ni film (left), and C) free-standing Ni nanowires (red) in 5 mmol L⁻¹ HCHO + 0.1 mol L⁻¹ NaOH solution at a scan rate 100 mV s⁻¹.

From these observations, it can be concluded that:

- 1) The as-deposited **fine-grained Ni film** was found to be capable of oxidising the HCHO due to the existence of α -Ni(OH)₂/γ-NiOOH surface species during potential cycling. The possible mechanism is the following: the α -Ni(OH)₂ is transformed to γ-NiOOH in the anodic region during potential cycling, and then γ-NiOOH oxidises HCHO (the mechanism is described in Chapter 1.3.2.3, see reactions 1.32 and 1.33). The process of transformation from α -Ni(OH)₂ to γ-NiOOH is in agreement with the theory presented by Bode [69] (Chapter 1.3.2.2, Figure 1.20).
- 2) The as-deposited **coarse-grained Ni film** and **Ni nanowires** gave the CV responses showing an electro-inactive behaviour towards HCHO in the potential range from ~0.2–0.7 V. The inactivity of these electrodes can be attributed to the formation of native crystalline NiO₂ or NiO, as it was explained by Miao et al. [48]. They indicated that Ni electrodes composed of the surface crystalline oxides show no catalytic activity towards HCHO.

From these observations, it was concluded that the HCHO could be electrochemically oxidised only by the active Ni(OH)₂/NiOOH redox couple. Also, for efficient electro-oxidation of HCHO, we should avoid the presence of native crystalline Ni-oxide by its transformation to hydroxides via KOH-modification process (i.e. potential cycling over Ni(OH)₂/NiOOH redox couple).

4.3.2 Electrochemical oxidation of HCHO on KOH-modified Ni electrodes

With the goal to induce changes of nickel-based deposits in terms of their chemical composition and crystallographic structures and build up the active Ni species (Ni(OH)₂/NiOOH) on the surface of coarse-grained Ni film and Ni nanowires, potential

cycling (i.e. KOH-modification) was introduced via cyclic voltammetry. Continuous cycling over the $\text{Ni}(\text{OH})_2/\text{NiOOH}$ redox peaks in KOH at relatively high positive potentials leads to the accelerated and controllable transformation from the native NiO or under layered metallic Ni to the surface hydroxide layer, i.e. $\text{Ni}(\text{OH})_2/\text{NiOOH}$ [48, 52]. The KOH-modification was also introduced to the fine-grained Ni film although it is already active in the as-deposited state, thus to further improve the HCHO oxidation ability of fine-grained Ni film by the formation of a higher amount of surface-active Ni species.

4.3.2.1 KOH-modification of Ni electrodes via potential cycling up to 1.5 V

First KOH-modification experiments (Figure 4.20) were performed on fine-grained Ni film, coarse-grained Ni film and Ni nanowires-based electrodes. The potential cycling was performed in 0.5 mol L⁻¹ KOH solution (pH = 13.6) in the potential range from 0 V to the 1.5 V and back to 0 V at a scan rate 200 mV s⁻¹. Each cycle was repeated 50 times for each electrode. From CV profiles of fine-grained Ni film (green), coarse-grained Ni film (blue) and Ni nanowires (red), two anodic peaks (a_{NiOOH} and a_{O_2}) and one cathodic peak ($c_{\text{Ni}(\text{OH})_2}$) were observed. In the forward scan, the anodic peak a_{NiOOH} at $E \approx +0.4$ V is attributed to the oxidation of Ni or NiO or $\text{Ni}(\text{OH})_2$ to NiOOH, according to the reactions: $\text{Ni} + 3\text{OH}^- - 3e^- \rightarrow \text{NiOOH}$, or $\text{NiO} + \text{OH}^- - e^- \rightarrow \text{NiOOH}$, or $\text{Ni}(\text{OH})_2 + \text{OH}^- - e^- \rightarrow \text{NiOOH}$, respectively. Potential cycling to more positive potentials is continued with the oxygen evolution region (a_{O_2} , at $E > 0.5$ V) that indicated the oxidation of hydroxyl ions to the molecular oxygen, according to the reaction: $4\text{OH}^- \rightarrow \text{O}_2 + \text{H}_2\text{O} + 4e^-$. This molecular oxygen penetrates to the Ni electrode surface or into inner Ni layers (e.g. Ni-Ni lattice) [31, 52], where it can be chemically adsorbed. In the reverse scan, the cathodic peak ($c_{\text{Ni}(\text{OH})_2}$) at $E \approx 0.3$ V indicates the reduction of NiOOH to $\text{Ni}(\text{OH})_2$.

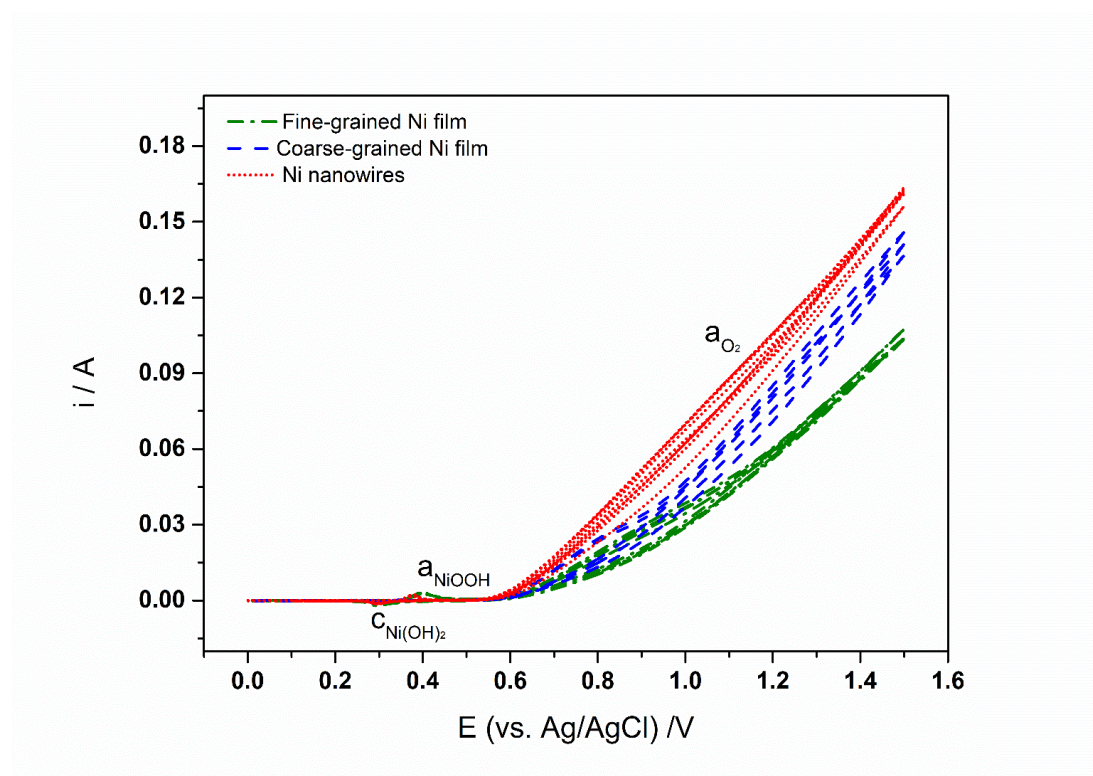


Figure 4.20: Cyclic voltammograms of fine-grained Ni film (green), coarse-grained Ni film (blue) and Ni nanowires (red) electrodes recorded in a de-aerated 0.5 mol L⁻¹ KOH solution from 0 V to +1.5 V at a scan rate of 200 mV s⁻¹ (1st – 50th cycle).

However, if the reaction of chemical adsorption of O₂ occurs (i.e. formation of Ni-oxides), the adsorbed oxygen might inhibit the HCHO detection [13] (as it was already proven in the

previous chapter). In order to confirm this prediction, the Ni electrodes that were KOH-modified in the potential range up to +1.5 V were tested in HCHO alkaline electrolyte.

4.3.2.2 Electrochemical oxidation of HCHO on Ni electrodes KOH-modified in the potential range up to +1.5 V

As mentioned above, the fine-grained and coarse-grained Ni films, and the Ni nanowires-based electrodes KOH-modified in the KOH solution at a potential range up to +1.5 V for 50 consecutive cycles have been tested for the HCHO detection via cyclic voltammetry. Figure 4.21 shows a typical CV profile of the KOH-modified A) fine-grained Ni film, B) coarse-grained Ni film and C) Ni nanowires in 0.1 mol L⁻¹ NaOH solution (dot curves) or 5 mmol L⁻¹ HCHO + 0.1 mol L⁻¹ NaOH solution (solid curves) at a scan rate 100 mV s⁻¹.

From CV curves recorded only in a 0.1 mol L⁻¹ NaOH solution (dot curves), the following anodic and cathodic peaks were observed. The anodic peaks (a_{NiOOH}) at $E=0.55$ V, 0.7 V, and 0.55 V for fine-grained Ni film, coarse-grained Ni film, and Ni nanowires, respectively. Also, a strong oxygen evolution (a_{O_2}) was observed at $E > \sim 0.5$ V in the anodic region. The cathodic peaks ($c_{\text{Ni(OH)}_2}$) were observed at $E = 0.4$ V, 0.35 V, and 0.4 V for fine-grained Ni film, coarse-grained Ni film, and Ni nanowires, respectively. A_{NiOOH} and $C_{\text{Ni(OH)}_2}$ correspond to the reversible reaction of $\text{Ni(OH)}_2 + \text{OH}^- \leftrightarrow \text{NiO(OH)} + \text{e}^-$.

As stated in the literature [33-36], upon the addition of HCHO to alkaline electrolyte the slight increase in the anodic peak (a_{NiOOH}) current densities should be observed due to the production of Ni(OH)_2 through the reaction between NiOOH and HCHO (as described in Introduction, Section 1.3.2.3, Figure 1.23, and reactions 1.32 and 1.33). However, Ni electrodes (Figure 4.21, A-C) KOH-modified in the potential range up to +1.5 V showed completely different and unexpected CV behaviour after the addition of 5 mmol L⁻¹ HCHO into the 0.1 mol L⁻¹ NaOH solution. Instead of increased current densities of the a_{NiOOH} , its decrease was observed. Based on these results, it is reasonable to conclude that the excessive production of oxygen in the KOH-modification process blocks the active sites of Ni electrodes and inhibits the electro-oxidation of HCHO. In other words, it is difficult to measure the oxidation current of HCHO because it is difficult to obtain a surface free Ni from adsorbed O_2 [31].

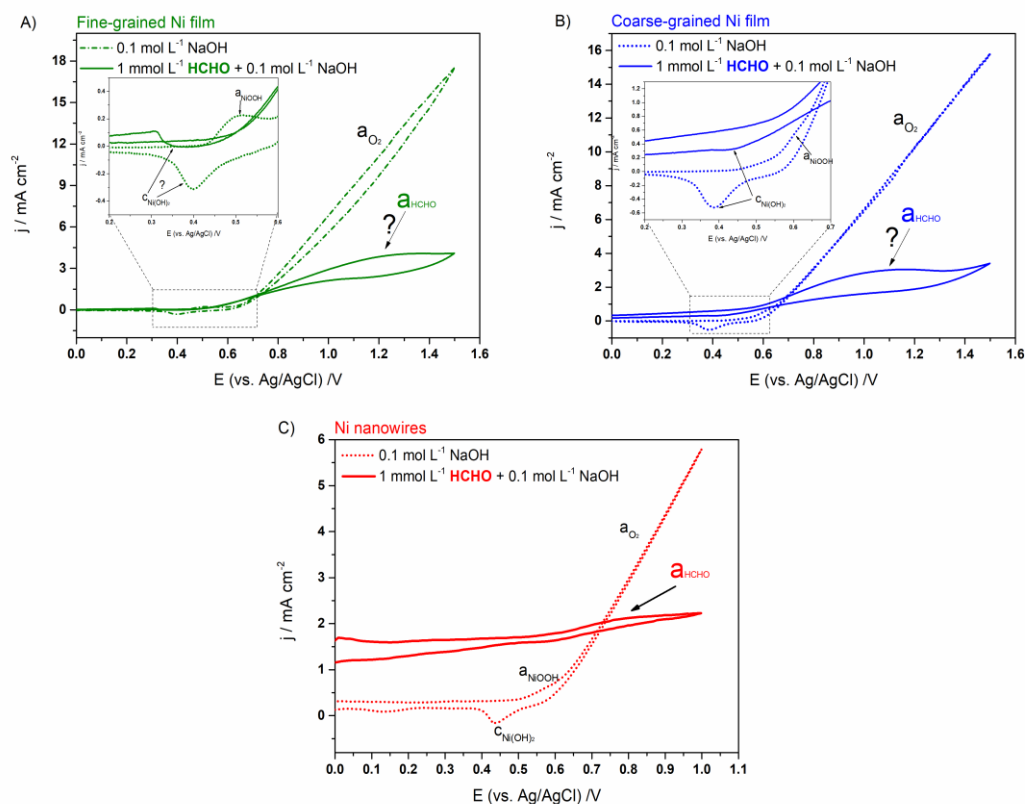


Figure 4.21: The CV profiles of the A) fine-grained Ni film, B) coarse-grained Ni film and C) Ni nanowires modified in KOH up to +1.5 V observed in 0.1 mol L⁻¹ NaOH solution or 5 mmol L⁻¹ HCHO + 0.1 mol L⁻¹ NaOH solution at a scan rate 100 mV s⁻¹.

These results confirmed the uselessness of KOH-modification process up to +1.5 V because the Ni surface is sensitive and gets blocked by adsorbed molecular oxygen, and thus the detection of the HCHO is disabled. The KOH-modification process (up to +1.5 V) is proven to be unsuitable to increase the amount of active Ni(OH)₂/NiOOH on the surface.

4.3.2.3 KOH-modification of Ni electrodes via potential cycling up to 0.6 V

In order to avoid a pronounced evolution of a molecular oxygen that can adsorb on the surface Ni, the KOH-modification process was performed in the potential range up to +0.6 V. Thus, selected upper potential of +0.6 V limits the oxygen evolution reaction (a_{O_2}) and still enables a continuous potential cycling over the Ni(OH)₂/NiOOH redox peaks. Figure 4.22 presents CVs of as-deposited fine-grained Ni film (A, B), as-deposited coarse-grained Ni film (C, D), and free-standing Ni nanowires (E, F) in 0.5 mol L⁻¹ KOH obtained at a scan rate 200 mV s⁻¹. Cycles 1, 10, 20, 50 and 60 are included in order to show the evolution of the CVs behaviour with the increasing number of cycles. Figure 4.22 (A, C and E) demonstrates CV profiles in the 1st cycle where the potential window was chosen to be from -1.0 V to +0.6 V in the anodic region and then the scan was reversed back to 0 V (for fine-grained and coarse-grained Ni film) or 0.2 V (for Ni nanowires) in cathodic region. The first increase in the anodic current density (a_1) was observed at potentials of -0.7 V (A)/-0.5 V (B)/-0.2 V (C) and corresponded to the following reaction: $Ni + 2OH^- \leftrightarrow \alpha-Ni(OH)_2 + 2e^-$. The plots reveal the differences in the observed a_1 current densities: in the case of fine-grained Ni film, the current density reaches the value of ~0.01 mA cm⁻², demonstrating that a small amount of newly formed $\alpha-Ni(OH)_2$ surface species is formed in the 1st cycle of the

KOH-modification process. This observation can be justified by the fact that most of the surface Ni species, i.e. α -Ni(OH)₂, are already formed during the Ni electrodeposition (proved by XRD, Figure 4.16, B). In the case of coarse-grained Ni film, the greater increase in the anodic current peak a_1 was observed ($j \approx 0.5 \text{ mA cm}^{-2}$) due to the more prominent conversion of surface Ni/NiO₂ to α -Ni(OH)₂ in comparison to that one observed on fine-grained Ni film. In other words, the as-deposited coarse-grained Ni film surface is mostly composed of Ni and NiO₂ (Figure 4.16, C) which are transformed to α -Ni(OH)₂ during the 1st scan of the KOH-modification process. Furthermore, the largest increase in the anodic peak current density of a_1 was observed in the case of Ni nanowires electrode. This observation can be assigned to the transformation of the largest surface/volume from Ni/NiO to the α -Ni(OH)₂. Also, the peak potential of Ni /NiO to α -Ni(OH)₂ transformation varies between individual Ni electrodes, as seen from the graphs presented in Figure 4.22 (A, C, E). It should be noted that this reaction represents an electro-crystallisation process, meaning that electrochemical reaction (transfer of electron) is also accompanied by atomic rearrangements, i.e. (re)crystallisation of the material. For example, from fcc Ni structures to a distorted hexagonal α -Ni(OH)₂ structures. As for the differences in the initial texture, i.e. the crystallographic orientation, the chemical and the crystal phase composition of Ni electrode surfaces, each of these electrodes needs a certain driving force (i.e. potential) for electro-crystallisation of α -Ni(OH)₂ [124, 125]. This fact is the main reason for the shift in peak potentials of a_1 (α -Ni(OH)₂ formation) in between the fine-grained Ni film, coarse-grained Ni film and Ni nanowire electrodes.

Following a potential excursion to the more positive potentials causes irreversible dehydration of α -Ni(OH)₂ to β -Ni(OH)₂ (a_2) [69]. Once the β phase is formed, it cannot be electrochemically reduced back to α -Ni(OH)₂ or metallic Ni due to its high electrochemical stability [36]. Continuing potential cycling to positive potential region, the next increase in the current densities was observed at $E \approx 0.4\text{--}0.5 \text{ V}$ (a_3), where the β -Ni(OH)₂ (formed at a_2) is oxidised to β -NiOOH. Also, the a_3 current densities increase might be a result of oxidation of Ni/NiO “inner” layers to β -NiOOH (reactions 1.28 and 1.29; explained in Chapter 1.3.2.2).

Once the formation of β -NiOOH occurred, the scans were immediately reversed (back to 0 V or 0.2 V) to avoid the massive production of molecular oxygen (at a_4). In the cathodic region, one cathodic peak (c_1) was observed (Figure 4.22, A, C, E) at $E \approx -0.3\text{--}-0.4 \text{ V}$ where the β -NiOOH (formed at a_3) is reduced to β -Ni(OH)₂.

In order to increase the amount of the surface-active species of Ni(OH)₂/NiOOH, the Ni electrodes were continuously cycled up to 50 times. Figure 4.22, B, D and F, shows the CV profiles of fine-grained Ni film (B), coarse-grained Ni film (D) and Ni nanowires (F) electrodes for the 10th, 20th, 50th and 60th cycle, observed at a scan rate 200 mV s^{-1} . With increasing numbers of cycles from 10 to 50, the current densities of the anodic (a_3) and cathodic (c_1) peaks increase until a steady state is reached and there is no significant current-density increase for cycles ≥ 50 (see cycle 50 and 60). From obtained results it can be deduced that the increase of the current densities of anodic (a_3) and cathodic (c_1) peaks shows the enrichment of the electroactive species of Ni(OH)₂ and NiOOH at the surface of the Ni electrodes due to the entry of OH⁻ into the Ni surface layers, see reactions 1.27–1.29, Chapter 1.3.2.2 [35, 48, 52].

However, the change in the current densities of the a_3 anodic peak from the 10th and 50th cycle ($\Delta j_{a_3} = j_{50^{th}} - j_{10^{th}}$) differs between Ni electrodes. The CV profiles reveal a small increase in the current densities of a_3 anodic peak ($\Delta j_{a_3} \approx 0.05 \text{ mA cm}^{-2}$) for fine-grained and coarse-grained Ni films, while this difference in the a_3 anodic peak is much more pronounced ($\Delta j_{a_3} > 0.5 \text{ mA cm}^{-2}$) in the case of Ni nanowires electrode. Regarding this observation (Δj_{a_3} from 1st to 50th cycle), we could assume that potential cycling (10th–50th cycle) causes significant changes in surface composition of the Ni nanowires and less significant changes in the case of fine-grained and coarse-grained films. In order to find how KOH-modification influences the composition/crystallinity of these electrodes, the surfaces of KOH-modified Ni electrodes were investigated by XRD, TEM/SAED and FT-IR.

In the following chapters of the thesis, the Ni electrodes (fine-/coarse-grained Ni films or Ni nanowires) KOH-modified in the potential range up to +0.6 V, at a scan rate of 200 mV s⁻¹ and up to 50 cycles were named and used as KOH-modified fine-grained Ni film, KOH-modified coarse-grained Ni film, and KOH-modified Ni nanowires.

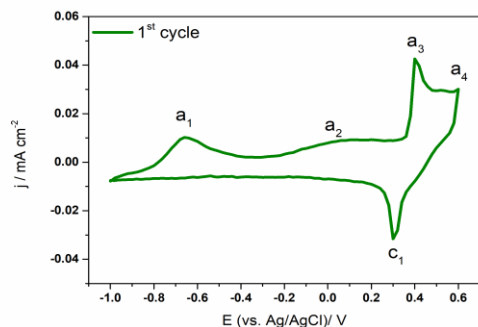
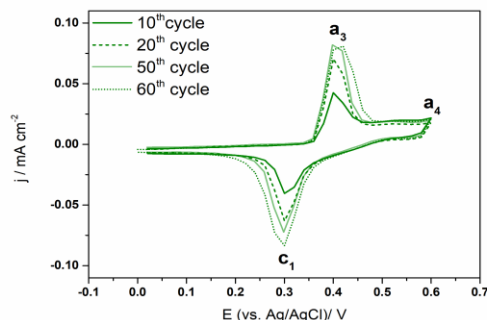
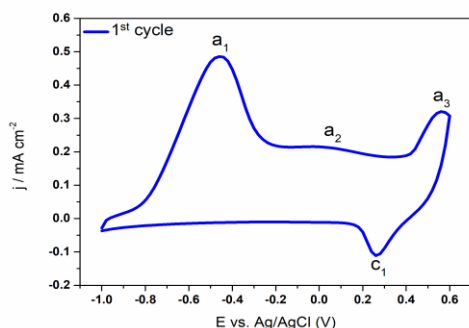
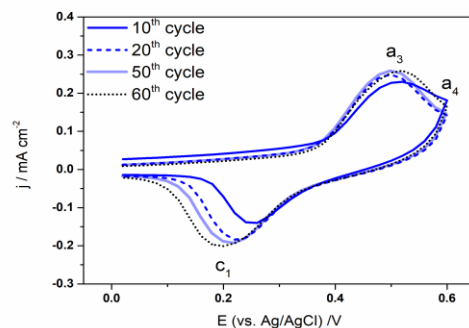
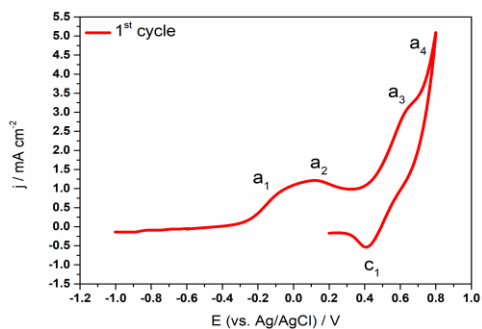
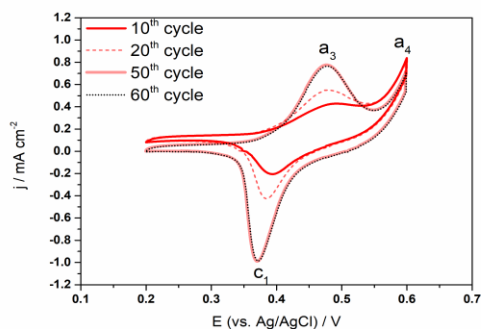
A) Fine-grained Ni film; cycle 1**B) Fine-grained Ni film; cycle 2-50****C) Coarse-grained Ni film; cycle 1****D) Coarse-grained Ni film; cycle 2-50****E) Ni nanowires; cycle 1****F) Ni nanowires; cycle 2-50**

Figure 4.22: CV profiles of fine-grained Ni film (A,B), coarse-grained Ni film (C,D) and Ni nanowires (E,F) electrodes recorded in a de-aerated 0.5 mol L⁻¹ KOH solution from -1.0 V to +0.6 V in the 1st cycle and from 0/0.2 V to +0.6 V in the 10th–60th cycle at a scan rate of 200 mV s⁻¹.

4.3.2.4 Characterisation of KOH-modified Ni electrodes

4.3.2.4.1 XRD of KOH-modified fine-grained Ni film

Figure 4.23 (green curves) shows the XRD patterns of KOH-modified fine-grained Ni film observed in the 2-theta range from A) 10–90°, B) 10–25°, C) 32–36° and D) 41–44°. In order to demonstrate the changes in composition on the surface of the electrode after the KOH-

modification, the graphs B–D also include the XRD patterns of the as-deposited (i.e. non-modified) fine-grained film (grey curves).

The XRD pattern of KOH-modified fine-grained Ni film obtained in 2-theta range from 10–90° (Figure 4.23, A) does not show any differences in comparison to as-deposited fine-grained Ni film (Figure 4.16, B), as the following diffraction peaks were observed: SiO₂/Cr/Au substrate with the broad hump for SiO₂ at 20–25° (ICDD 00-033-1161), two characteristic peaks for cubic Cr at 36.5° and 81.7° (ICDD 00-006-0694); three characteristic peaks for cubic Au at 38.2°, 77.5° and 81.7° (ICDD 01-089-3697) with the preferential growth orientation of Au (1 1 1) plane; and two characteristic peaks at 2-theta of 44.5° and 76.5° that indicate the presence of electrodeposited fcc Ni (ICDD 00-001-1258) with the preferential growth orientation of Ni (1 1 1) plane.

Furthermore, Figure 4.23, B–D, represents the XRD patterns of KOH-modified (green curves) and as-deposited, i.e. non-modified (grey curves) fine-grained Ni film at 2-theta ranges of 10–25° (B), 32–36° (C) and 41–44° (D).

Based on the comparison of these two electrodes, we concluded:

- 1) KOH-modification induces slight changes of Ni surface; the characteristic peaks for hexagonal α -Ni(OH)₂ (ICDD 00-0358-0715, ICDD 00-022-0444) were identified at 2-theta of 11.7°, 12.5°, 34.3° and 42.6°, with a mild increase in their intensity.
- 2) These results can be correlated with the CV profile (Figure 4.22, B) of fine-grained Ni film, where only a slight increase in the current density of a₃ anodic peak current was observed between the 10th and the 50th cycle ($\Delta j_{a_3} = j_{50^{th}} - j_{10^{th}} \approx 0.05 \text{ mA}$).

KOH-modification of the fine-grained film did not enrich the surface with the electroactive α -Ni(OH)₂/ γ -NiOOH or β -Ni(OH)₂/ β -NiOOH or amorphous-Ni(OH)₂/ β -NiOOH. By these observations it was confirmed that α -Ni(OH)₂ is definitely precipitated during the electrodeposition of fine-grained Ni film.

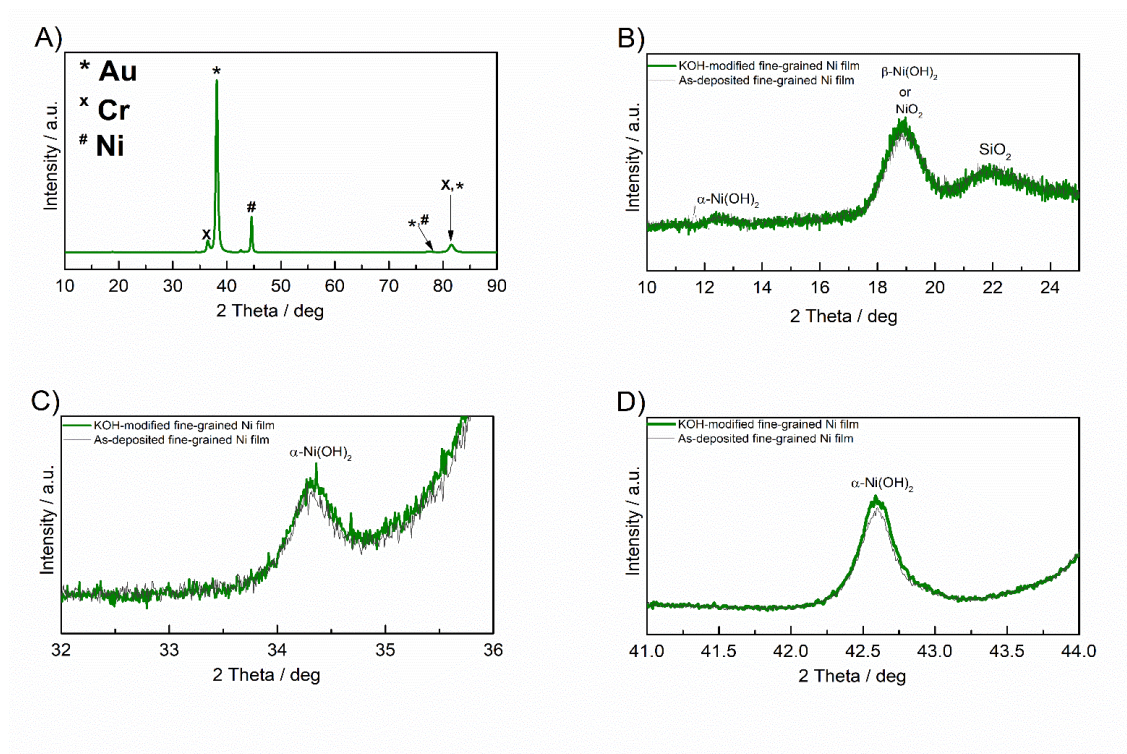


Figure 4.23: XRD spectra of the KOH-modified fine-grained Ni film electrode collected at 2-theta of 10–90° (A). The XRD spectra B–D corresponds to the magnified regions of spectra A, where the characteristic peaks for β -Ni(OH)₂/NiO₂ and α -Ni(OH)₂ were expected.

4.3.2.4.2 XRD and FT-IR of KOH-modified coarse-grained Ni film

Figure 4.24 (blue curves) shows the XRD patterns of KOH-modified coarse-grained Ni film observed in the 2-theta range from A) 10–90°, B) 10–25°, and C) 32–36°. In order to demonstrate the changes in composition on the surface of the electrode after the KOH-modification, the graphs B and C also include the XRD patterns of the as-deposited (i.e. non-modified) coarse-grained film (grey curves).

From the XRD pattern of KOH-modified coarse-grained Ni film obtained in 2-theta range from 10–90° (Figure 4.24, A), the following diffraction peaks for SiO₂/Cr/Au substrate were observed: broad hump for SiO₂ at 20–25° (ICDD 00-033-1161), two characteristic peaks for cubic Cr at 36.5° and 81.7° (ICDD 00-006-0694), and three characteristic peaks for cubic Au at 38.2°, 77.5° and 81.7° (ICDD 01-089-3697) with the preferential growth orientation of Au (1 1 1) plane. Furthermore, diffraction peaks that indicate the presence of fcc Ni with the preferential growth orientation of Ni (1 1 1) plane were observed at 2-theta of 44.5° and 76.5° (ICDD 00-001-1258).

The significant differences between as-deposited (grey curves) and KOH-modified (blue curves) coarse-grained Ni film were observed in 2-theta regions from 10–25° (Figure 4.24, B) and 32–36° (Figure 4.24, C). The XRD pattern of KOH-modified fine-grained Ni film (blue) indicates the presence of two different chemically assembled hexagonal α -Ni(OH)₂; characteristic peaks at 12.0°, 23.4°, 33.8° and 34.3° can be attributed to the 3Ni(OH)₂ × 2H₂O (ICDD 00-022-0444), and characteristic peaks at 12.5°, 24.1°, 33.9° and 42.6° ascribed to the Ni(OH)₂ × 0.75H₂O (ICDD 00-038-0715).

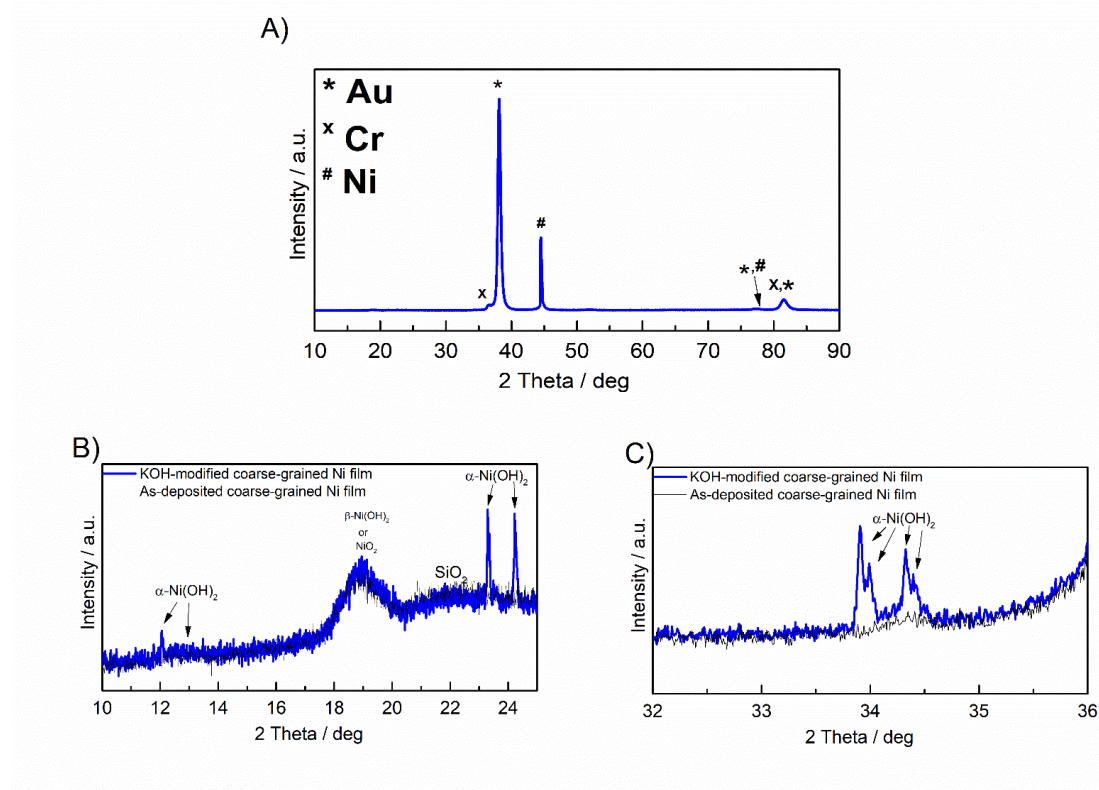


Figure 4.24: XRD spectra of the KOH-modified coarse-grained Ni film electrode collected at 2-theta of 10–90° (A). The XRD spectra B and C correspond to the magnified region of XRD spectra A, where the characteristic peaks for β -Ni(OH)₂/NiO₂ and α -Ni(OH)₂ were expected.

From these observations, it can be concluded:

- 1) As KOH-modification is introduced to the coarse-grained film, the Ni surface is transformed to the α -Ni(OH)₂ due to the electrochemical reaction with the OH⁻ ions (see reaction 1.29, Chapter 1.3.2.2).
- 2) KOH-modified coarse-grained Ni film still contains a small amount of NiO₂ indicated by a diffraction peak at 19°, which means that the coarse-grained Ni

film contains a small amount of Ni (IV) species that cannot be completely transformed to the $\text{Ni}(\text{OH})_2$ during charging in KOH-modification process up to +0.6 V.

Furthermore, the presence of $\alpha\text{-Ni}(\text{OH})_2$ or rather -O-H bond on coarse-grained Ni film was further confirmed by FT-IR. Figure 4.25 shows typical FT-IR spectra of KOH-modified coarse-grained Ni film. The spectrum was measured following the same procedure as for the as-deposited coarse-grained film (Figure 4.17, B). The spectrum shows vibration bands for the -O-H at 3500 cm^{-1} , -OH functional group at 1720 cm^{-1} , as well as Ni-O-H vibration at 610 cm^{-1} and Ni-O bond vibrations at 410 cm^{-1} and 520 cm^{-1} .

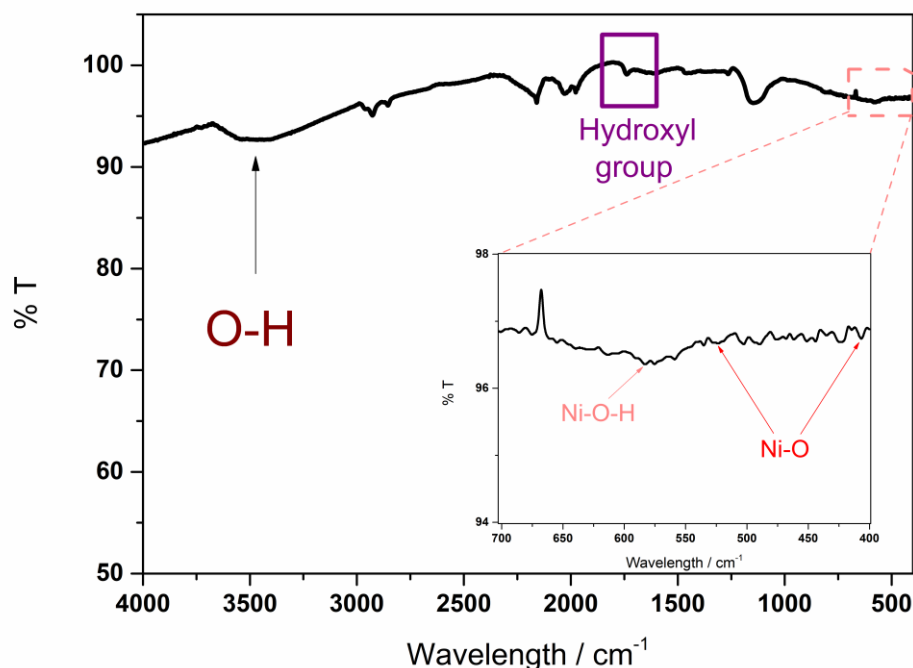


Figure 4.25: FT-IR spectrum of coarse-grained Ni film KOH-modified in the potential range up to +0.6 V at a scan rate 200 mV s^{-1} with an inset of the wavelength range from $400\text{--}700\text{ cm}^{-1}$ for better clarity.

4.3.2.4.3 XRD, TEM/SAED and FT-IR of KOH-modified Ni nanowires

The XRD pattern of free-standing KOH-modified Ni nanowires is presented in Figure 4.26, A–C. The composition and crystal structure obtained in 2-theta range from $10\text{--}90^\circ$ (Figure 4.26, A) does not show any differences in comparison to the free-standing non-modified Ni nanowires (Figure 4.18); and indicates the presence of cubic Au (ICDD 01-089-3697) without any preferential orientation (five characteristic peaks at 38.0° , 44.4° , 64.5° , 77.6° and 81.7°) and fcc Ni (ICDD 00-001-1258) that does not show any texturing (three characteristic peaks at 44.5° , 51.9° and 76.4°). In order to investigate the presence of $\alpha\text{-}/\beta\text{-Ni}(\text{OH})_2$ after KOH-modification, the XRD patterns were collected in a narrow 2-theta range from $5\text{--}35^\circ$ (Figure 4.26, B). For better clarity, Figure 4.26, B includes the XRD spectrum of non-modified Ni nanowires electrode (grey). Rough indexing of the XRD pattern of KOH-modified Ni nanowires electrode (red curve) does not imply the reflections of crystalline NiO (ICDD 04-006-6545) which was found in the XRD pattern of the non-modified Ni nanowires electrode (grey curve). This means that surface Ni is completely transformed to $\text{Ni}(\text{OH})_2$ during the KOH-modification process (Figure 4.22, E and F) and according to the

reaction 1.28 presented in Chapter 1.3.2.2 However, no defined diffraction peaks could be attributed to either hexagonal α -/ β -Ni(OH)₂, but a broad hump at 10° indicating the possibility of the presence of poorly crystalline or amorphous Ni(OH)₂ as described by Oliva et al. [58].

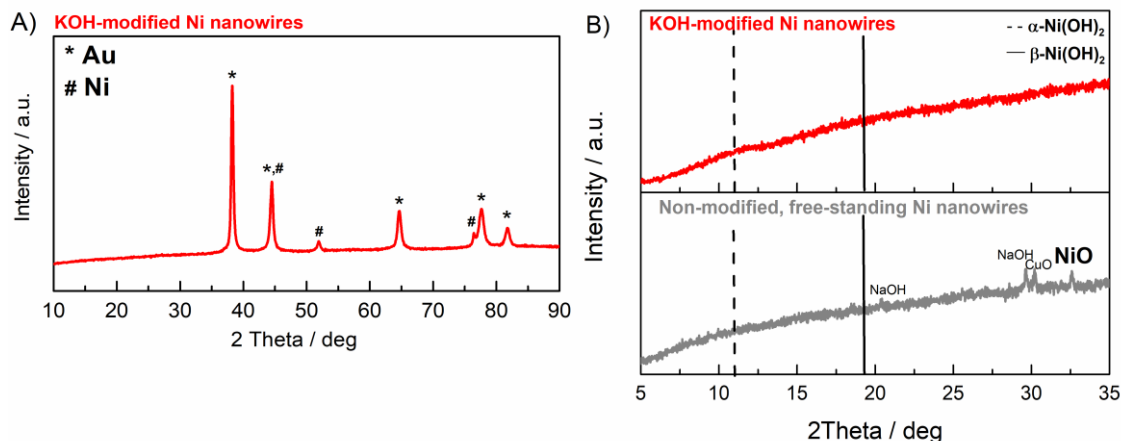


Figure 4.26: A) XRD spectra of the Ni nanowires electrode recorded after the KOH-modification process in the potential range up to +0.6 V at a scan rate 200 mV s⁻¹, collected at 2-theta of 10–90°, and B) the inset XRD spectra of KOH-modified Ni nanowires electrode (red) and non-modified, i.e. free-standing, Ni nanowires electrode (grey), collected at 2-theta of 5–35°.

As when using the XRD we were not able to confirm in detail the crystal structure of the surface after the KOH-modification of Ni nanowires electrode, we additionally investigated its structure and phase composition in the TEM (Figure 4.27). Although the 200 ± 50 nm-thick NWs are not transparent in the 200 kV TEM, we avoided the conventional thinning sample preparation in order to mitigate the sample-preparation-induced artefacts. The KOH-modified Ni nanowires were sonicated in absolute ethanol and directly transferred to commercial Cu grids. TEM image of single Ni nanowire deposited on Au branched nanowire is shown in Figure 4.27, A. From Figure 4.27, B the interface between Au and Ni is clearly seen, moreover, it is seen that the KOH-modification layer is present only on the Ni part of the nanowire and absent from the initial Au branched regions (see orange square). From Figure 4.27, C, we were able to observe the thickness of the Ni modification layer (i.e. nickel hydroxide), and it was 8–10 nm thin. Figure 4.27, D represents a close-up selected-area electron diffraction (SAED) pattern which was obtained on the modification layer. This analysis revealed an amorphous Ni-oxide/hydroxide phase, with the only Ni lattice visible (inset). Our observation indicates that the modified Ni-based layer covering the Ni nanowires is amorphous, without any long-range ordering.

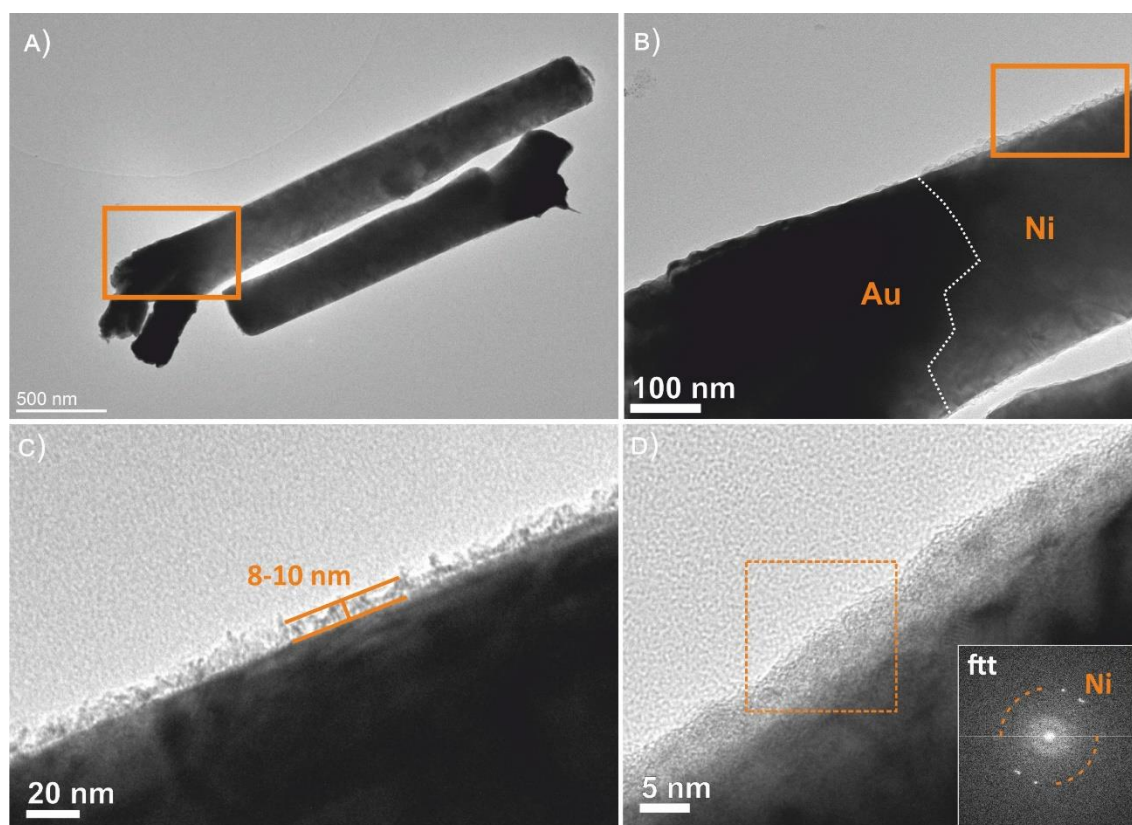


Figure 4.27: A) Conventional TEM micrograph of KOH-modified Ni NWs, showing the remains of the branched Au substrate; B) surface KOH-modification can only be observed on the Ni parts of the NWs, indicating the Ni-based origin; C) the thickness of the modified layer is uniform, 8–10 nm; and D) shows no long- or short-range ordering.

Additionally, FT-IR spectra of KOH-modified Ni nanowires were recorded to examine the presence of the following chemical bonds: –O–H, Ni–O–H and Ni–O. Figure 4.28 shows FT-IR spectrum of KOH-modified Ni nanowires observed from A) 400–4000 cm^{-1} together with magnified wavelength ranges from B) 2500–4000 cm^{-1} , C) 1500–1800 cm^{-1} and D) 400–700 cm^{-1} for better clarity. The broad peak around 3400 cm^{-1} (spectrum B) indicates the existence of the O–H bond and the absorption band at approximately 1720 cm^{-1} (spectrum C) can be attributed to a hydroxyl group. Further, the spectrum C revealed the presence of Ni–O vibration bond at around 410 cm^{-1} and 520 cm^{-1} , and the Ni–O–H stretching bond peak at 610 cm^{-1} [126, 127].

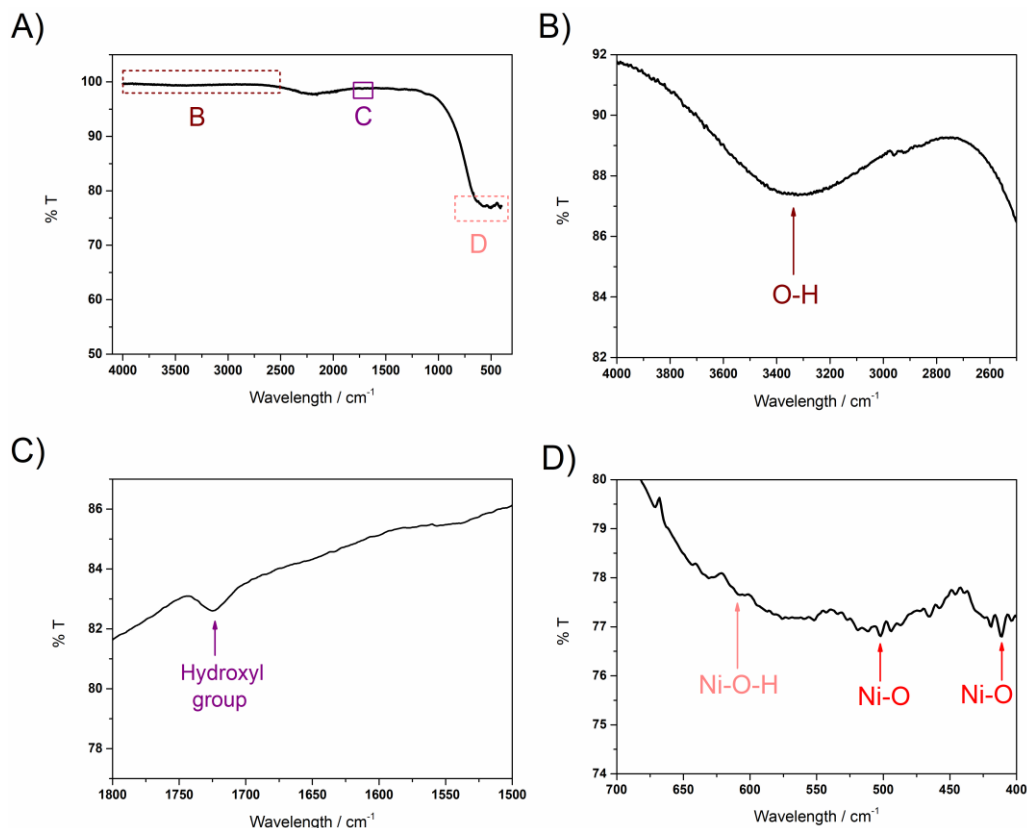


Figure 4.28: Right: FT-IR spectrum of Ni nanowires KOH-modified in the potential range up to +0.6 V at a scan rate 200 mV s⁻¹. Left: Magnified original FT-IR at wavelength ranges of A) 2500–4000 cm⁻¹; B) 1500–1800 cm⁻¹ and C) 400–700 cm⁻¹.

The findings obtained by XRD, FT-IR, or TEM analysis (Chapter 4.3.2.4) in correlation with CV profiles of KOH-modification processes (Chapter 4.3.2.3) lead to the following conclusions:

1. In the case of **fine-grained Ni films**: the surface of this film after electrodeposition is mostly composed of α -Ni(OH)₂ that is formed during cathodic electrodeposition from Ni²⁺ acidic electrolytes (pH = 2.5). Furthermore, the studies revealed that KOH-modification process does not induce significant changes in the surface composition of fine-grained Ni film. Based on the CV behaviour (Figure 4.22) in the 1st cycle, we conclude that there is a small enrichment of α -Ni(OH)₂ ($j(a_1)$ is low) which is most probably formed on the native Ni/NiO surface. Also, there is a small enrichment of β -Ni(OH)₂ on the surface in the 1st cycle ($j(a_3) > j(a_1)$), however, the amount of β -Ni(OH)₂ does not increase significantly with the increasing number of cycles up to 50 (small changes of anodic (a_3) and cathodic (c_1) peak current densities; $\Delta j = j_{50^{th}} - j_{10^{th}} \approx 0.05 \text{ mA}$). These observations showed that the amount of β -phase formed during KOH-modification is negligible compared to the α -phase.

** Figure 4.29 represents a scheme of the surface transformation of fine-grained Ni film during the modification process in KOH electrolyte (at certain anodic or cathodic peak potentials from the 1st to the 50th cycle).*

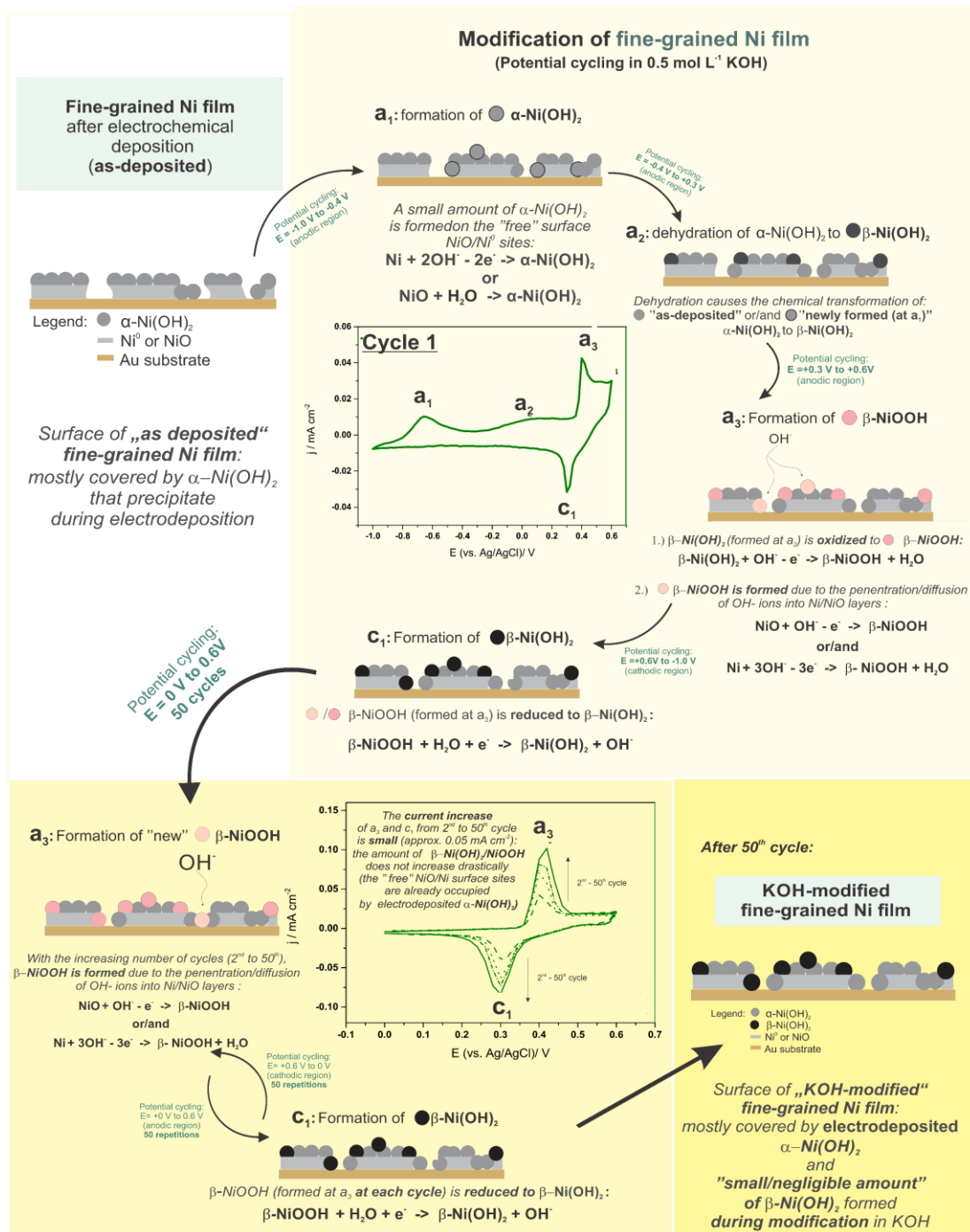


Figure 4.29: Schematic presentation of the surface transformation of a fine-grained Ni film during the modification process in the KOH electrolyte.

- In the case of **coarse-grained Ni films**: the surface of this film is mostly composed of α -Ni(OH)₂ that is formed during the KOH-modification process of an as-deposited electrode (composed of Ni or NiO) at a₁ in the 1st cycle (significant increase in the a₁ current density). Also, there is no significant enrichment of β -Ni(OH)₂ on the surface during KOH-modification, as there is a small increase in the a₃ and c₁ current densities between the 10th and the 50th cycle; $\Delta j = j_{50^{th}} - j_{10^{th}} \approx 0.05 \text{ mA}$. From CV observations and XRD results, it was concluded that the amount of β -phase formed during KOH-modification is negligible compared

to the α -phase. However, we assume that the coarse-grained Ni film contains a higher amount of β -Ni(OH)₂ in comparison to the fine-grained Ni film due to the higher current density values observed at a_3 current peak.

* Figure 4.30 represents a scheme of the surface transformation of coarse-grained Ni film during the modification process in KOH electrolyte (at certain anodic or cathodic peak potentials from the 1st to the 50th cycle).

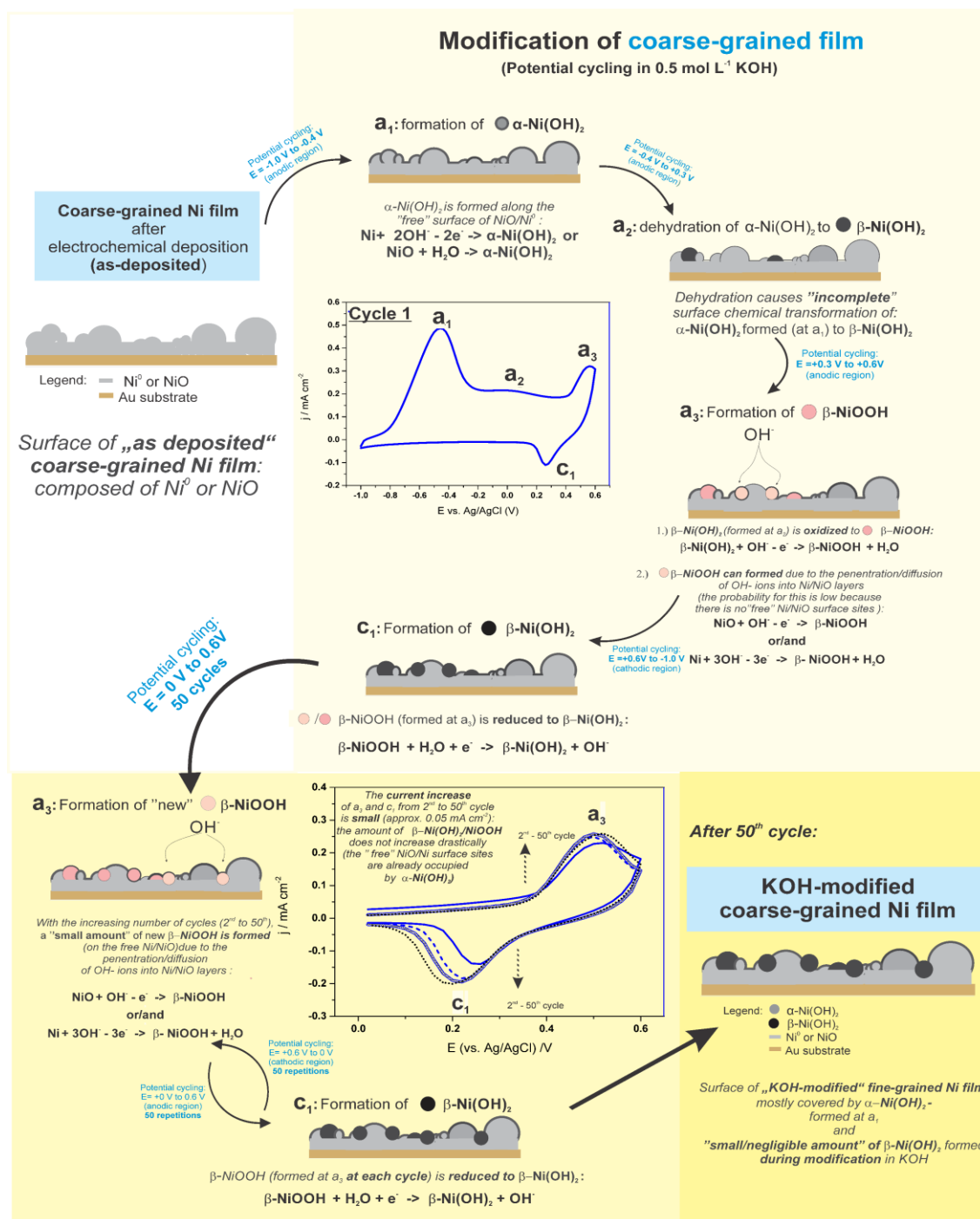


Figure 4.30: Schematic presentation of the surface transformation of a coarse-grained Ni film during the modification process in the KOH electrolyte.

3. In the case of **Ni nanowires**: the TEM/SAED and FT-IR investigation revealed the formation of a several-nm-thick amorphous layer of Ni(OH)_2 throughout the whole of the surfaces of the nanowires which is formed during KOH-modification between the 1st and the 50th cycle. We assumed that the small amount of $\alpha\text{-Ni(OH)}_2$ is formed (at a_1) and is further transformed to the $\beta\text{-Ni(OH)}_2$ (at a_3) in the 1st cycle. However, the most significant transformation of the Ni/NiO surface to amorphous Ni(OH)_2 occurs due to the oxidation reaction of OH^- with the $\beta\text{-Ni(OH)}_2$ or NiO or Ni (at a_3) during the 10th and the 50th cycle (a huge increase in the a_3 and c_1 current densities; $\Delta j = j_{50^{th}} - j_{10^{th}} \approx 0.5 \text{ mA}$).

**Figure 4.31 represents a scheme of the surface transformation of Ni nanowires during the modification process in KOH electrolyte (at certain anodic or cathodic peak potentials from the 1st to the 50th cycle).*

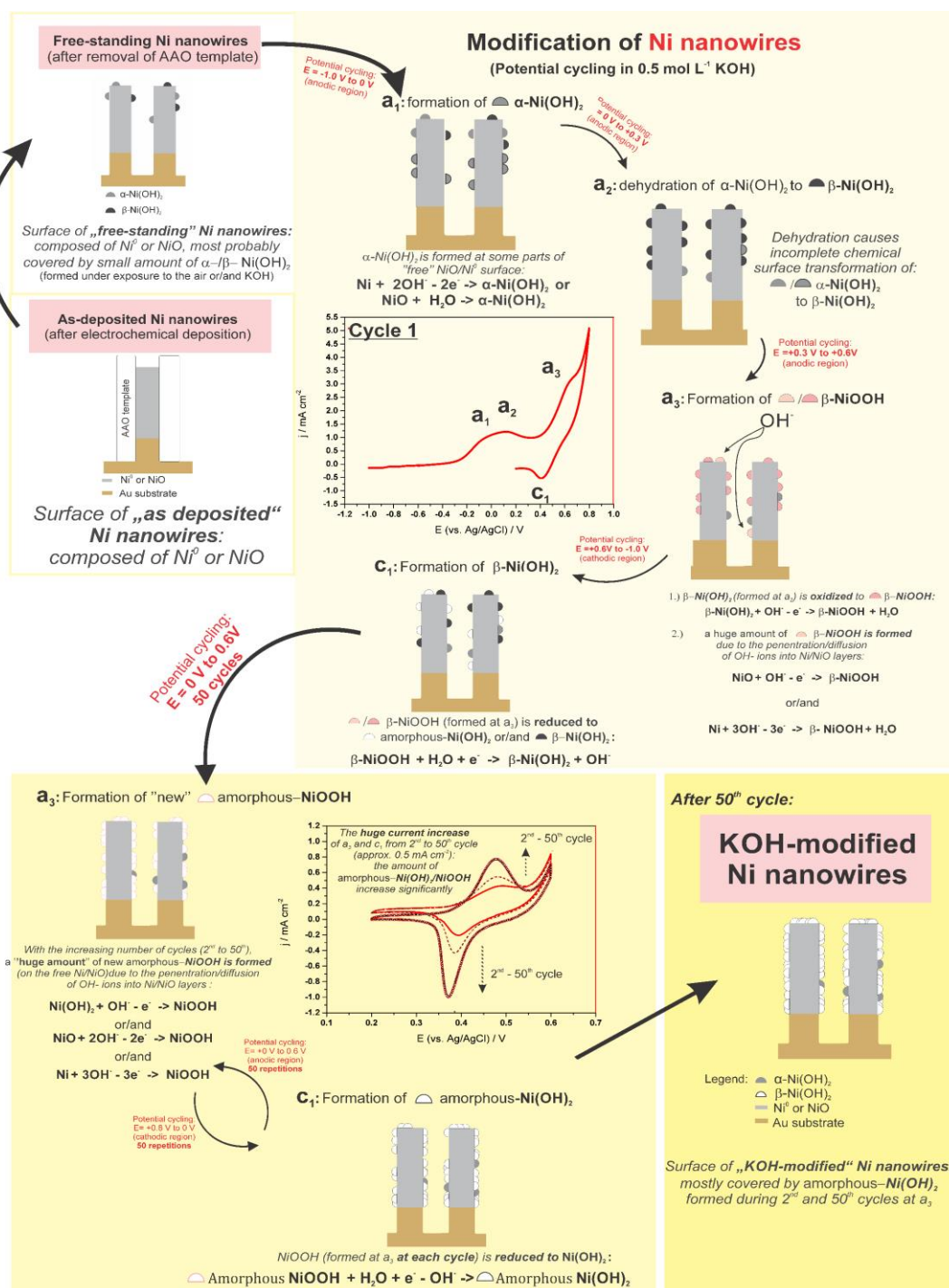


Figure 4.31: Schematic presentation of the surface transformation of Ni nanowires during the modification process in the KOH electrolyte.

Comparing CV, XRD, FT-IR and TEM results we concluded that the growth of $\text{Ni}(\text{OH})_2$ is related to the crystal structure of electrodeposited Ni and the orientation of Au substrate. In our case, hexagonal $\alpha\text{-Ni}(\text{OH})_2$ has grown on a preferentially (1 1 1)-oriented fcc Ni that was electrodeposited on an Au substrate with a preferential crystallographic (1 1 1)-orientation. On the other hand, amorphous $\text{Ni}(\text{OH})_2$ has been electrochemically formed on the surface of the isotropic Ni-Au substrate.

4.3.2.5 Electrochemical oxidation of HCHO on Ni electrodes KOH-modified in the potential range up to +0.6 V

All produced Ni-based electrodes that were KOH-modified in the potential range up to +0.6 V were further exposed to the HCHO containing alkaline electrolytes in order to investigate their electro-oxidation ability. Figure 4.32 shows the electrochemical behaviour of KOH-modified Ni electrodes, including fine-grained Ni film (A, green), coarse-grained Ni film (B, blue) and Ni nanowires (C, red) in 0.1 mol L⁻¹ NaOH solution and 1 mmol L⁻¹ HCHO + 0.1 mol L⁻¹ NaOH solution. In parallel, the bare Au substrates (Au nanowires or Au films) were also tested considering the fact that Au is known to be capable of electro-oxidising different organic compounds, including HCHO [103]. The CVs of bare Au electrodes in 1 mmol L⁻¹ HCHO + 0.1 mol L⁻¹ NaOH solution are included on each graph separately (grey dash).

The electrochemical responses of KOH-modified Ni electrodes observed in the solution containing only 0.1 mol L⁻¹ NaOH (Figure 4.32, A-C, black curves) exhibit well-defined anodic (aNiOOH) and cathodic (cNi(OH)₂) peaks associated with the Ni(OH)₂/NiOOH redox couple that corresponds to the reversible reaction of $\text{Ni(OH)}_2 + \text{OH}^- \leftrightarrow \text{NiO(OH)} + \text{e}^-$. After the addition of 1 mmol L⁻¹ HCHO into 0.1 mol L⁻¹ NaOH solution (Figure 4.32, A-C), the increment in the anodic peak current (aHCHO) and a slight reduction in the cathodic peak current were observed for:

- A) The fine-grained Ni film (green); anodic peak (aHCHO) at $E = 0.7$ V and cathodic peak at $E = 0.35$ V,
- B) The coarse-grained Ni film (blue); anodic peak (aHCHO) at $E = 0.8$ V (aNiOOH) and cathodic peak at $E = 0.25$ V, and
- C) The Ni nanowires (red); anodic peak (aHCHO) at $E = 0.7$ V and cathodic peak at $E = 0.35$ V.

It is observed that the current density of KOH-modified Ni nanowires electrode ($j \approx 0.5$ mA cm⁻²) is much larger than the current density of KOH-modified coarse-grained ($j \approx 0.25$ mA cm⁻²) and fine-grained ($j \approx 0.13$ mA cm⁻²) Ni films. Also, the onset over-potential of Ni nanowires electrode ($E \approx 0.3$ V) is smaller than that of coarse-grained ($E \approx 0.35$ V) and fine-grained ($E \approx 0.45$ V) Ni films. Moreover, the intensity of the cathodic peak (cNi(OH)₂) that is the resultant of the reduction of NiOOH to Ni(OH)₂ reduces with the addition of HCHO. This might be due to the partial reduction of NiOOH by HCHO.

Furthermore, the addition of 1 mmol L⁻¹ HCHO into 0.1 mol L⁻¹ NaOH solution (Figure 4.32, grey) gave no signal for HCHO electro-oxidation on bare Au electrodes (film or nanowires). These results indicate that the bare Au electrodes show no affinity towards HCHO electro-oxidation in the potential regions where Ni(OH)₂/NiOOH transformations occur (at $E > 0.5$ V).

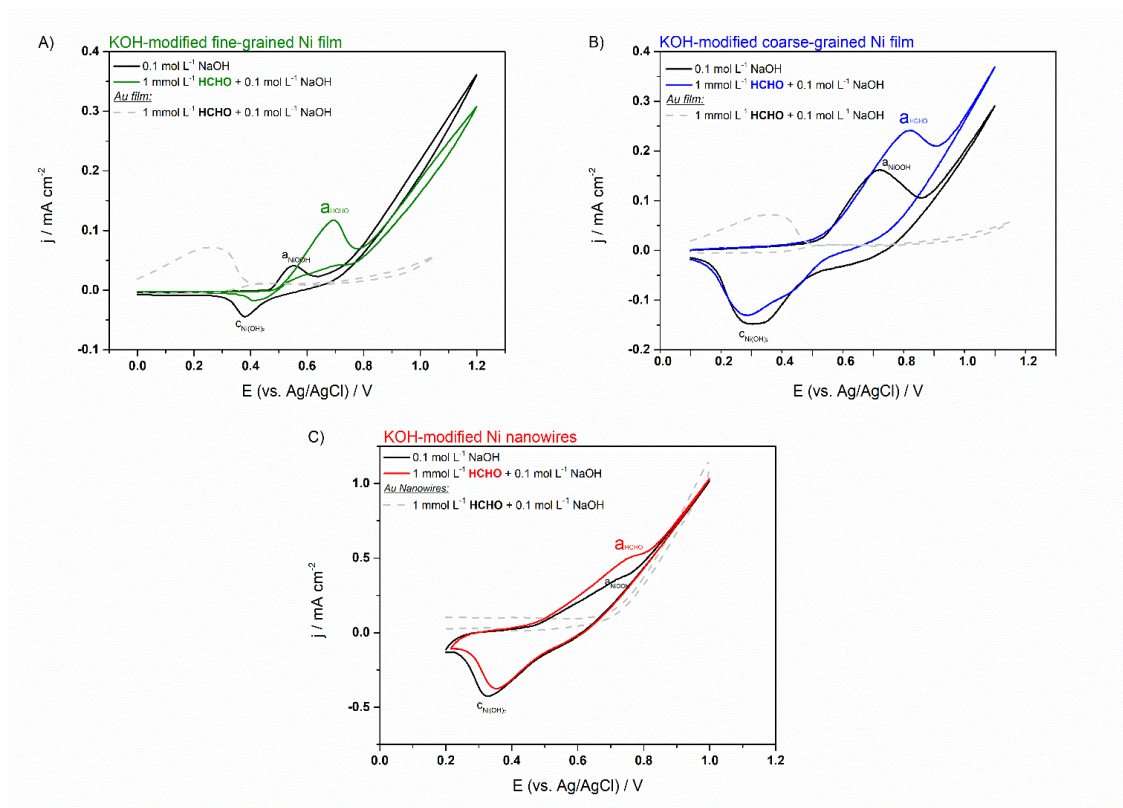


Figure 4.32: The CV profiles of the A) fine-grained Ni film, B) coarse-grained Ni film and C) Ni nanowires modified in KOH up to +0.6 V observed in 0.1 mol L⁻¹ NaOH solution (black curves) or 1 mmol L⁻¹ HCHO + 0.1 mol L⁻¹ NaOH solution at a scan rate 100 mV s⁻¹. The graphs A-C, grey curves, include the CV profiles of the bare Au electrodes (films or wires) observed in 1 mmol L⁻¹ HCHO + 0.1 mol L⁻¹ NaOH solution at a scan rate 100 mV s⁻¹.

These observations indicate that the HCHO is indeed oxidized by active Ni species on the Ni-based electrodes (fine-grained Ni film, coarse-grained Ni film and Ni nanowires) that were KOH-modified in the potential range up to 0.6 V. Depending on the CVs behaviour we can confirm that electro-oxidation of the HCHO in alkaline media occurs via Ni(OH)₂/NiOOH mediated electrolysis (Chapter 1.3.2.3).

4.3.3 Electrochemical catalysis of as-derived Ni electrodes

According to the above-obtained results, it was assumed that the best catalytic properties exhibit KOH-modified Ni nanowires.

In order to prove this, we combined and adapted CV curves of the KOH-modified Ni electrodes observed in 1 mmol L⁻¹ HCHO in 0.1 mol L⁻¹ NaOH solution, as it is shown in Figure 4.33, A. From this CV profiles, it can be seen that the increased current densities and decreased onset over-potentials were achieved in the sequence fine-grained Ni film < coarse-grained Ni film < Ni nanowires, meaning that KOH-modified Ni nanowires exhibit the best catalytic activity for HCHO detection. The output current values represented in Figure 4.33, A are normalized to the electrochemically active surface areas (A_{ecsa}) – see Chapter 4.2.

The electrocatalytic HCHO oxidation was therefore examined by Tafel plots (Chapter 1.1.1.2). The Tafel plot is an important indicator for evaluating HCHO catalysts, as it describes the influence of over-potential on the steady-state current. Based on the CV curves, the corresponding Tafel curves were constructed (Figure 4.33, B). A slope of the Tafel plots which reflects the charge transfer kinetics is determined by fitting CV data to the equation of $\eta = a + b \times \log|j|$, where η is an over-potential, b is the slope of Tafel curve and j

is the current density. From Figure 4.33, B it was observed that the slope for the Ni nanowires is slightly smaller than that for coarse-grained Ni film, and smaller than fine-grained Ni film, showing that the Ni nanowires electrode outperforms the Ni films-based electrodes.

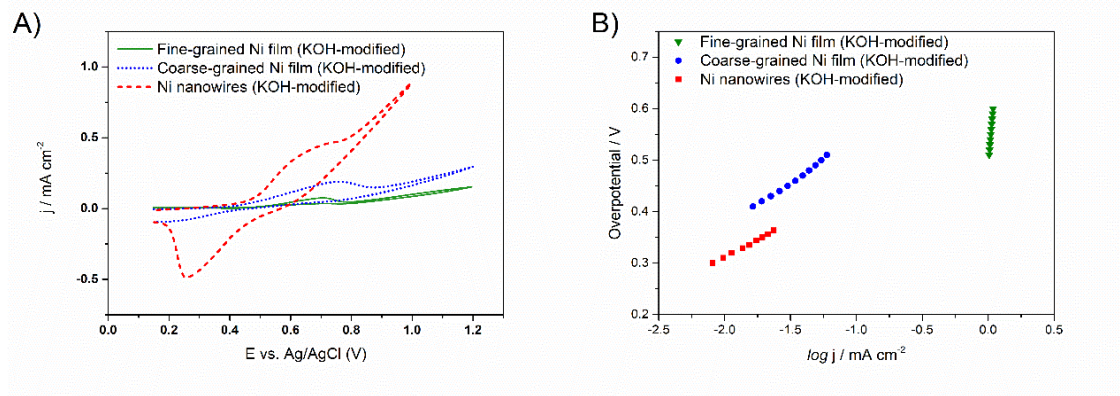


Figure 4.33: A) CV profile of KOH-modified Ni electrodes: green- fine-grained film, blue- coarse-grained film and red- nanowires; collected in 1 mmol L⁻¹ HCHO in 0.1 mol L⁻¹ NaOH solution at a scan rate of 100 mV s⁻¹; *current density values (j) = output current/ A_{ecsa}* . B) Tafel curves of KOH-modified Ni fine-grained film (green), coarse-grained film (blue) and nanowires (red); obtained from Figure A

In this chapter, it was shown that the KOH-modified Ni nanowires exhibit better catalytic activity compared to the KOH-modified fine-grained and coarse-grained Ni films. The improved catalytic properties, i.e. low onset over-potential and higher current density, can be correlated with the crystal structure of active Ni species (as it was already explained in Section 1.3.2.3.2). The amorphous nature of the formed Ni(OH)₂/NiOOH on the surface of nanowires that was proven by TEM and FT-IR contributes to the enhanced activity [75, 128]. It is known that due to their lattice distortion, abundant surface defects and electrochemical and mechanical stability [42, 76, 77, 129], amorphous/disordered Ni(OH)₂/NiOOH surface layer exhibit an improved performance in comparison to crystalline α - or β - phase [46, 75, 128, 130]. The crystalline α - or β -Ni(OH)₂/NiOOH-based catalysts have some disadvantages, e.g., low stability during the long electrochemical reactions [46, 52, 75].

Furthermore, according to Bode's diagram (Figure 1.20), the α -phase of Ni(OH)₂ is transformed into the γ -phase of NiOOH during the charging and discharging process in alkaline electrolyte. The $\alpha \leftrightarrow \gamma$ transformation requires the transfer of more than one electron (~ 1.6 – 1.67) since γ -NiOOH includes Ni(IV) cations. On the other hand, the transformation of disordered/amorphous Ni(OH)₂/NiOOH species on the surface of Ni nanowires includes the transfer of one-electron during the charging and discharging process in alkaline electrolyte. This fact can explain why the KOH-modified fine-grained and coarse-grained Ni film, containing α -Ni(OH)₂ surface species, display relatively poor electrocatalytic activity compared to the nanowires, containing disordered Ni surface species.

Moreover, given that the surface of both films is mostly composed by α -phase, it raises a question: "Why the KOH-modified fine-grained Ni films exhibit poorer catalytic activity towards HCHO in comparison to the KOH-modified coarse-grained Ni film?" The answer for this most probably originates from electrode preparation/transformation in KOH, i.e. KOH-modification. As it was already explained (Chapter 4.3.2.4.3., Figure 4.29 and Figure 4.30), both films probably contain a small amount of β -Ni(OH)₂ (the amount of surface α -phase $\gg$ the amount of surface β -phase) that is formed during potential cycling in KOH between the 10th and the 50th cycle (Figure 4.22, B and D). However, the coarse-grained Ni film may contain a slightly higher amount of β -Ni(OH)₂ compared to the fine-grained film according to the higher current densities of anodic (a_3) and cathodic (c_1) peak current densities observed in CVs presented in Figure 4.22, B and D. Due to these observations we can confirm that the slightly improved electro-catalysis of the coarse-grained film compared to the fine-grained film is a result of surface composition, since the coarse-grained film contains a

slightly higher amount of β -Ni(OH)₂. This surface β -phase contributes to the enhanced activity as it accelerates the HCHO electro-oxidation, because β -Ni(OH)₂/ β -NiOOH transformation requires the transfer of 1 electron, while α -/ γ -transformation requires ~ 1.6 electrons.

4.3.4 Electrochemical oxidation of HCHO on Ni nanowires KOH-modified at a different scan rate

Throughout the study, it was shown that the KOH-modified Ni nanowires exhibit the best catalytic activity towards HCHO in comparison to the other Ni electrodes (i.e. fine- and coarse-grained Ni films). At this point, we were wondering if we are able to improve the catalytic performance of Ni nanowires even more by manipulation of the thickness of the Ni(OH)₂/NiOOH active surface layer by changing certain parameters in the KOH-modification processes. It was already shown that the electro-catalytic oxidation of HCHO is sensitive to various KOH-modification parameters, such as the potential range and the number of scans. However, the effect of the scan rate in the KOH-modification process has still been unexplored. For the experiments above, a constant scan rate of 200 mV s⁻¹ was chosen according to the results obtained in Chapter 4.2.4. and the observations presented by Hall et al. [75] and Drunen et al. [85]. To verify the effect of the KOH-modification scan rate on the Ni(OH)₂/NiOOH formation and its HCHO electro-catalytic activity, as well as the electrode's surface composition and its thickness, various scan rates were used in KOH-modification processes.

4.3.4.1 KOH-modification of Ni nanowires at different scan rates

The free-standing Ni nanowire electrodes were KOH-modified at three different scan rates: 10 mV s⁻¹, 200 mV s⁻¹ and 400 mV s⁻¹. The CV profiles presented in Figure 4.34 were examined in 0.5 mol L⁻¹ KOH solution in a potential window from -1.0 V to 0.7 V in the 1st cycle (left) and from 0.2 V to 0.7 V in the 10th to the 50th cycle (right). As seen from the grey (10 mV s⁻¹), red (200 mV s⁻¹) and purple (400 mV s⁻¹) curves, the anodic peak potentials (a_1 - a_3) and the cathodic peak potentials (c_1) change with the variation of the scan rate. A major difference was observed in the 1st cycle at anodic peak potential for the formation of α -Ni(OH)₂(a_1), Figure 4.34, A. The CV profiles demonstrate that an increase of the scan rate (from 10–200 mV s⁻¹) shifts the peak a_1 towards more positive potential values and increases the peak current density. This phenomenon was explained by Alsabet et al. [47], where it was shown that KOH-formation of α -Ni(OH)₂ is accompanied by significant changes in its structure, i.e. huge atomic rearrangement, from Ni or NiO structures to turbostratic (brucite type) and distorted cubic α -Ni(OH)₂ structures. The rearrangement of adsorbed species (i.e. electro-crystallisation) could influence the structure and thickness of surface hydroxide layer and result in a scan rate/potential dependence relationship. Thus, the surface atomic rearrangement can be speculated to be the main reason for a shift in a peak potential of a_1 while changing the scan rate. With the continuation of potential cycling to the more positive potentials, the dehydration reaction occurs (a_2), which leads to the formation of stable and irreversible β -Ni(OH)₂. Also, this reaction includes an atomic rearrangement, meaning that this reaction occurs at a different potential while increasing the scan rates (as it was already explained). Once the stable β -Ni(OH)₂ is formed, enormous atomic rearrangements are no longer expected. The next increase in the anodic current densities occurs at a_3 due to the oxidation of Ni(OH)₂ to NiOOH. As it can be seen from Figure 4.34, A, the anodic current peaks (a_1 and a_2) cannot be observed from the CV of Ni nanowires sample that was KOH-modified at a scan rate of 400 mV s⁻¹. Nevertheless, the transformation of surface Ni/NiO to α -Ni(OH)₂ and then to β -Ni(OH)₂ most probably occurs according to the behaviour of this sample in the following cycles (explained below). However, the amount of surface species that are transformed in the 1st cycle is low due to the highest selected scan rate.

Figure 4.34, B presents a series of CV profiles for free-standing Ni nanowire electrodes recorded at different scan rates, 10 mV s⁻¹ (grey), 200 mV s⁻¹ (red) and 400 mV s⁻¹ (purple) from 10th–50th cycle. From CV plots, an increase of anodic peak (a_3) and cathodic peak (c_1) current densities was observed with increasing numbers of cycles from 10 to 50. However, the comparison of a_3 current densities of Ni nanowires KOH-modified at a scan rate of 10

(grey), 200 (red) and 400 (purple) mV s^{-1} for the 10th, 20th and 50th cycle leads to the following observations about the mechanism of thickening of Ni surface layers (NiO or $\text{Ni(OH)}_2/\text{NiOOH}$):

- 1) Ni nanowires KOH-modified at **10 mV s^{-1}** : from a comparison of a_3 current density values (Table 4.1), it can be deduced that the slight increase of a_3 current densities with increasing the number of cycles showing no significant enrichment of NiOOH layer from 10–50 cycles. This means that the thickening of NiOOH layer (by the migration of OH^- ; see reactions 1.27–1.29) occurs mostly in the first 10 cycles due to the slow scan rate. Although some reports [57] suggest that NiO can also be developed due to the migration of O_2 into Ni-Ni layer at a slow scan rate; this suggestion might explain why the current density of a_3 in the 10th cycle at a scan rate of 10 mV s^{-1} is higher than the current density of a_3 in the 10th cycle at a scan rate of 200 mV s^{-1} . To confirm this, i.e. the formation of NiO, an XRD analysis was taken (explained in the following chapter).
- 2) Ni nanowires KOH-modified at **200 mV s^{-1}** : from a comparison of a_3 current density values (Table 4.1) it can be concluded that the increase of a_3 current densities with increasing the number of cycles showing significant enrichment of NiOOH layer between 10–50 cycles due to the entry of OH^- into the Ni surface layers, see reactions 1.27–1.29, Chapter 1.3.2.2 [35, 48, 52]. However, it was already proven that the high scan rate limits the distribution of molecular oxygen into the Ni-Ni layer, and thus, limits the formation of cubic NiO.
- 3) Ni nanowires KOH-modified at **400 mV s^{-1}** : from a comparison of a_3 current density values (Table 4.1), it was assumed that there is no significant enrichment of NiOOH layer from 10th–50th cycle due to the very high scan rate. Furthermore, at such a high scan rate, the anodic current peak is shifted towards higher potentials, meaning that the resulting a_3 current density might be due to two phenomena occurring concurrently, namely, the formation of Ni(OH)_2 and oxygen evolution reaction (a_4) [47, 56].

Table 4.1: The a_3 current density values for Ni nanowire electrodes KOH-modified at different scan rates at the 10th, 20th and 50th cycle.

	$j(a_3) [\text{mA cm}^{-2}]$ 10th cycle	$j(a_3) [\text{mA cm}^{-2}]$ 20th cycle	$j(a_3) [\text{mA cm}^{-2}]$ 50th cycle
Ni nanowires KOH-modified at 10 mV s^{-1}	0.52	0.53	0.56
Ni nanowires KOH-modified at 200 mV s^{-1}	0.39	0.56	0.74
Ni nanowires KOH-modified at 400 mV s^{-1}	0.98	0.98	0.99

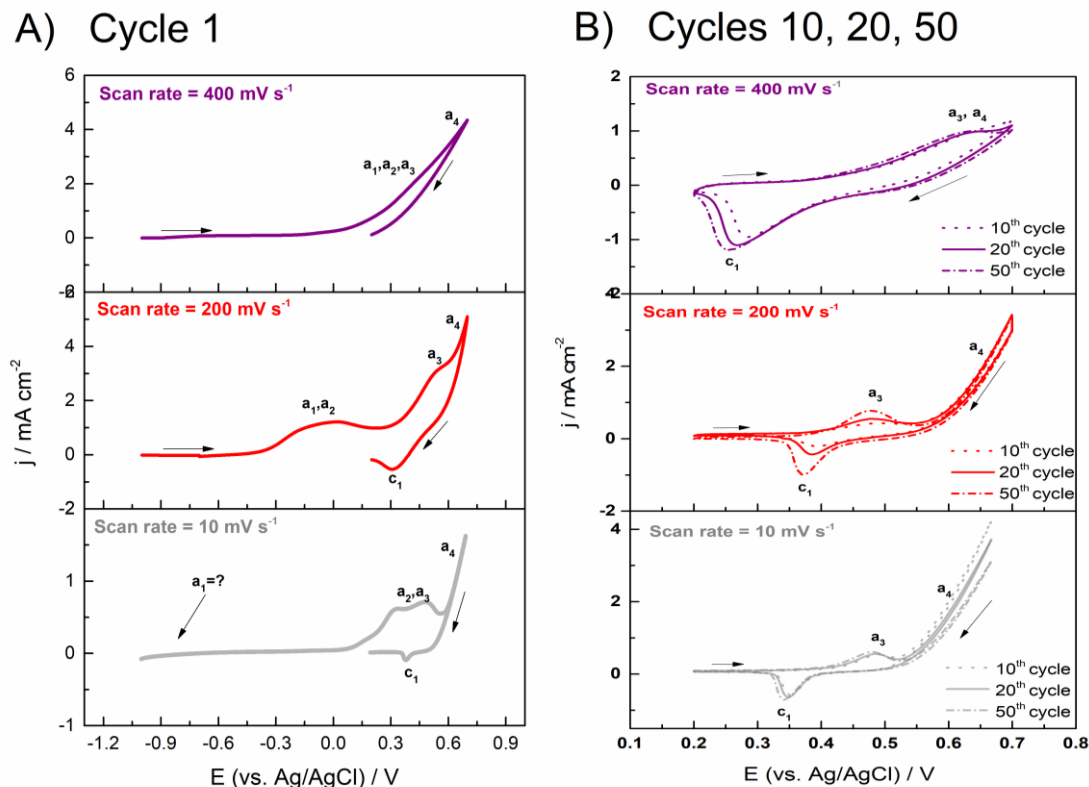


Figure 4.34: CV profiles of free-standing Ni nanowires electrode recorded in a de-aerated 0.5 mol L⁻¹ KOH solution from A) -1.0 V to +0.7 V in the 1st cycle and B) from 0.2 V to +0.7 V in the 10th–50th cycle at scan rates of 10 (grey), 200 (red) and 400 (purple) mV s^{-1} .

4.3.4.2 XRD of KOH-modified Ni nanowires at different scan rates

In order to investigate the composition and crystal structure of Ni nanowires after the KOH-modification (up to 50 cycles) at various scan rates, the Ni nanowire electrodes were analysed using XRD. Figure 4.35 A-C presents a typical XRD pattern of the composition of Ni nanowire electrodes recorded in the 2-theta range of 10–90° after KOH-modification (50 cycles) in KOH at a scan rate of 10 mV s^{-1} (A, grey), 200 mV s^{-1} (B, red) and 400 mV s^{-1} (C, purple). For all three samples, similar patterns were obtained in the 2-theta range from 35° to 90°. In this 2-theta range the XRD patterns confirm the presence of (1 1 1), (2 0 0) and (2 2 0) planes of fcc Ni (ICDD 00-001-1258) and the (1 1 1), (2 0 0), (2 2 1), (3 1 1) and (2 2 2) crystalline planes of the cubic Au (ICDD 01-089-3697).

By comparing the insets obtained in a narrow 2-theta range (5–35°), certain differences have been observed among samples that were KOH-modified at different scan rates. XRD measurements of Ni nanowires electrode KOH-modified at a scan rate of 10 mV s^{-1} (Figure 4.35 A, inset) showed the presence of a cubic (1 1 1)-oriented NiO at 32.5° (ICDD 04-006-6545), while this diffraction peak was not indexed in the other two samples (B and C) that were KOH-modified at faster scan rates. Furthermore, in Figure 4.35, A and B, a broad hump at 10° is observed in the XRD pattern of the samples KOH-modified at 10 mV s^{-1} and 200 mV s^{-1} , indicating poor crystallinity of the Ni(OH)₂. On the basis of the XRD results, the absence of well-crystalline surface β -Ni(OH)₂ was confirmed. However, the amorphous nature of surface Ni(OH)₂ on the surface of sample B – KOH-modified at a scan rate of 200 mV s^{-1} – was already proven by TEM (Figure 4.27). The XRD data (Figure 4.35, A and C) also revealed the presence of NaOH (reflection at ~30°) which precipitates during AAO etching.

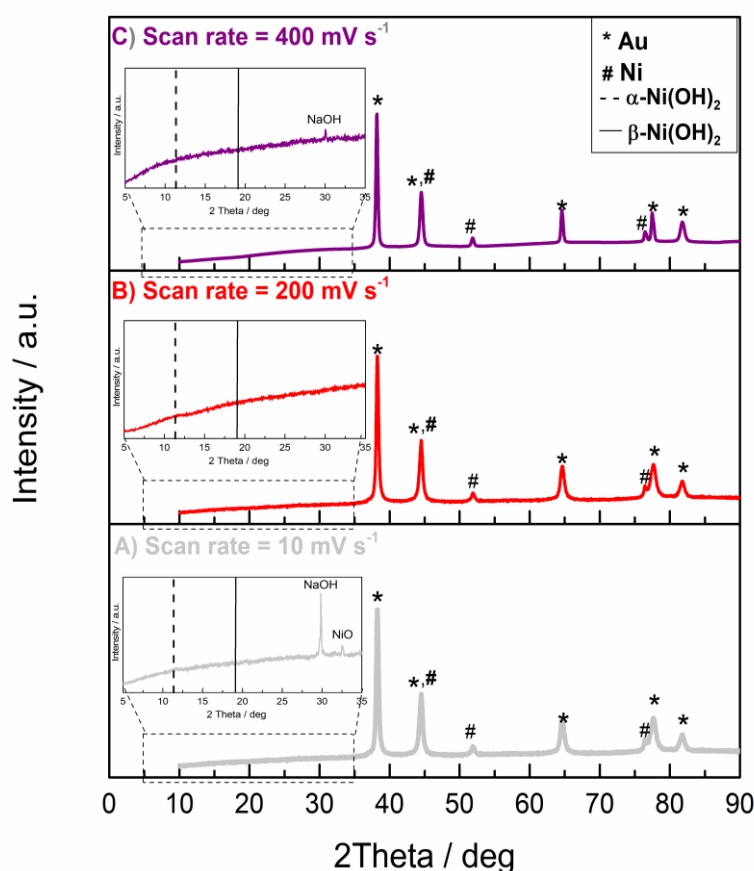


Figure 4.35: XRD spectra of the free-standing Ni nanowires electrode, KOH-modified at scan rates: A) 10 (grey), B) 200 (red) and C) 400 (purple) mV s^{-1} . XRD spectra were collected at 2 theta of 10–90° and 5–35° (inset). The inset corresponds to the region where the characteristic peaks for Ni_xO_y and α - or β - $\text{Ni}(\text{OH})_2$ were expected.

However, the XRD results in correlation with CV curves presented in Figure 4.34 brought us to a conclusion about the surface transformation after KOH-modification (after 50 cycles):

- 1) **The surface composition of Ni nanowires electrode that was KOH-modified at a scan rate of 10 mV s^{-1}** (Figure 4.36): the relatively slow potential cycling (10 mV s^{-1}) increases the thickness of both the outer hydroxide layer (most probably amorphous) and the inner (1 1 1)-oriented NiO layer (detailed explanation of thickening surface layers is described in Introduction – Chapter 1.3.2.2):
 - a) The thickening of the outer hydroxide layer occurs at the anodic current peak a_3 (Figure 4.34, B, grey curve) due to the OH^- ions dispersion into the I) $\text{Ni}(\text{OH})_2$ outer layer ($\text{Ni}(\text{OH})_2 + \text{OH}^- - e^- \rightarrow \text{NiOOH} + \text{H}_2\text{O}$), II) (1 1 1)-oriented NiO interlayer ($\text{NiO} + \text{OH}^- - e^- \rightarrow \text{NiOOH}$) or III) Ni inner layer ($\text{Ni} + 3\text{OH}^- - 3e^- \rightarrow \text{NiOOH}$) layers.
 - b) The thickening of the inner NiO layer occurs by the application of higher potentials (Figure 4.34, grey curve, see anodic peak a_4) which leads to the production of molecular oxygen that can be trapped into the Ni-Ni layer.

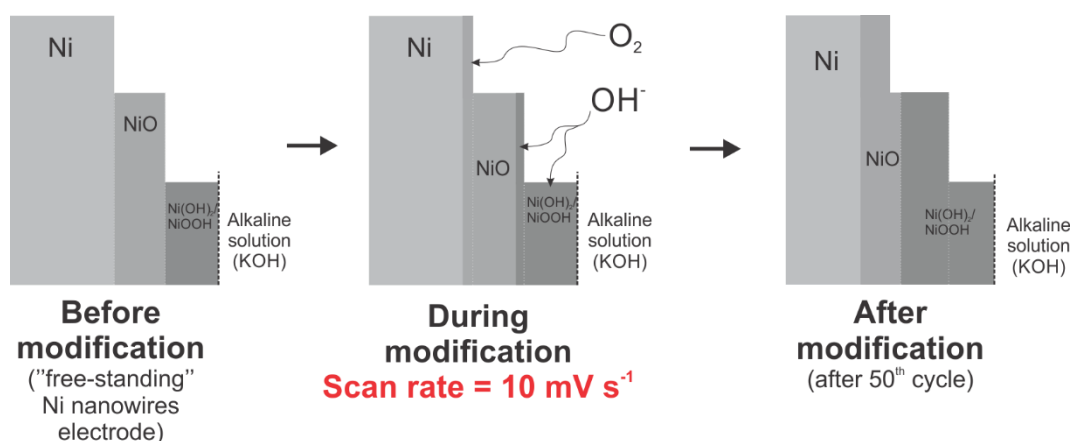


Figure 4.36: The schematic presentation of the Ni nanowires-based surface layers transformation during KOH-modification at a scan rate of 10 mV s^{-1} .

- 2) **The surface composition of Ni nanowires electrode that was KOH-modified at a scan rate of 200 mV s^{-1}** (Figure 4.37): a KOH-modification of the Ni nanowires electrode at a higher scan rate (200 mV s^{-1}) shows some significant changes in the composition of surface (NiO and Ni(OH)_2) layers. XRD data showed that such a modified electrode does not show the presence of NiO (1 1 1)-oriented as it is removed/transformed during the oxidation/reduction cycling at a scan rate of 200 mV s^{-1} . The potential cycling of 200 mV s^{-1} , therefore, increases the thickness of only the outer hydroxide layer (amorphous, proved by TEM):

- The redox peak a_3 in KOH-modification process (Figure 4.34, B, red curve) can be accounted for I) by OH^- migration to the surface Ni(OH)_2 , II) OH^- adsorption into (1 1 1)-oriented NiO and/or III) OH^- adsorption into Ni inner.
- The scan rate of 200 mV s^{-1} is high and most probably limits the thickening of the NiO layer by the fast diffusion of OH^- to the underlying Ni layer. Upon that the propagation of oxygen molecules into the Ni lattice is inhibited.

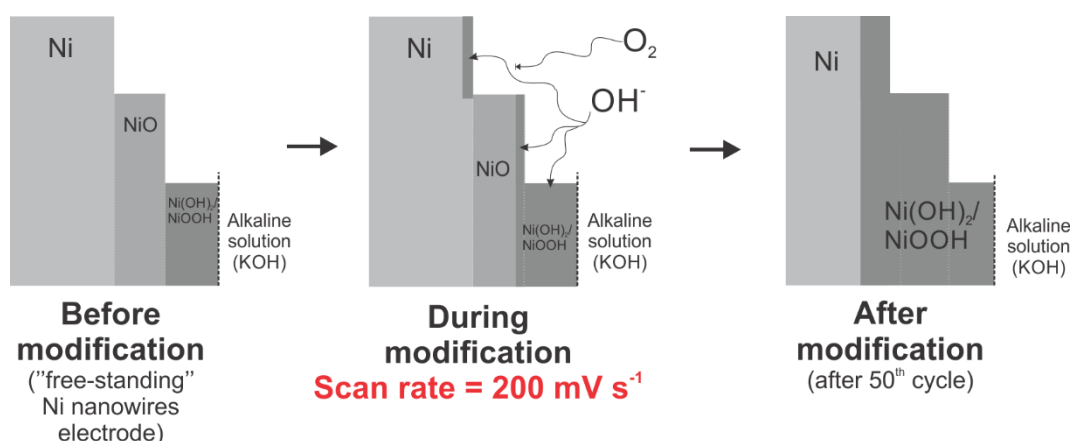


Figure 4.37: The schematic presentation of the Ni nanowires-based surface layers transformation during KOH-modification at a scan rate of 200 mV s^{-1} .

- 3) **The surface composition of Ni nanowires electrode that was KOH-modified at a scan rate of 400 mV s^{-1}** (Figure 4.38): for the electrode that was KOH-modified at an even higher scan rate (400 mV s^{-1}), it was assumed that:

- The thickening of the outer hydroxide layer occurs at the anodic current peak a_3 (Figure 4.34, B, purple curve) due to the OH^- ions dispersion into the I) $\text{Ni}(\text{OH})_2$ outer layer ($\text{Ni}(\text{OH})_2 + \text{OH}^- - e^- \rightarrow \text{NiOOH} + \text{H}_2\text{O}$), and II) (1 1 1)-oriented NiO interlayer ($\text{NiO} + \text{OH}^- - e^- \rightarrow \text{NiOOH}$), while the diffusion of the OH^- to the Ni lattice ($\text{Ni} + 3\text{OH}^- - 3e^- \rightarrow \text{NiOOH}$) is limited due to the extremely high scan rate. Therefore, such a modified sample (at a scan rate of 400 mV s^{-1}) contains less $\text{Ni}(\text{OH})_2$ surface species than the sample that was KOH-modified at a scan rate of 200 mV s^{-1} .
- The potential cycling is too fast to increase the thickness of the NiO layer by the propagation of O_2 into the inner layers.

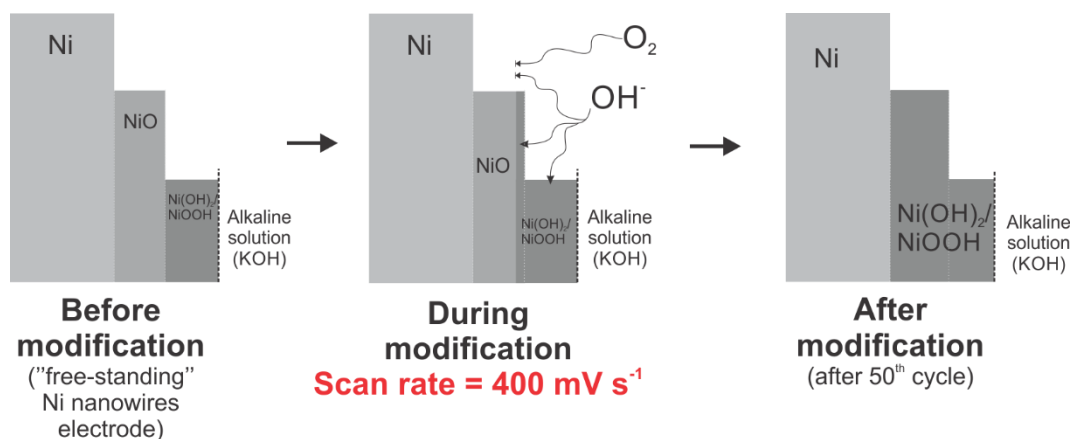


Figure 4.38: The schematic presentation of the Ni nanowires-based surface layers transformation during KOH-modification at a scan rate of 400 mV s^{-1} .

Thus, from XRD results it was concluded that the scan rate is a very important parameter which induces significant changes of the Ni-based layers in terms of chemical composition and crystallographic structures of surface-active species indicative of HCHO electro-oxidation.

4.3.4.3 Electrochemical oxidation of HCHO on KOH-modified Ni nanowires at different scan rates

The electro-catalytic activity of differently KOH-modified Ni nanowire electrodes towards the oxidation of HCHO was investigated by voltammetric responses (Figure 4.39). The CV profiles of Ni nanowires that were KOH-modified at a scan rate of 10 mV s^{-1} (grey), 200 mV s^{-1} (red) and 400 mV s^{-1} (purple) were observed in 4 mmol L^{-1} HCHO and 0.1 mol L^{-1} NaOH solution at a scan rate of 100 mV s^{-1} . Figure 4.39 (red curve) represents a Ni nanowires electrode that was KOH-modified at a scan rate of 200 mV s^{-1} , where a redox couple peaked around 0.75 V in anodic region/ 0.3 V in the cathodic region were observed. These peaks can be attributed to the conversion between $\text{Ni}(\text{OH})_2$ and NiOOH (detailed explanation in Chapter 4.3.2.5, Figure 4.32, C). Also, a rapid rising of an anodic current density at potentials $> 0.85 \text{ V}$ that correspond to oxygen-evolving.

Furthermore, there is a small current densities increase in the anodic peaks of HCHO oxidation (a_{HCHO}), 0.25 mA cm^{-2} and 0.2 mA cm^{-2} , and in the cathodic current peaks (c_{HCHO}), -0.19 mA cm^{-2} and -0.17 mA cm^{-2} , at Ni nanowire electrodes that were KOH-modified at a scan rate of 10 mV s^{-1} (grey) and 400 mV s^{-1} (purple), respectively. In the HCHO-containing electrolyte, the anodic peak a_{HCHO} can be ascribed to the oxidation of $\text{Ni}(\text{OH})_2$ to NiOOH and the production of a $\text{Ni}(\text{OH})_2$ through the reaction of NiOOH and HCHO (described in Chapter 1.3.2.3, $\text{Ni}(\text{OH})_2/\text{NiOOH}$ mediated electrolysis). These results show that HCHO may be oxidised by Ni nanowire electrodes KOH-modified at a scan rate of 10 (grey) and 400 (purple) mV s^{-1} , but the catalytic activity of these two electrodes is much lower, i.e. decreased current density ($\geq 50\%$) and higher onset over-potential ($\geq 20\%$) compared to the Ni nanowires electrode that was KOH-modified at a scan rate of 200 mV s^{-1} (red).

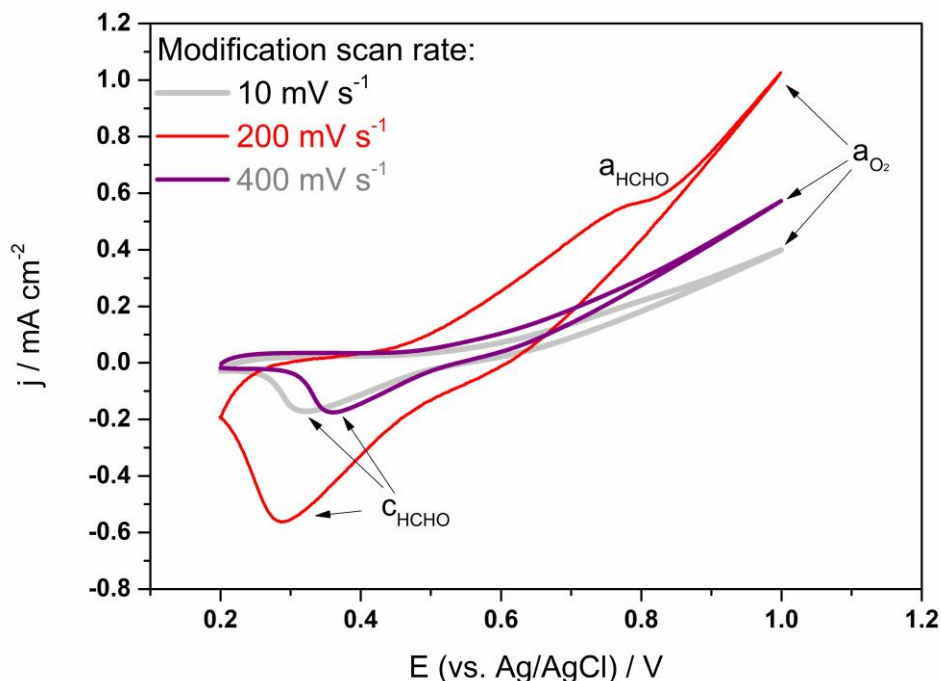


Figure 4.39: CV profiles of KOH-modified Ni electrodes at a scan rate of 10 (grey), 200 (red) and 400 (purple) 100 mV s^{-1} ; collected in 4 mmol L^{-1} HCHO in 0.1 mol L^{-1} NaOH solution at a scan rate of 100 mV s^{-1} .

To summarise this chapter, it was proven that the composition of Ni surface species and their electro-catalytic efficiency towards HCHO oxidation (Figure 4.39) could be controlled by varying the scan rate in the KOH-modification process. These crystallographic, morphological and chemical changes in alkaline solutions upon potential cycling play a crucial role in the electro-catalytic oxidation of HCHO by accelerating or hindering the electron transfer. Based on the XRD (Figure 4.35) and CV (Figure 4.34) results we concluded that the presence of native NiO interlayer, which is present in the surface of Ni nanowires electrode that was KOH-modified at a scan rate of 10 mV s^{-1} , is the underlying reason for the drop of electrocatalytic activity of Ni nanowires electrode towards HCHO. The main reason for the lower electro-catalytic performance can be explained by the electron injection mechanism to manipulate the work function and to shift the Fermi level of catalytic active NiOOH species (presented by Wang et al. [46] and described in detail in Chapter 1.3.2.3.1). If the thin layer of NiOOH is in direct contact with the metallic Ni, the electrons from the metallic Ni can be easily transferred to the NiOOH. Electron injection builds up a strong internal electric field at the Ni/NiOOH interface that lifts the Fermi surface of the catalysts and enhances the electron transfer. Such behaviour can be attributed to the Ni nanowires electrode that was KOH-modified at a scan rate of 200 mV s^{-1} . However, once the direct contact is interrupted with the interlayer of native NiO, the distance between the electron-rich substrate (Ni) and electroactive NiOOH exceeds the value of d , as presented in Figure 4.40. The electron injection is inhibited, the corresponding work function of NiOOH increases, and further, the electron transfer is slower. Consequently, the onset overpotential of Ni/NiO/NiOOH nanowires electrode tends to increase, and the current density decreases. Such behaviour can be ascribed to the Ni nanowires electrode that was KOH-modified at a scan rate of 10 mV s^{-1} .

The Ni nanowires electrode KOH-modified at a scan rate of 400 mV s^{-1} was found to gain better electro-catalytic activity in comparison to the one KOH-modified at 10 mV s^{-1} (higher current density, $\sim 20\%$ and lower onset-overpotential, $\sim 10\%$), due to the absence of native NiO. Based on the HCHO-CV behaviour (Figure 4.39, purple), the surface of this electrode is

covered by $\text{Ni}(\text{OH})_2$ which is most probably amorphous, since its presence could not be confirmed by XRD. However, the catalytic activity is still inferior to that KOH-modified at 200 mV s^{-1} . The lower electro-catalytic-activity, in this case, can be ascribed to the corresponding decrease in the amount of active sites of NiOOH due to the fast scan rate in the KOH-modification process, as described in the previous chapter.

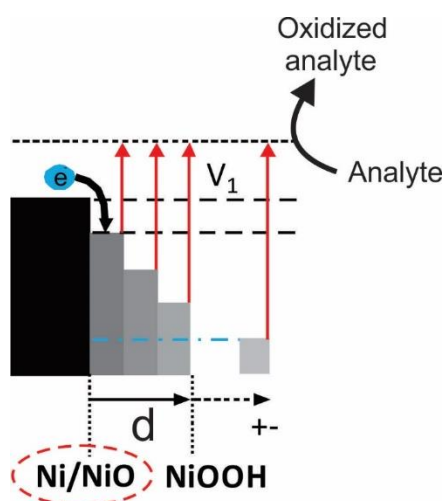


Figure 4.40: Schematic presentation of $\text{NiOOH}/\text{NiO}/\text{Ni}$ catalysts, where d represents the thickness of the NiO layer, and red arrows the values of the work function.

In this chapter, it was shown that the modification (potential cycling) in KOH is essential to modify the as-deposited Ni nanowire surfaces to consist of surface-active species ($\text{Ni}(\text{OH})_2/\text{NiOOH}$). It was found that a scan rate of 200 mV s^{-1} is suitable for the formation of a several-nanometres-thick layer of $\text{Ni}(\text{OH})_2/\text{NiOOH}$, without the presence of native NiO which hinders the electron transfer in HCHO electro-catalytic oxidation. Benefitting from the structural merits, i.e. amorphous nature (proved by TEM, Section 4.3.2.4.3), and the manipulated surface work function of the NiOOH , KOH-modified amorphous $\text{Ni}(\text{OH})_2\text{-Ni}$ nanowires exhibit an enhanced electron transfer, high HCHO oxidation currents and high signal-to-noise ratios in comparison to non-modified Ni NWs.

4.3.5 Sensory properties and characteristics of KOH-modified Ni electrodes

Sensory properties and characteristics are usually characterised by a number of analytical merits such as linear dynamic range, sensitivity and detection limit [10]. To gain an insight into the sensory performance of the KOH-modified Ni electrodes (fine-grained Ni film, coarse-grained Ni film and Ni nanowires) for HCHO electro-oxidation, we studied the effect of different concentrations of HCHO on the electrode's voltammetric and amperometric response.

4.3.5.1 Cyclic voltammetry study

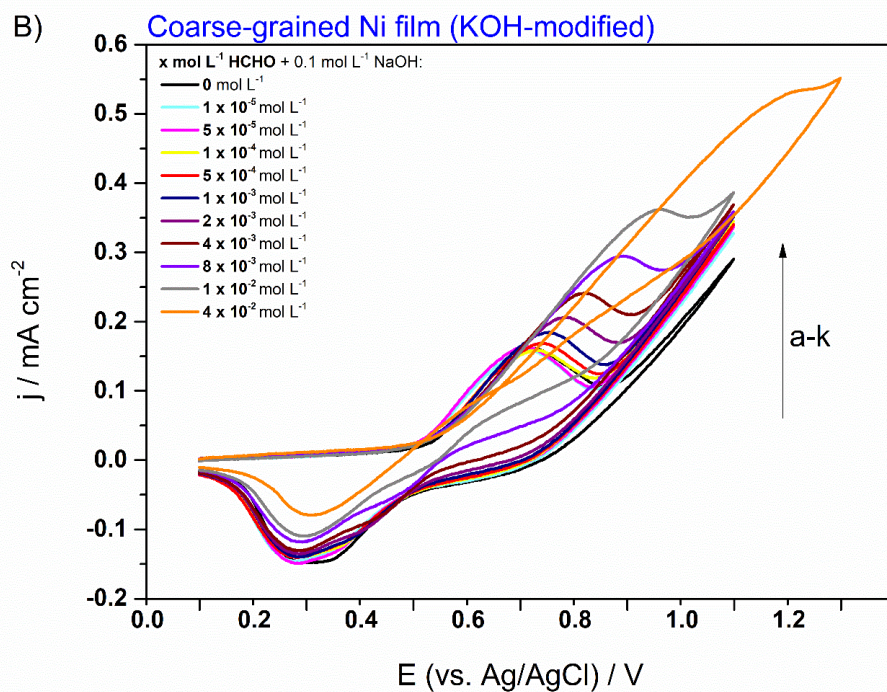
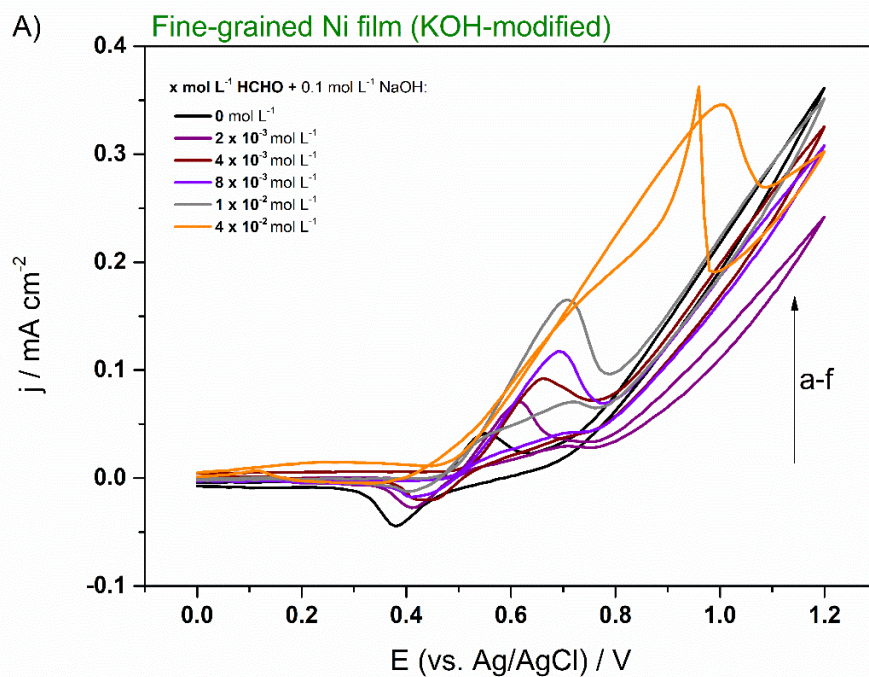
Cyclic voltammetry studies were performed on Ni electrodes KOH-modified in the potential window up to 0.6 V. Figure 4.41 shows the CV behaviour of A) fine-grained Ni film, B) coarse-grained Ni film and C) Ni nanowires each observed in the various concentrations of HCHO in 0.1 mol L^{-1} NaOH solution at a scan rate of 200 mV s^{-1} .

The CVs of fine-grained Ni film (Figure 4.41, A) were recorded in an HCHO concentration range of $0 - 4 \times 10^{-2} \text{ mol L}^{-1}$ from 0 V to the 1.2 V. The CV profile recorded only in 0.1 mol L^{-1} NaOH solution (black) showed the behaviour as it was already described in Figure 4.32, A. After the addition of various HCHO concentrations ranging from $2 \times 10^{-3} - 4 \times 10^{-2} \text{ mol L}^{-1}$ into the 0.1 mol L^{-1} NaOH solution, the HCHO oxidation peak potential shifted to more positive potentials (from the 0.6 V to the 1.0 V) and the HCHO oxidation peaks current

density increases from $0.05\text{--}0.35\text{ mA cm}^{-2}$ with increasing the HCHO concentrations. Quite an unusual CV profile was observed from the orange curve where 40 mmol L^{-1} HCHO was used; the apex that appeared in the reverse scan most probably indicates the saturation of the electrode.

The CVs of coarse-grained Ni film (Figure 4.41, B) showed similar behaviour to those observed for fine-grained Ni film. In the absence of HCHO (black curve), expected anodic and cathodic current peaks were observed (described in Figure 4.32, B). After the addition of different HCHO concentrations ($1 \times 10^{-5} - 4 \times 10^{-2}\text{ mol L}^{-1}$) into the NaOH solution, the oxidation peaks current density increases (from $0.15\text{--}0.5\text{ mA cm}^{-2}$) and, as expected, also the oxidation peak potentials shifted to a more positive region (from $0.7\text{--}1.2\text{ V}$).

Also, the CV responses of the Ni nanowires were similar to those observed on the fine- and coarse-grained Ni films. Various HCHO concentrations, ranging from $1 \times 10^{-6} - 1 \times 10^{-2}\text{ mol L}^{-1}$ of HCHO in 0.1 mol L^{-1} NaOH, were used (Figure 4.41, C). In the absence of HCHO (black curve), one couple of well-defined $\text{Ni(OH)}_2/\text{NiOOH}$ redox peaks was observed (already described in Figure 4.32, C). Once the HCHO was added into 0.1 mol L^{-1} NaOH, the anodic peak current increased (from $0.35\text{--}0.8\text{ mA cm}^{-2}$), and the peak potential slightly shifted to more positive potentials (from $0.5\text{--}0.9\text{ V}$).



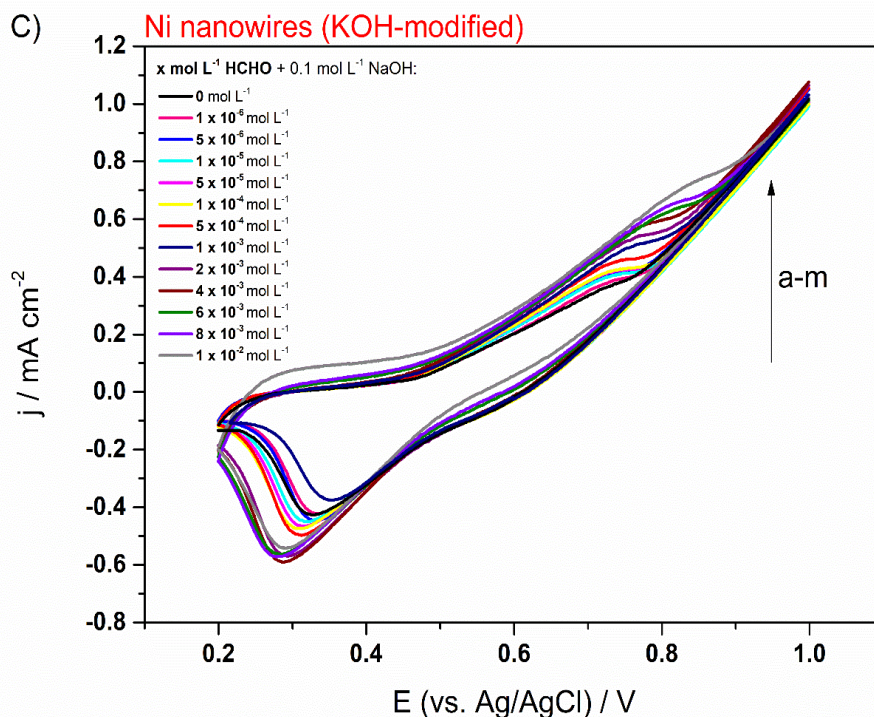


Figure 4.41: CV curves of the KOH-modified Ni-based electrodes; obtained in different concentration ranges of HCHO in 0.1 mol L⁻¹ NaOH solution at a scan rate of 100 mV s⁻¹: A) fine-grained Ni film (0 – 4 × 10⁻² mol L⁻¹ HCHO), B) coarse-grained Ni film (0 – 4 × 10⁻² mol L⁻¹ HCHO), and C) Ni nanowires (0 – 1 × 10⁻² mmol L⁻¹ of HCHO).

From CVs of KOH-modified Ni-based electrodes, including fine-grained Ni film, coarse-grained Ni films and Ni nanowire electrodes, several important pieces of information were observed:

- The examination of CVs shows that upon the addition of HCHO, the anodic peak current mainly arises from the oxidation of Ni(OH)₂ species to NiOOH. Moreover, the one with the higher valence oxidises formaldehyde via chemical reaction followed by the generation of low-valence nickel, Ni(OH)₂. Taking into account all these observations and in agreement with the literature [33-37], we reconfirmed the mechanism of mediated HCHO electro-oxidation (explained in Chapter 1.3.2.3).
- From CV curves, we also observed that the anodic peak potential shifts to high potential, which may be attributed to the IR drop arising from high current density values at high HCHO concentrations [30].
- At potentials ~1.0 V the HCHO anodic peak current (*a*_{HCHO}) is shifted to the region where the reaction of oxygen evolution is dominant; meaning that the Ni surface can be saturated by O₂ (this can explain the quite unusual shape of the CV in the reverse scan of the orange curve in Figure 4.41, A). To find the concentration at which the electrode surface is saturated, the graph that represents the HCHO concentration as a function of HCHO oxidation peak potential was constructed for all three Ni electrodes (Figure 4.42, A-C). From Figure 4.42, A-C, it can be observed that the current peak potential linearly increases with increasing the HCHO concentration up to 0.04 mol L⁻¹, after which the concentration reached almost a constant value. Thus, a concentration value of 0.04 mol L⁻¹ represents a critical concentration after which the adsorption of the oxygen at the electrode surface causes the hindrance of HCHO further oxidation [30]. Above the critical concentration, the electrode is saturated with oxygen, and the measurements of higher HCHO concentrations are no longer reliable.

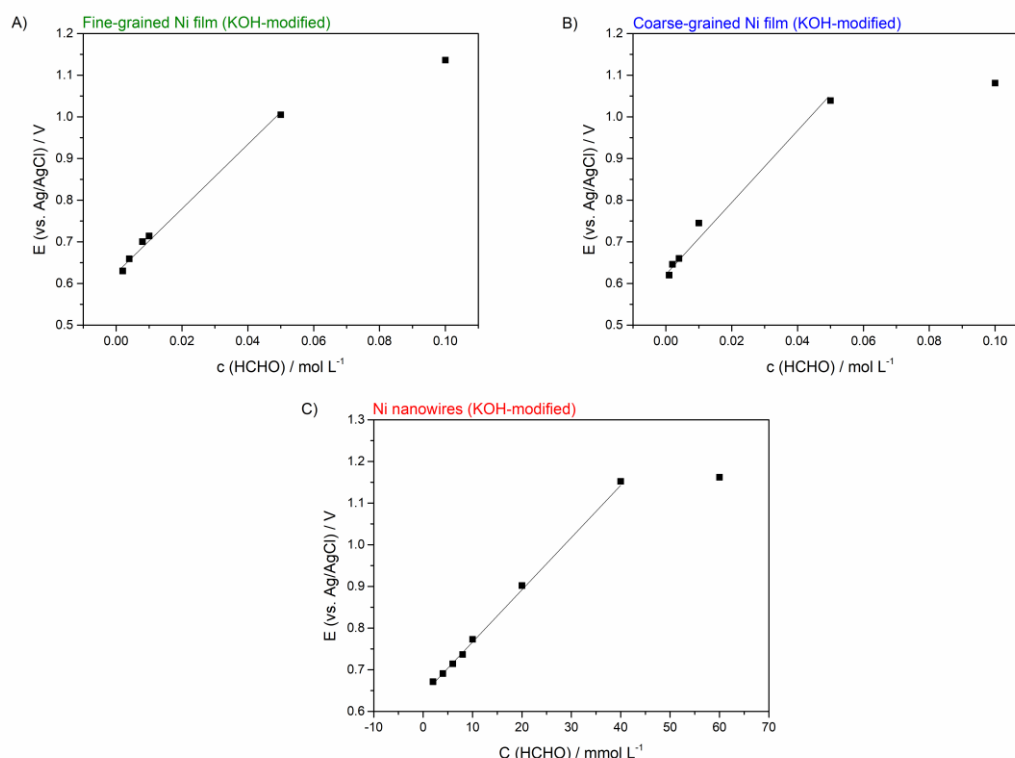


Figure 4.42: Variation of the peak potential of HCHO oxidation with its concentration on A) fine-grained Ni electrode, B) coarse-grained Ni electrode, and C) Ni nanowires electrode.

4.3.5.2 Chronoamperometry study

Rapid, sensitive and accurate detection of HCHO has become a major concern because it is a by-product of several important oxidation reactions. To evaluate the response time, the sensitivity and detection limit of the KOH-modified Ni electrodes, amperometric measurements were performed at various concentrations of HCHO under optimal potentials (determined based on oxidation peak potential from CVs in Figure 4.41).

A typical current-time plot of the KOH-modified fine-grained Ni film after the addition of certain concentration of HCHO (from 0.1 – 80 mmol L⁻¹) into 0.1 mol L⁻¹ NaOH is given in Figure 4.43. The working potential was set at 0.7 V for 10 s. It was found that the current density increases as the HCHO concentration increases, from 0.1 – 60 mmol L⁻¹ (curve a-l). This result supports the observation obtained from CVs (Figure 4.41, A). At the concentration of 80 mmol L⁻¹ (black dot curve) a slight decrease in the current density was observed, which indicates that the electrode is already saturated.

CA measurements were employed to further examine the response time of KOH-modified fine-grained Ni film electrode. As shown in Figure 4.43 the electrode responded rapidly, since the sharp rise in the current density was observed in the first second. This means that HCHO oxidation starts directly after the formation of the first NiOOH molecules (as presented by reactions 1.32 and 1.33) on the surface of the electrode. Furthermore, the KOH-modified fine-grained Ni electrode reached a steady-state within 5 s after the addition of 4 mmol L⁻¹ (burgundy) – 60 mmol L⁻¹ (green) HCHO into the NaOH solution. However, after the addition of lower HCHO concentrations (from 0.1 – 4 mmol L⁻¹), the steady-state was reached in time from 8 to 10 s. These results demonstrate that the KOH-modified fine-grained Ni film electrode has a fast response time only in a narrow HCHO concentration range from 4 mmol L⁻¹– 60 mmol L⁻¹.

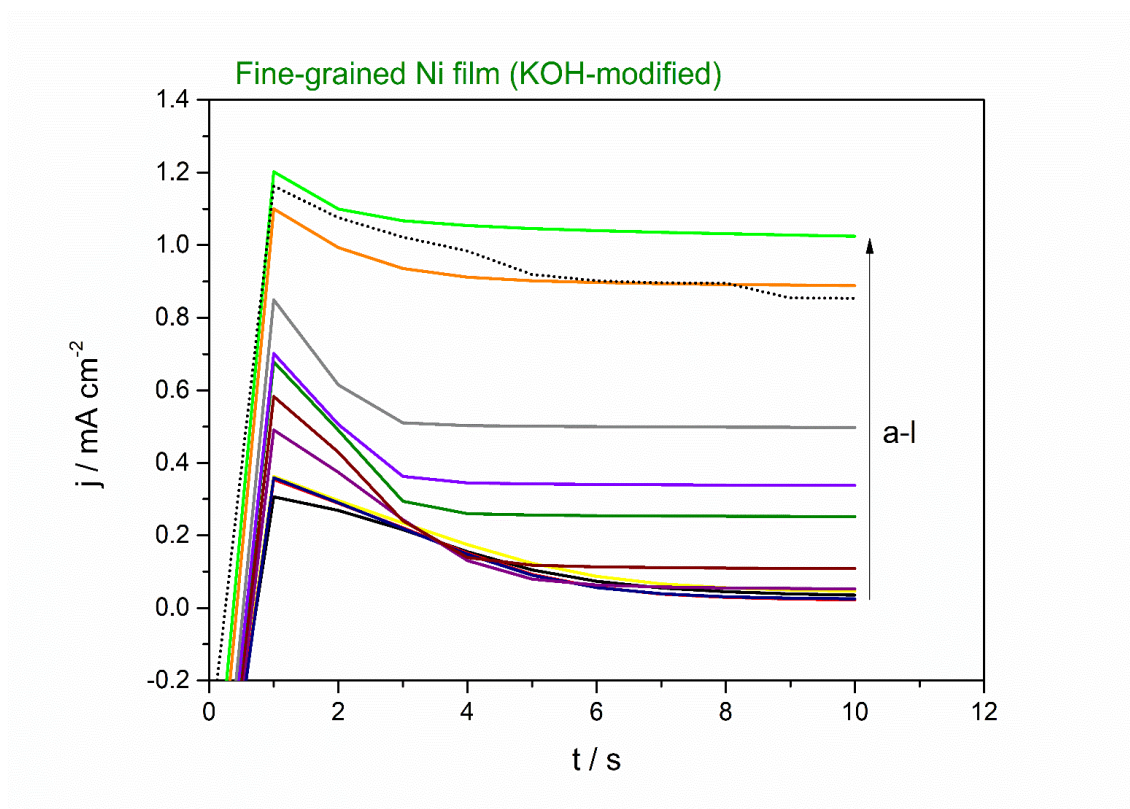


Figure 4.43: Chronoamperograms obtained at the KOH-modified fine-grained Ni film-based electrode a) in the absence of HCHO (black) and in the presence of b) 0.1 (yellow), c) 0.5 (red), d) 1.0 (navy blue), e) 2.0 (purple), f) 4.0 (burgundy), g) 6.0 (olive green), h) 10 (violet), i) 20 (grey), j) 40 (orange), k) 60 (green) and l) 80 (black dots) mmol L⁻¹ HCHO in a 0.1 mol L⁻¹ NaOH solution; observed under a constant potential of 0.7 V for 10 s.

Figure 4.44 shows the chronoamperograms for the KOH-modified coarse-grained Ni film electrode obtained by setting the working electrode potential at 0.7 V for 10 s for various concentrations of HCHO (0.01 – 100 mmol L⁻¹) in 0.1 mol L⁻¹ NaOH. As can be seen from results, the current density increases as the HCHO concentration increases from 0.01 mmol L⁻¹ (cyan, $j \approx 0.45$ mA cm⁻²) to 80 mmol L⁻¹ (pink, $j \approx 1.45$ mA cm⁻²). At the HCHO concentration of 100 mmol L⁻¹ (black dot curve, $j < 1.4$ mA cm⁻²), a slight decrease in the current density was observed meaning that the electrode is already saturated. These results confirm the observation from the potential-concentration plot (Figure 4.42, B) where the saturation of the coarse-grained Ni film was determined to be in the range from 40 – 100 mmol L⁻¹.

When certain concentrations of HCHO were added to the 0.1 mol L⁻¹ NaOH, the KOH-modified coarse-grained Ni film responded rapidly, as it is seen from the sharp current density rise in the 1st second (Figure 4.44). This was followed by an exponential drop until the steady-state was reached: within 8 s for all the concentrations.

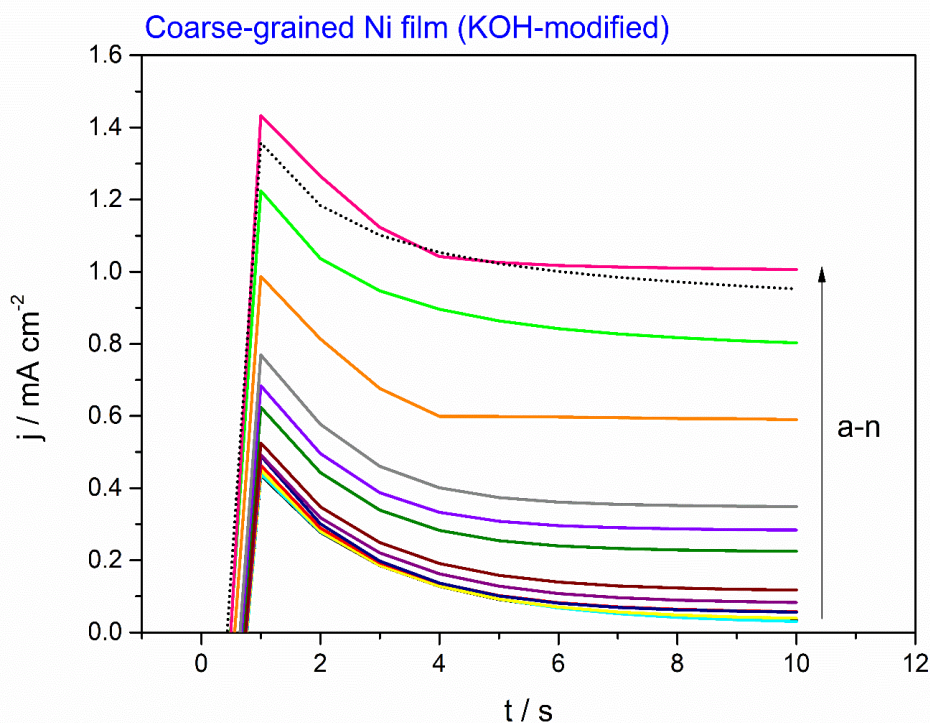


Figure 4.44: Chronoamperograms obtained at the KOH-modified coarse-grained Ni film-based electrode a) in the absence of HCHO (black) and in the presence of b) 0.01 (cyan), c) 0.1 (yellow), d) 0.5 (red), e) 1.0 (navy blue), f) 2.0 (purple), g) 4.0 (burgundy), h) 6.0 (olive green), i) 10 (violet), j) 20 (grey), k) 40 (orange), l) 60 (green), m) 80 (pink) and n) 100 (black dots) mmol L⁻¹ HCHO in a 0.1 mol L⁻¹ NaOH solution; observed under a constant potential of 0.7 V for 10 s.

Figure 4.45 shows the current-time curves of the KOH-modified Ni nanowires electrode in the absence (black) and the presence of the desired concentrations of HCHO (from 0.8 to 60 mmol L⁻¹) in a 0.1 mol L⁻¹ NaOH solution. The amperometric response was measured at an applied potential of 0.7 V, corresponding to the HCHO anodic current peak in CV (Figure 4.41, C). In the absence of HCHO (black) and by the addition of the desired HCHO concentrations, the current densities reached the maximum current density in the 1st second. As the HCHO concentration increases from 0.8–40 mmol L⁻¹, the current density increases, which is consistent with that of the CV. At HCHO concentrations higher than 40 mmol L⁻¹, the current density reached almost a constant value (black dots), indicating that the electrode is saturated in between 40 – 60 mmol L⁻¹ HCHO concentration in the 0.1 mol L⁻¹ NaOH solution. Regarding the response time, Figure 4.45 shows a sharp rise in the current density in the 1st second for all the applied HCHO concentrations. This indicates that the oxidation of HCHO occurs quickly as soon as the first molecules of NiOOH are formed and reaches the steady-state within 4 s.

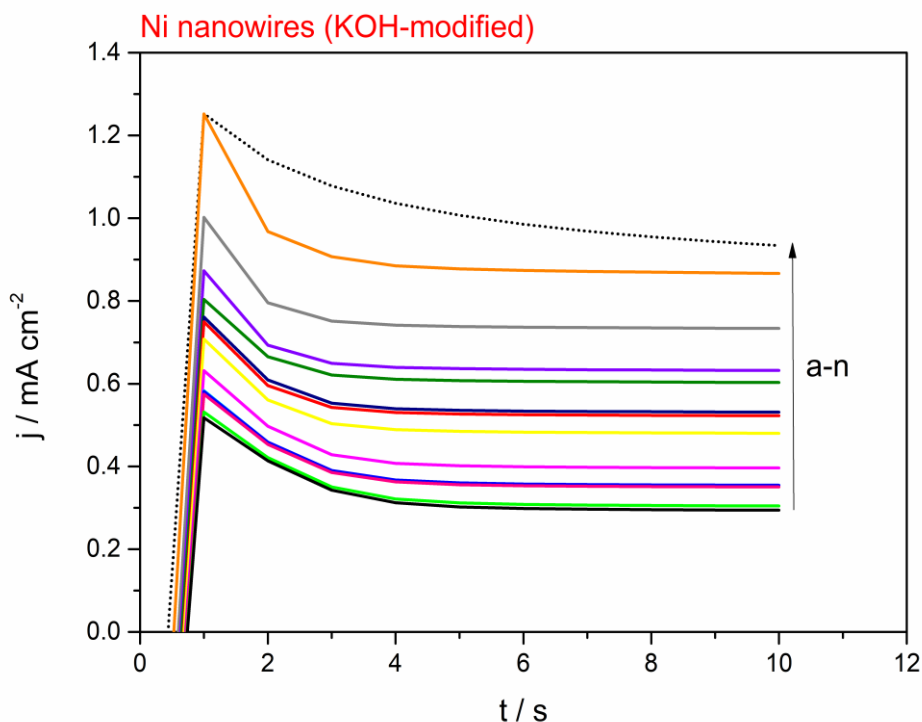


Figure 4.45: Chronoamperograms obtained at the KOH-modified Ni nanowire-based electrode a) in the absence of HCHO (black) and in the presence of b) 0.0008 (green), c) 0.001 (pink), d) 0.005 (blue), e) 0.01 (cyan), f) 0.05 (magenta), g) 0.1 (yellow), h) 0.5 (red), i) 1.0 (navy blue), j) 6.0 (olive green), k) 10 (violet), l) 20 (grey), m) 40 (orange), and n) 60 (black dots) mmol L⁻¹ HCHO in a 0.1 mol L⁻¹ NaOH solution; observed under a constant potential of 0.7 V for 10 s.

4.3.5.3 The sensitivity of Ni electrodes

The additional figure of merit that is commonly used for reporting the analytical results of receptor elements is sensitivity. Thus, the calibration plots were constructed for KOH-modified Ni electrodes, and the sensitivity was determined from the slope of the calibration curve.

The calibration plot of KOH-modified fine-grained Ni film (Figure 4.46, A) is linear in two HCHO concentration ranges from 0.1–4 mmol L⁻¹ (red curve) and 4–60 mmol L⁻¹ (blue curve), with the sensitivity of 49.7 $\mu\text{A cm}^{-2} \text{ L mol}^{-1}$ and 9.1 $\mu\text{A cm}^{-2} \text{ L mol}^{-1}$, respectively. Error bars represent the standard deviation from the mean of three replicates. As it is seen from the graph, the maximum concentration of HCHO that can be measured before the electrode's saturation was confirmed to be 60 mmol L⁻¹. In addition, the limit of detection (LOD) was obtained from experimental measurements. Figure 4.46, B, represents the concentration-current plot of KOH-modified fine-grained Ni film obtained in the HCHO concentration range from 0–0.01 mol L⁻¹. The current density values for each concentration presented on this plot were obtained from amperometric measurements observed at a constant applied potential of 0.7 V. The experimental LOD was determined to be 80–100 $\mu\text{mol L}^{-1}$; therefore, this value was determined at the HCHO concentrations range where the standard deviation from the mean of three replicates is out of the range for the standard deviation of background measurements.

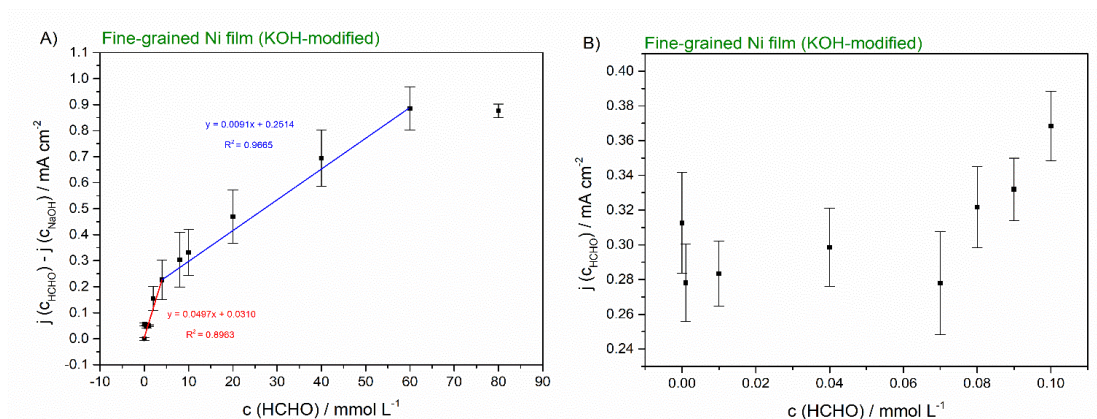


Figure 4.46: A) Linear calibration curves of a steady-state current vs the concentration of HCHO in a 0.1 mol L⁻¹ NaOH solution of the KOH-modified fine-grained Ni film. B) The steady-state currents vs lower concentration of HCHO, from which the experimental LOD was determined. Error bars represent the standard deviation from the mean of three replicates.

The calibration plot of KOH-modified coarse-grained Ni film (Figure 4.47, A) shows a linear correlation to HCHO in two ranges from 0.01–10 mmol L⁻¹ (red curve) and from 10–80 mmol L⁻¹ (blue curve), thus 80 mmol L⁻¹ represents a critical concentration, after which the adsorption of the oxygen at the electrode surface hinders further HCHO oxidation (already shown in Figure 4.44). The sensitivity was determined to be 69.7 $\mu\text{A cm}^{-2} \text{L mol}^{-1}$ and 12.0 $\mu\text{A cm}^{-2} \text{L mol}^{-1}$. The experimentally determined LOD of KOH-modified coarse-grained Ni film was obtained from the concentration-current plot, as presented in Figure 4.47, B. The current values were determined in the HCHO concentration range from 0–0.01 mol L⁻¹ from amperometric measurements (observed at a constant applied potential of 0.7 V). The experimental LOD was determined to be 8–10 $\mu\text{mol L}^{-1}$; therefore, the experimental LOD value was determined at the HCHO concentrations range where the standard deviation from the mean of three replicates is out of the range for the standard deviation of background measurements.

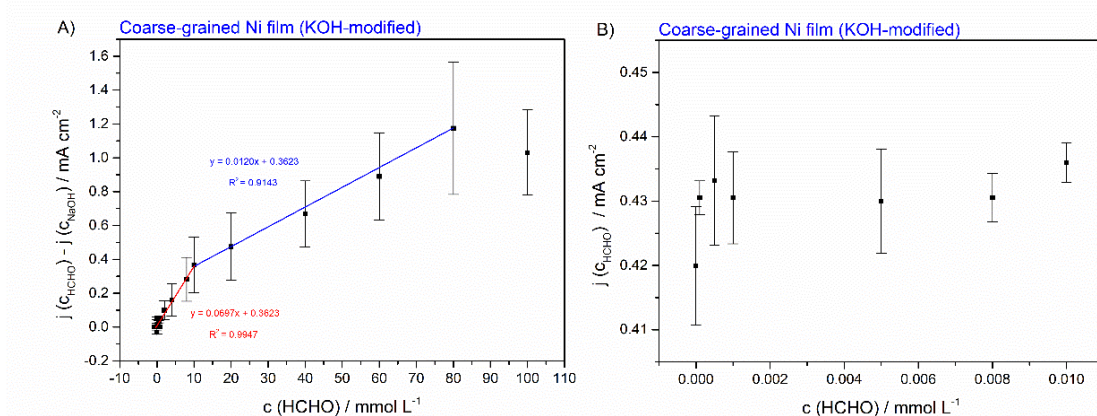


Figure 4.47: A) Linear calibration curves of a steady-state current vs the concentration of HCHO in a 0.1 mol L⁻¹ NaOH solution of the KOH-modified coarse-grained Ni film. B) The steady-state currents vs lower concentration of HCHO, from which the experimental LOD was determined. Error bars represent the standard deviation from the mean of three replicates.

As indicated in Figure 4.48, A, two linear ranges of 0.001–2 mmol L⁻¹ (red curve) and from 2–40 mmol L⁻¹ (blue curve) were observed for the KOH-modified Ni nanowires electrode with calculated sensitivities of 91.1 $\mu\text{A cm}^{-2} \text{L mol}^{-1}$ and 13.7 $\mu\text{A cm}^{-2} \text{L mol}^{-1}$, respectively. Considering the limit of detection that was experimentally determined, the value for KOH-

modified Ni nanowires was obtained to be 0.8–0.9 $\mu\text{mol L}^{-1}$ (Figure 4.48, B). The LOD was experimentally determined from the concentration-current plot as already explained for the fine- and coarse-grained Ni film.

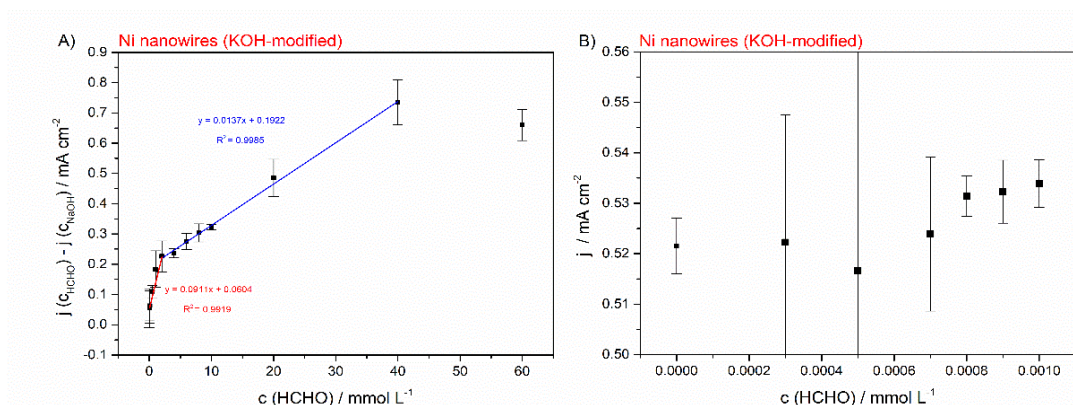


Figure 4.48: A) Linear calibration curves of a steady-state current vs the concentration of HCHO in a 0.1 mol L⁻¹ NaOH solution of the KOH-modified Ni nanowires. B) The steady-state currents vs lower concentration of HCHO, from which the experimental LOD was determined. Error bars represent the standard deviation from the mean of three replicates.

The calibration plots presented in Figure 4.46, Figure 4.47, and Figure 4.48 were also used to precisely and accurately determine the LOD of the KOH-modified Ni electrodes (fine- and coarse-grained Ni films, and Ni nanowires) by Equation 4.5:

$$\text{LOD} = \frac{k s_b}{m} \quad (4.6)$$

Where k is a confidence factor ($k = 3$), s_b is a standard deviation of blank and m is a calibration sensitivity (the slope of the calibration curves). The calculated LODs for Ni electrodes are presented in Table 4.2. As it shows, the calculated LOD values for fine-grained Ni film and Ni nanowires are in the range of experimentally determined LODs. In the case of the coarse-grained Ni film, a calculated value is out of range of experimentally determined, but still in the same magnitude order. However, this deviation is negligible since it is probably a result of experimental error.

Table 4.2: LOD of Ni electrodes.

LOD / $\mu\text{mol L}^{-1}$	Fine-grained Ni film	Coarse-grained Ni film	Ni nanowires
Calculated by Eq. 1.35	84.61	6.58	0.84
Experimentally determined	90–100	8–10	0.8–1.0

Furthermore, the comparison of linear ranges and LODs of KOH-modified Ni electrodes with other reported HCHO receptor elements that are based on noble- or non-noble metals are presented in Table 4.3. The overall performance reveals that the KOH-modified Ni nanowires receptor element displays a good superiority in terms of linear calibration and LOD.

In terms of linear range, not only the Ni nanowires receptor element but also other Ni-based electrodes presented in Table 4.3 enable the measurements at a higher concentration of HCHO. These observations can be attributed to the mechanisms themselves and the “poisoning” effect. To the best of our knowledge, noble metals-based (Pd, Pt, Au, etc.) active sites of receptor elements become occupied and deactivated by adsorbed intermediates (e.g. carbon monoxide). The formation of the surface poisoning species leads to the narrow linear calibration ranges.

Regarding the LOD, the value of the KOH-modified Ni nanowires receptor element is comparable to that achieved with the noble-metal-based receptor elements and even

surpasses the already reported lowest LOD for Ni-based receptor element (Ni/P-CPE), as listed in Table 4.3.

Table 4.3: Comparison of linear ranges of various HCHO receptor elements.

Receptor element	Linear range / $\mu\text{mol L}^{-1}$	LOD / $\mu\text{mol L}^{-1}$	References
Pd nanowires array/GCE ^a	2–1,000	0.5	[29]
Pd-doped SCE ^b	10–10,000	2	[131]
Pt-Pd nanoparticles/Nafion modified GCE ^a	10–1,000	3	[97]
Au cluster	1,000–10,000	930	[103]
Ni/P-CPE ^c	20–11,500	5.8	[37]
KOH-modified fine-grained Ni film	100–4000 and 4,000–60,000	84	Our work
KOH-modified coarse-grained Ni film	10–10,000 and 10,000–80,000	6.5	Our work
KOH-modified Ni nanowires	1–1,000 and 2,000–20,000	0.8	Our work

^aGlassy carbon electrode, ^bScreen printed electrode, ^ccarbon paste electrode

As indicated in this chapter, KOH-modified Ni nanowires were proven to exhibit the most advantageous sensory performance, including fast response, the highest sensitivity and the lowest detection limit among all examined electrodes. The fact that KOH-modified nanowires exhibit such an excellent performance in HCHO detection was expected since we already proved and described their enhanced catalytic activity and its source in Chapter 4.3.3. By all of these observations, we concluded that the KOH-modified Ni nanowires electrode displays superiority in terms of sensory and catalytic properties towards HCHO electro-oxidation in comparison to the KOH-modified fine- and coarse-grained Ni films. This, of course, is related to the composition and structure of surface-active species ($\text{Ni}(\text{OH})_2/\text{NiOOH}$).

4.3.5.4 The selectivity and repeatability of Ni nanowires

The Ni nanowires-based electrode that was KOH-modified at a scan rate of 200 mV s^{-1} showed the best catalytic and sensory properties towards HCHO. Due to this fact, the KOH-modified (200 mV s^{-1}) Ni nanowires-based electrode was evaluated by two additional sensory parameters, i.e. selectivity and repeatability.

The selectivity is one of the main properties for the electrochemical sensors to discriminate interfering analytes with a similar structure and functional groups. The influence of various foreign species, including ethanol (EtOH), 1-propanol (1-PrOH), acetaldehyde (MeCHO) and hydrogen peroxide (H_2O_2), was tested by measuring the amperometric response. Figure 4.49 shows the current-time response of the KOH-modified Ni nanowires obtained at a constant applied potential of 0.7 V. The same volume of the 1 mmol L^{-1} of HCHO, MeCHO, EtOH, 1-PrOH and H_2O_2 was successively added every 10 s into the 0.1 mol L^{-1} NaOH solution. From results, it was concluded that the current response is negligible when 1-PrOH, EtOH, MeCHO and H_2O_2 were added, while a significant current increase was observed after adding HCHO (after the 50s) to the 0.1 mol L^{-1} NaOH solution. Results indicated that the response of KOH-modified Ni nanowires electrode towards formaldehyde in the presence of interfering species is considerably high.

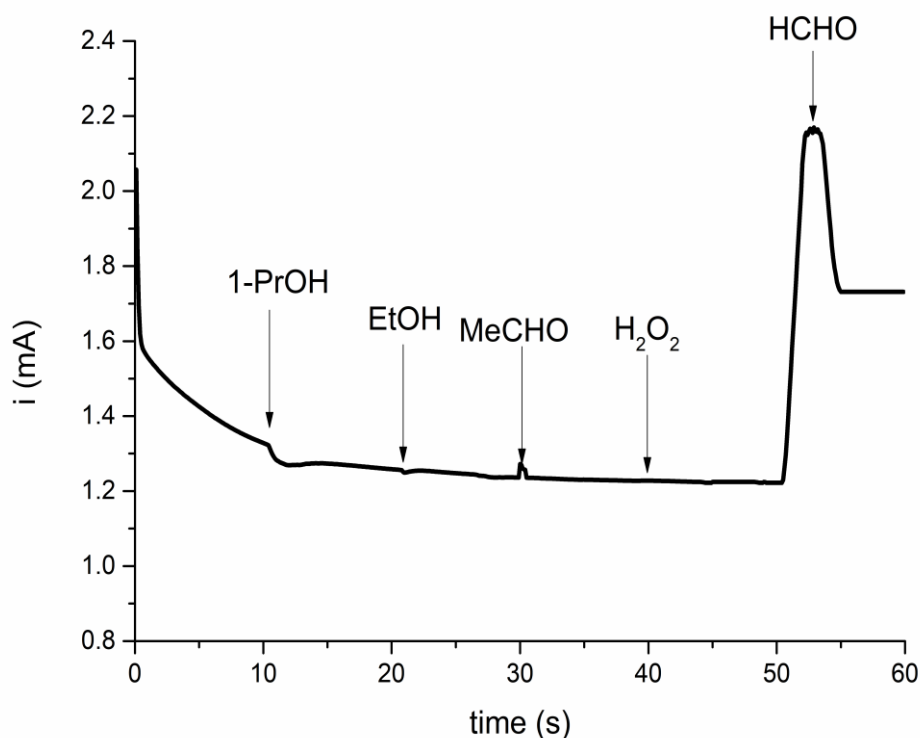


Figure 4.49: CA response of the KOH-modified Ni nanowires electrode for successive addition of 1 mmol L^{-1} 1-PrOH, EtOH, MeCHO, H_2O_2 and HCHO to the 0.1 mol L^{-1} NaOH solution at the fixed potential of 0.8 V .

The repeatability of the experiments is also an important parameter in evaluating the performance of the sensor. The repeatability of the KOH-modified Ni nanowires was determined using chronoamperometry by measuring the current densities response in a 1 mmol L^{-1} HCHO and 0.1 mol L^{-1} NaOH solution. Figure 4.50 shows the current values of the ten different amperometric measurements observed at a constant applied potential of 0.8 V after steady-state was reached. The results imply that the electrode has good repeatability as the current density responses remain constant after ten measurements with the relative standard deviation (RSD) of 0.63% (inset). Repeatability of the proposed electrode was compared with some other previously reported modified electrodes, and the RSD of Ni nanowires electrode that was KOH-modified at a scan rate of 200 mV s^{-1} was lower than for the electrodes based on noble metals (Pd nanowires – $\text{RSD} = 1.1\%$ or Pt-Pd nanoparticles – $\text{RSD} = 3.2\%$ [29, 97]) or Ni-based electrodes (Ni/P nanozeolite – $\text{RSD} = 3.45\%$ [37]). These observations reveal the good stability and satisfactory recovery of Ni nanowires.

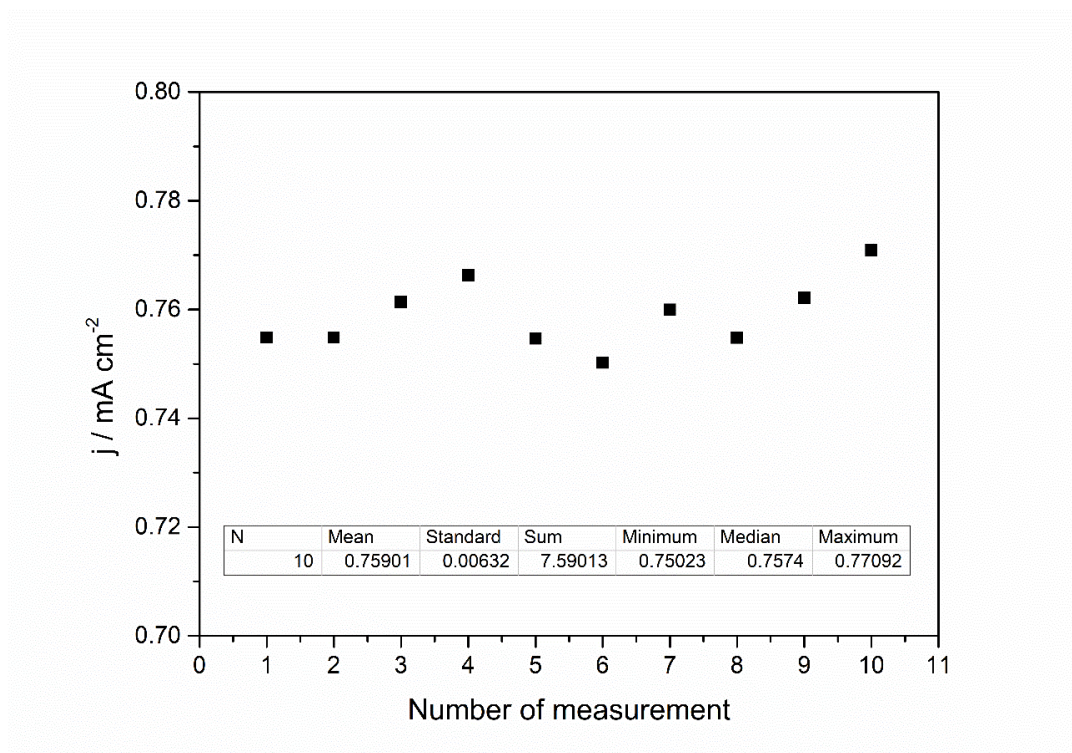


Figure 4.50: Repeatability of amperometric measurements of the KOH-modified Ni nanowires. Inset: statistics of the measurements.

To conclude, in this chapter we clearly showed the selectivity of the KOH-modified (at a scan rate 200 mV s^{-1}) Ni nanowires-based receptor element, as the interferences from the oxidation of common interfering species such as MeCHO, EtOH, 1-PrOH and H_2O_2 are effectively avoided. Our observations of the sensitivity are comparable to the results reported in the literature for HCHO receptor elements, based on non-noble and noble metals [29] [131] [97] [103] [37]. Besides, this electrode has good repeatability, which means that the electrode can be used for at least 10 measurements without greater changes in current signals. However, the comparison of the repeatability with the previously reported sensors [29, 97, 108] offers some advantages over noble-metal-based electrodes where the decrease in current densities after each measurement can be attributed to the generation of surface poisonous organic compounds (carbon monoxide), as described in Chapter 1.4.1. Due to the formation of poisoning intermediates the noble-metals-based receptor elements generally become deactivated. In the case of Ni-based receptor elements, the mechanisms of HCHO electro-oxidation are different, and the active side of the electrodes cannot be occupied by adsorbed intermediates (see Chapter 1.4.1). Overall, regarding the sensory performance, the proposed nanowires-based receptor element has potential applications in practical analyses.

Chapter 5

Conclusions

In this chapter, we will summarise the main achievements and conclusions of this thesis reached throughout the last four years. This thesis provides a review on the research of HCHO receptor elements based on various electrodeposited Ni nanostructured materials, 2-D films and 1-D nanowires. The attractive and unique properties of electrodeposited 1-D and 2-D Ni-based nanostructures led towards the development of receptor systems exhibiting promising analytical and catalytic behaviour towards HCHO electrochemical detection. The first part of the thesis is depicted by the electrodeposition of Ni-based nanostructured systems, the second part is focused on the electrochemical determination of electrochemically active surface areas of as-prepared Ni electrodes using the oxalate method, and the last part is dedicated to the investigation of Ni electrodes surfaces transformation from Ni to oxides or hydroxides and their oxidation ability in alkaline media for HCHO detection.

The first part of the thesis was dedicated to the electrodeposition of the Ni-based electrodes, i.e. 2-D films and 1-D nanowires. Ni films were electrodeposited on Au-glass substrates from two Ni-sulfate solutions with a different pH (2.5 and 5.5) by cathodic electrodeposition using the same reduction potential of $E = -1.0$ V. The FEG-SEM analysis revealed that the morphology, the shape and the size of Ni crystallites vary with the electrolyte pH. At a lower pH, the intensive hydrogen evolution reaction occurred (due to the water decomposition). Consequently, it increased the pH value in the vicinity of the electrode, reduced the diffusion layer thickness, and therefore changed the growth and nucleation process. The resulting film (i.e. fine-grained Ni film) electrodeposited from electrolyte with pH=2.5 was smoother and composed of Ni grains in the size of 50–70 nm. On the other hand, when the deposition was carried out from electrolyte with a higher pH (5.5), the resulting film (i.e. coarse-grained Ni film) was composed of bigger crystallites in the size of 100–300 nm. Furthermore, the influence of electrolyte pH on the composition of Ni films was examined by XRD. Two main Ni chemical species, reduced metallic (Ni^0) and hydroxide ($\text{Ni}(\text{OH})_2$) were detected in the case of fine-grained Ni film. The reduced species are a product of the electrochemical reaction of Ni^{2+} and exhibit a preferential crystallographic orientation of Ni with the (1 1 1) orientation. The hydroxide species are a result of chemical precipitation due to the intensified hydrogen evolution. In the case of the coarse-grained film, the main detected Ni species were reduced fcc Ni (with a preferential (1 1 1) orientation). The Ni nanowires have been successfully electrodeposited in the pores of AAO template under the potentiostatic regime at $E = -1.0$ V. FEG-SEM observation of wires in the pores indicates the uniform diameter of 200 nm, the length of 2–3 μm , and the parallel-ordered arrangement after dissolving the AAO membrane.

In order to normalise the output currents and to be able to compare the as-prepared Ni electrodes current response with the literature, the second part of the thesis was focused on the determination of electrochemically active surface areas A_{ecsa} of as-deposited Ni electrodes (fine- and coarse-grained Ni films, and Ni nanowires). On the basis of the literature, the oxalate method was selected since it provides *in-situ* measurements of A_{ecsa} of Ni electrodes that have to be oxide-free by adding oxalic acid to the alkaline electrolyte. The formation of an adsorbed oxalate layer at the Ni electrode surfaces was utilised by the literature to stabilise the surface nickel hydroxides/oxy-hydroxides and to limit its growth to a few atomic layers. First, the electrochemical formation of oxalate-stabilised- $\text{Ni}(\text{OH})_2$ and oxalate-stabilized- NiOOH in alkaline media was studied on standard Ni electrode (Ni foil). We showed that the use of experimental conditions that include a scan rate of 200 mV

s⁻¹, the oxalic acid concentration of 0.08 mol L⁻¹ and the KOH concentration of 0.5 mol L⁻¹, leads to reproducible results, and favoured the formation of a Ni(OH)₂ and NiOOH layer (anticipated from the literature to be a few atomic layers thick) on Ni foil. The same experimental conditions were applied to as-deposited Ni films and free-standing Ni nanowire electrodes. The faradaic oxidation and reduction of stabilised-Ni(OH)₂/NiOOH surface layer was measured, and the corresponding Coulombic charge was used to calculate A_{eCSA} of as-deposited Ni electrodes. Furthermore, the determined A_{eCSA} were compared to the geometrically determined surface areas of Ni-based electrodes. However, the values were ~40% for fine-grained, ~50% for coarse-grained Ni film and ~30 % for Ni nanowires in favour of the electrochemically active surface area. By this comparison, we showed the importance of using the oxalate method to accurately determine the A_{eCSA} (i.e. an indicator of the “amount” of active Ni(OH)₂/NiOOH surface species,). A_{eCSA} values were further used for the normalisation of output currents in HCHO electro-catalytic detection.

In the last part of the thesis, the studies were focused on the surface transformation of as-deposited Ni electrodes from Ni to oxides, hydroxides/oxyhydroxides during the exposure to air and an alkaline electrolyte, or after KOH-modification. The non- and KOH-modified electrodes were investigated via XRD, TEM/SAED and FT-IR analysis, and subjected to electrochemical testing to investigate the electro-catalytic oxidation of the HCHO in alkaline media and the final sensory properties.

Throughout the study, it was shown that electro-catalytic oxidation of HCHO is highly dependent on the surface chemical composition of Ni electrodes, the formation of which can be controlled by electrodeposition conditions (substrate, pH, etc.) and by changing certain parameters in the KOH-modification processes (e.g. potential range, number of scans, and scan rate). The catalytically-active hexagonal α -Ni(OH)₂ (crystal structure has been proven by XRD) was directly electrodeposited by using a textured (1 1 1)-oriented Au substrate at low pH (<2) which provided an intensified hydrogen evolution with a local pH increase, and consequently a direct precipitation of α -Ni(OH)₂ on the surface of the Ni electrode. The electrodeposited hydroxide, α -Ni(OH)₂, present on the surface of the Ni film, i.e. fine-grained Ni film, has been assigned to have an ability to oxidise HCHO via electro-catalytic reaction in the alkaline electrolyte. It was shown that the precipitation of catalytically-active α -Ni(OH)₂ does not occur by using different electrodeposition conditions: higher pH of electrolyte (in the case of coarse-grained Ni film) or isotropic Au substrate (in the case of Ni nanowires). Those electro-deposits consisted of metallic Ni and air-formed crystalline surface Ni-oxides. In comparison to the fine-grained Ni film, the as-deposited coarse-grained Ni film and as-deposited Ni nanowires were showing an electro-inactive behaviour towards HCHO that was assigned to the formation of surface Ni oxides.

Furthermore, we have been able to transform the electro-inactive as-deposited Ni-based electrodes (coarse-grained Ni film and Ni nanowires) to active, by inducing significant surface changes in terms of their chemical composition and their crystallographic structures. This was achieved by the KOH-modification process via potential cycling at 200 mV s⁻¹. This process enables the transformation of inactive surface species (NiO) to catalytically active species (Ni(OH)₂/NiOOH). However, the various experimental parameters were considered in the KOH-modification process, including the potential range, the number of scans, and the scan rate.

We have shown that the potential range in KOH-modification must be selected in the potential region where the reaction of oxygen evolution does not occur. The produced O₂ is adsorbed at the electrode's surface, blocks the active Ni sites (Ni(OH)₂/NiOOH), and therefore inhibits the oxidation/detection of HCHO. Due to this fact, the potential in KOH-modification was selected to be up to 0.6 V in the case of fine- and coarse-grained Ni films, and Ni nanowires, since it still enables the reaction of OH⁻ ions with surface Ni or NiO, and thus enables a continuous potential cycling over the Ni(OH)₂/NiOOH redox peaks.

Furthermore, we have shown that the number of scans is important from a perspective of thickening of the active surface layer (Ni(OH)₂/NiOOH.) The impact of this parameter was negligible in the case of fine-grained Ni film, as the electrode surface got saturated with α -Ni(OH)₂ during electrodeposition. In the case of the coarse-grained film, the first cycle was the most important, where the surface transformation of Ni or NiO to α -Ni(OH)₂ occurred. However, the most significant transformation of the Ni/NiO surface species to Ni(OH)₂ occurred at the Ni nanowires electrode during the KOH-modification process (from the 1st to the 50th cycle). The surface layer of Ni(OH)₂/NiOOH at the nanowires electrode became thicker due to the entry of OH⁻ into the Ni/NiO layers. So far, we also provide an up-to-date guide on how different crystallographic structures of α -Ni(OH)₂ or amorphous Ni(OH)₂ can

be formed depending on the selection of the Ni-based substrate. The crystalline hexagonal α -Ni(OH)₂ grew on the preferentially (1 1 1)-oriented fcc Ni substrate, while amorphous Ni(OH)₂ grew on the isotropic Ni without a pronounced texture.

Furthermore, Ni-based electrodes KOH-modified in KOH at a potential range up to +0.6 V were tested in the electrocatalytic reaction of HCHO oxidation. The cyclic voltammetry studies confirmed the HCHO oxidation ability for all three KOH-modified electrodes. The obtained HCHO anodic peak current densities for these electrodes decrease in the following order: 0.5 mA cm⁻² – Ni nanowires, 0.25 mA cm⁻² – coarse-grained Ni film and 0.13 mA cm⁻², and the onset HCHO over-potential increase in the following order: 0.3 V – Ni nanowires, 0.35 V – coarse-grained Ni film and 0.33 V. Based on these results, it was shown that the KOH-modified Ni nanowires electrode exhibits the best catalytic activity, as it reaches the highest anodic current density and the lowest over-potential for HCHO oxidation. The exceptionally high catalytic activity of the nanowires was assigned to the amorphous nature of Ni(OH)₂/NiOOH. Both, KOH-modified fine- and coarse-grained Ni films show catalytic activity towards HCHO oxidation, but less active than KOH-modified Ni nanowires electrode. According to the Bode's diagram, our results suggest that the reduced electrocatalytic activity of KOH-modified Ni films is correlated with the fact that more than one electron is needed (1.6–1.67) for the transformation between α -Ni(OH)₂/ γ -NiOOH during potential cycling in the alkaline electrolyte. Therefore, KOH-modified Ni films as catalysts need higher input energy for electro-catalytic oxidation of HCHO.

As KOH-modified Ni nanowire electrodes showed the best catalytic performance towards HCHO oxidation, their surface-active species Ni(OH)₂/NiOOH were tackled via KOH-modification at different scan rates. It has been shown that a slow scan rate (10 mV s⁻¹) increases the thickness of the NiO layer by the propagation of O₂ into inner Ni-based layers, while the thickening of the NiO layer is limited by fast diffusion of OH⁻ at higher scan rates (200 and 400 mV s⁻¹). This means that surface NiO is completely transformed to the Ni(OH)₂ at high scan rates > 200 mV s⁻¹. On the other hand, the highest scan rate (400 mV s⁻¹) limits the thickening of the Ni(OH)₂ layer by diffusion of OH⁻ to the Ni lattice (Ni + 3OH⁻ - 3e⁻ → NiOOH). Thus, the samples KOH-modified at the highest scan rate (400 mV s⁻¹) contain less Ni(OH)₂ surface species than the samples KOH-modified at lower scan rates (10 and 200 mV s⁻¹). Those changes (crystallographic, morphological and chemical) play a crucial role in the electro-catalytic oxidation of HCHO as they accelerate or hinder the electron transfer process. The Ni nanowires electrode KOH-modified at a scan rate of 200 mV s⁻¹ was found to gain better electrocatalytic activity (increased current density (~50%) and lower onset over-potential (~20%) in comparison to the electrodes KOH-modified at 10 and 400 mV s⁻¹. These results have brought us to the conclusion that better catalytic activity of sample KOH-modified at a scan rate of 200 mV s⁻¹ can be ascribed to the highest amount of catalytically-active Ni(OH)₂/NiOOH species and the absence of NiO which hinders the electron transfer in HCHO electro-catalytic oxidation.

Along with those studies, the sensory properties of KOH-modified fine-grained Ni film, KOH-modified coarse-grained Ni film and KOH-modified Ni nanowires were determined by the number of analytical merits such as linear dynamic range, sensitivity and detection limit. The analytical properties of the electrodes, i.e. sensory properties, were determined by measuring the voltammetric and amperometric response of each electrode at different concentrations of HCHO in alkaline media. KOH-modified Ni nanowires yielded the most advantageous performance, as they exhibited fast response (1 s) which reached a steady state within 4 s, the highest sensitivity (1.4 μ A cm⁻² mol L⁻¹ and 91.1 μ A cm⁻² mol L⁻¹) and the lower detection limit (0.8 μ mol L⁻¹) in comparison to the KOH-modified fine-grained Ni film and coarse-grained Ni film, which is in accordance with the electrode catalytical performances studied within this thesis.

To summarise, this dissertation provides routes towards the successful electrochemical synthesis of efficient HCHO Ni-based receptor elements. It opens an avenue for rational design and controllable preparation of the nanomaterial with a well-defined structure, shape, and composition to achieve high-performance electro-catalysis reflected in high output currents. These represent a solid base to achieve excellent sensory characteristics, including high sensitivity, low detection limit, high selectivity, and good reproducibility. The developed Ni-based electrodes surpass other Ni-based nanostructured electrodes and reach the sensory values comparable to noble-metals-based electrodes. As such they show great potential for the successful implementation in future sensing applications.

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Publications Related to the Thesis

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- Š. Trafela, J. Zavašnik, S. Šturm and K. Žužek Rožman, "Formation of a Ni(OH)₂/NiOOH active redox couple on nickel nanowires for formaldehyde detection in alkaline media," *Electrochimica Acta*, vol. 309, pp. 346-353, 2019.

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Biography

The author of this thesis Špela Trafela was born on July 1, 1990, in Ptuj, Slovenia. She finished primary education in 2005 at Osnovna šola Podlehnik and secondary education in 2009 at Gimnazija Ptuj. She proceeded with her university study programme in Chemistry at the Faculty of Chemistry and Chemical Technology at the University of Ljubljana. She obtained the Bachelor Degree in Organic chemistry on September 26th, 2012 under the supervision of Prof. Dr. Janez Košmrlj. She obtained the Master Degree in Organic chemistry on September 10th, 2015 under the supervision of Prof. Dr. Bogdan Štefane. In October 2015, she continued with her PhD studies at Jožef Stefan Postgraduate School in the field of Nanosciences and Nanotechnologies, and she was enrolled as a young researcher under supervision of Prof. Dr. Kristina Žužek Rožman at the Department for Nanostructured Materials, Jožef Stefan Institute, Ljubljana, Slovenia.