The two Janus faces in oxygen electrocatalysis: Activity versus stability of transition metal based electrocatalysts

Dissertation

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1 Introduction

The rapid growth of the world’s population and economy, especially in China and India, is expected to raise the global energy demand by about 30 % by 2040 [1,2]. It is not possible to satisfy such a demand based on fossil fuel dominated energy production. Moreover, fossil fuel based energy production causes significant harm to the environment since its use inadvertently releases greenhouse gases into the atmosphere. Greenhouse gases are identified to exacerbate global warming and climate change, hence reducing their production is of utmost importance. This importance received a global face when 194 member states of the United Nations Framework Convention on Climate Change (UNFCCC) signed the so called Paris Agreement in 2016 for united global action to reduce global warming. The Paris Agreement on climate change will cause a game-changing development in the global energy framework [1]. Well before 2016 and the Paris Agreement, there have been on-going efforts to change from fossil fuel based energies to renewable energy production, including hydropower, wind, solar, and geothermal among others [3]. Energy produced by renewables sources provided around 19.2 % of the global energy consumption in 2014, which grew up to 23.7 % in 2015 [3]. Among the different existing renewable energy sources, solar and wind energy are of highest interest in recent years, manifested in the global annual average growth rate of their capacity of 28 % and 17 %, respectively, in 2015 [3]. Envisaging solar and wind as the main energy sources for the future, their uncontrollable intermittency becomes a serious bottleneck, hampering a faster development. Surplus energy during peak production has to be stored in order to ensure grid stability, and conversely, to be provided again when needed [4,5]. Energy storage in chemical bonds, especially the hydrogen-hydrogen bond, appears to be very appealing, since hydrogen is a highly versatile energy carrier and can be inexhaustibly obtained from water. Renewable based hydrogen is not only desirable for energy production on demand through its oxidation in fuel cells, but can also be used for replacing fossil fuel based hydrogen in the chemical industry, which is currently dominantly produced by steam reforming of natural gas. For the conversion of renewable energy into storable hydrogen, electrochemical water splitting turns out to be among the most promising approaches [6]. Besides the storage of energy in the form of hydrogen, battery technologies are another prominent method for electrochemical energy storage. The necessity for a high energy density at low cost combined with increased safety and environmental compatibility are increasingly explored for advanced metal-air batteries, because of their theoretically high specific energy comparable to gasoline [7]. The research presented in this thesis is dedicated to contribute to the field of electrocatalysis, specifically, the
development and characterization of earth-abundant electrocatalysts and their stable fixation on electrode surfaces for the envisaged application in water electrolysis, fuel cells and metal-air batteries.
2 State of the art

2.1 Electrochemical energy conversion and storage

Surplus energy, produced by intermittent renewable sources, e.g. wind and solar, has to be stored in order to stabilize the grid, and further, to deliver it again on demand. Electrochemistry offers various approaches and is the basis of many technologies for energy conversion, storage and “green” mobility. The storage of energy in chemical bonds, especially the hydrogen-hydrogen bond, appears to be a highly promising approach [6]. The hydrogen can be stored or used for chemical reactions, e.g. as fuel in hydrogen fuel cell driven vehicles or as fuel for a decentralized energy production scenario. Renewable hydrogen is produced by water electrolysis either in an acidic or an alkaline environment. Electrolysis in acidic electrolytes makes the use of precious noble metals as electrocatalysts inevitable, hence preventing the envisaged technical application owing to the high cost and scarcity of the catalysts. Low-cost and earth abundant electrocatalysts based on transition metals like Co, Ni, Mn or Fe are not stable in an acidic environment. Thus, electrolysis in alkaline media is necessary in order to develop low-cost transition metal catalysts. Surplus energy can also be stored in batteries in the form of redox states. The theoretically high energy density of metal-air batteries makes them highly interesting for potential large scale electrochemical energy storage, being able to release energy on demand without having to be coupled to a second device like a fuel cell. Therefore, the following sections focus on alkaline water electrolysis and metal-air batteries, and their main respective electrochemical reactions, i.e. hydrogen evolution, oxygen evolution and oxygen reduction reaction.

2.1.1 Alkaline electrolysis

Alkaline water electrolysis is a promising means for electrochemical conversion of surplus renewable energy into storable hydrogen. Hydrogen is the cornerstone for the so called “hydrogen economy”, in which hydrogen is proposed to be the major fuel for stationary and mobile power generation, as well as the dominant energy fuel [8–10]. Electrochemically produced hydrogen from renewables is perceived as a clean fuel since it emits only water as the waste during energy production in hydrogen fuel cells, and oxygen as the only by-product during its production. Generally, alkaline water electrolysis proceeds via oxygen evolution at the anode and hydrogen evolution at the cathode according to equation (1)-(3). A simple alkaline electrolysis cell consists of an anode, a cathode, electrolyte, typically KOH or NaOH, and a gas separator (Figure 1) [11].
2.1 Electrochemical energy conversion and storage

Water is reduced at the cathode under the formation of hydrogen and hydroxide ions. The evolved hydrogen can be captured and stored or directly used as a feedstock for further chemical conversions. Hydroxide ions follow the resulting pH gradient and cross the gas separator towards the anode compartment, where they are oxidized to release electrons and to form oxygen and water as by-products of the hydrogen evolution. Although electrochemical water splitting appears to be a relatively simple process, several limiting issues need to be addressed before the envisaged wide spread application of water electrolysis has developed as the main technology for hydrogen production. Several energy barriers have to be overcome for electrochemical water splitting to proceed efficiently. In analogy to an electric circuit, these barriers can be expressed as resistances, which can be differentiated into different types, namely: (i) electrical resistances of the external circuitry, e.g. wiring and connections, (ii) transport-related resistances due to gas bubble formation leading to physical blockage of the electrode surface, and the transport resistance of ions through the electrolyte and the membrane, and (iii) resistances which originate from the electrochemical reactions themselves [11]. In order to overcome the activation barriers of the reactions at the anode and cathode, certain overpotentials have to be applied. These overpotentials are governed by the intrinsic surface properties of the electrode. Thus, an in depth understanding followed by a minimization of the electrochemical reaction resistances is essential for improvement of the energy efficiency of alkaline water electrolysis. From an electrochemical point of view, the latter resistances

\[ H_2O \rightarrow H_2 + \frac{1}{2} O_2 \]  

Cathode: \[ 2 H_2O + 2 e^- \rightarrow H_2 + 2 OH^- \]  

Anode: \[ 4 OH^- \rightarrow O_2 + 2 H_2O + 4 e^- \]
considering an electrified electrode/electrolyte interface are of the highest interest and therefore discussed further.

The concatenation of water molecules by hydrogen bonds makes water one of the most thermodynamically stable compounds in nature. Thus, the cleavage of a water molecule into hydrogen and oxygen can only be a thermodynamically uphill reaction. The minimum energy to be paid is determined by the equilibrium cell voltage $E^0$, which is the difference between the equilibrium potential of the anode and cathode reactions. The reversible water splitting potential is 1.23 V (vs. RHE) at room temperature, thus it is thermodynamically unfavored and can only proceed when sufficient energy is provided. However, even when this minimum energy is provided, the reactions are inherently slow, thus necessitating additional energy input, the reaction overpotentials, to facilitate the reactions at reasonable rates (Figure 2) [12,13]. The kinetics of electrode reactions, and thus of the evolution of hydrogen and oxygen, can be described by the Butler-Volmer equation (4) [14].

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

The Butler-Volmer equation describes the correlation between the current and the potential at an electrode, with $i_0$ as the exchange current density, $\alpha$ as the transfer coefficient, which is a measure of the fraction of the applied voltage effectively driving the desired electrochemical reaction, $R$ is the universal gas constant, $F$ the Faraday constant, $T$ the temperature, $n$ the number of exchanged electrons and $\eta$ is the reaction overpotential, defined as the difference of the applied potential $E_{\text{appl}}$ and the reversible potential $E^0$.

![Figure 2. Polarization curves for the hydrogen evolution, hydrogen oxidation, oxygen evolution and oxygen reduction reactions (potential given vs. RHE). Current vs. potential curves without (solid lines) and with (dashed lines) the necessity of an overpotential $\eta$.](image-url)
At the equilibrium potential \( i = i_0 \). The exchange current density is a measure of the reaction kinetics. According to equation (4) a higher \( i_0 \) correlates to faster kinetics and hence lower overpotential is needed and vice versa [14]. At high overpotentials and in the absence of mass transfer influences, either the anodic or the cathodic part of the Butler-Volmer equation becomes negligible and the equation can be written as the Tafel equation for anodic or cathodic reactions [15,16]. For high anodic overpotentials and \( i > 0 \), the equation can be expressed as equation (5) and for high cathodic overpotentials and \( i < 0 \), as equation (6).

\[
i = i_0 e^{\frac{(1-a)nF}{RT} - \eta a}
\]

(5)

\[
i = -i_0 e^{-anF}{RT} - \eta c
\]

(6)

Plotting of the logarithm of \( i \) versus the overpotential yields the Tafel plot from which Tafel slopes can be extracted. Tafel slopes are often used in order to extract mechanistic and kinetic information of the proceeding reactions. In the following, a deeper insight into the reactions taking place during alkaline water splitting, the hydrogen and oxygen evolution reaction, is provided.

### 2.1.1.1 Hydrogen evolution reaction (HER)

The hydrogen evolution reaction (HER) is the cathode reaction during electrochemical water splitting. In alkaline electrolytes, water dissociation is the first step (Volmer step). The reaction can then proceed either by the Heyrovsky or the Tafel step, or if the catalyst consists of different active sites, a mixture of both. In the former, the adsorbed hydrogen atom combines with an electron and a proton from the electrolyte to form hydrogen, while in the latter step two adjacent adsorbed hydrogen atoms combine to form a hydrogen molecule [17].

**HER in alkaline solution:**

\[
2H_2O + 2e^- \rightarrow H_2 + 2OH^- \quad (E^0 = 0 \text{ V vs. RHE})
\]

(7)

\[
H_2O + e^- + *H \rightarrow *H + OH^- \quad \text{(Volmer)}
\]

(8)

\[
H_2O + e^- + *H \rightarrow H_2 + OH^- \quad \text{(Heyrovsky)}
\]

(9)

or

\[
2*H \rightarrow H_2 \quad \text{(Tafel)}
\]

(10)

The HER overpotential can generally be described by the Tafel equation for cathodic reactions (Eq. (6)). Evidently, it is directly related to the exchange current density, which can be seen as
a measure of the rate constant of the reaction and which is strongly dependent on the surface properties of the electrode. For a deeper understanding of the reaction kinetics of a given electrocatalytic system, it is necessary to determine the rate-determining step. This can be achieved through analysis of the Tafel slope [18]. It is widely accepted that Tafel slopes of 120, 40 and 30 mV dec\(^{-1}\) indicate the Volmer, Heyrovsky and Tafel step, respectively, as the rate-determining step [19]. Thus, simple Tafel analysis can give information about the apparent HER mechanism, however, the obtained slopes may vary with the applied potential and hydrogen coverage [19]. Since the reaction rate and the overpotential are material specific properties, a deeper understanding of the coherence is necessary. If \(i_0\) is plotted against \(\Delta G_{\text{max}}(U^0)\) a volcano type graph is obtained (Figure 3). That volcano plot follows the Sabatier principle [14]. According to Sabatier, the optimal catalytic activity can be achieved when the reaction intermediates are neither bound too weakly nor too strongly [20]. If intermediates are bound too weakly, their activation at the catalyst’s surface is hindered, while if they are bound too strongly, the active sites stay occupied and the catalyst becomes poisoned. Thus, highly active catalysts have to offer a compromise between the aforementioned two extrema.

**Figure 3.** a) Volcano plot representing the relationship between exchange current density \(i_0\) and hydrogen adsorption free energy (adapted from [21]); b) Volcano plot representing HER \(i_0\) versus hydrogen adsorption free energy for various metals, alloys, and non-metallic compounds (adapted from [22]).

Platinum group metals, e.g. Rh, Pd, Ir, Ru and Pt itself, are close to the top of the volcano and thus exhibit high activities towards the HER. Their \(\Delta G_{H^*}\) is close to 0 and they provide a high exchange current density \(i_0\) [14]. However, their scarcity and therefore high costs prevent them...
from large-scale applications. Nevertheless, platinum was and still is in the main target of numerous studies, especially single crystals as models for mechanistic studies [23,24]. The alloying of precious metals with non-noble metals, specifically 3d transition metals, simultaneously enhances the electrocatalytic activity and reduces the use of the precious metals [25]. Metal heteroatom doping of Pt host structures can lead to an optimized d-band center and \( \Delta G_{\text{H}}^{*} \) [14]. It was shown for Pt(111) that a submonolayer of Ni(OH)\(_2\) substantially enhances the HER activity in alkaline media due to lowering of the energy barrier necessary for reorganization of the interfacial water network [26]. The underlying supporting substrate also influences the activity of the precious metal. Pt can be deposited on tungsten or molybdenum carbide substrates in various architectures by means of common physical vapor deposition techniques [27,28]. Such supported catalysts can achieve as high activity as the pure metals but with substantially lower precious metal loadings [29].

To completely avoid the utilization of precious metals, pure non-noble metal HER catalysts were developed. Simple Ni electrodes are commonly used in industrial alkaline water electrolysis because of their low cost and high corrosion resistance [30], however, they experience deactivation under continuous operation due to the formation of hydride species [31,32]. Raney-Nickel, a Ni-Al alloy, was an early attempt to stabilize the activity of Ni HER electrodes. The Al is leached out of the alloy in alkaline solution, thus forming a porous Ni network while the Al in the electrolyte can act as a stabilizing matrix [33]. Vasu et al. further explored binary transition metal alloys and found Ni-Mo alloys to exhibit the highest HER activity, delivering a low overpotential of 0.18 V at a high current density of 300 mA cm\(^{-2}\) and elevated temperature in concentrated alkaline solution for a time span of 1500 h of electrolysis [34]. The high catalytic activity can be attributed to hypo-hyper-d-electronic interactions, which can alter the HER activity of alloys containing transition metals from the left and the right half of the transition series as much that they outperform precious metal catalysts [35]. Besides alloying, hybridization of transition metals with other functional materials such as oxides and hydroxides can have a beneficial effect on the HER activity [36,37]. In alkaline media, the slow water dissociation step decreases the HER activity by about two to three orders of magnitude with respect to acidic media [36,37]. Hybridization with hydroxides or oxides may favor the water dissociation step and the formation of reactive hydrogen intermediates which later combine to a hydrogen molecule [36,37]. Several groups have shown the positive effect of such hybridization of precious metal d-orbitals with Ni based hydroxide and oxide on the HER activity [36–38]. Furthermore, it was shown that water dissociation is no longer the rate determining step in such hybrid HER catalysts [36,37].
Transition metal heteroatom structures, such as carbides [39–41], chalcogenides [42–45], borides [46–48], phosphides [49–51] and nitrides [39], are in the focus of current research interest. The varying surface and electronic properties of such materials compared to pure metals or alloys hampers the formulation of a universal HER descriptor, like the correlation based on $i_0$ and $\Delta G_H^*$ [14]. An exception are transition metal sulfides, which have been investigated in-depth both theoretically and experimentally in order to reveal the catalytically active site [42,44].

2.1.1.2 Oxygen evolution reaction (OER)

The oxygen evolution reaction (OER) is the anode reaction of electrochemical water splitting. It is a multistep reaction involving the transfer of four electrons, which suffers from slow kinetics and hence high overpotentials are necessary to drive the reaction at a meaningful rate, thus increasing the overall cell voltage and lowering the hydrogen production efficiency. Evidently, highly efficient oxygen evolution has to be achieved for a competitive production of renewable hydrogen. The mechanism of the OER can be separated into four discrete electron transfer steps [52].

OER in alkaline solution: \[ 4OH \rightarrow O_2 + 2H_2O + 4e^- \quad (E^0 = 1.23 \text{ V vs. RHE}) \] \[ \text{ (11) } \]

\[ * + OH \rightarrow *OH + e^- \] \[ \text{ (12) } \]

\[ *OH + OH \rightarrow *O + H_2O + e^- \] \[ \text{ (13) } \]

\[ *O + OH \rightarrow *OOH + e^- \] \[ \text{ (14) } \]

\[ *OOH + OH \rightarrow *O_2 + H_2O + e^- \] \[ \text{ (15) } \]

\[ *O_2 \rightarrow * + O_2 \] \[ \text{ (16) } \]

The direct combination of two adjacent $*O$ intermediates is also expected to produce $O_2$ [53]. One of the charge transfer steps is rate determining. Analogous to the HER, Tafel analysis allows for the determination of the rate determining step, exchange current density and expression of the necessary overpotential. Different groups elaborated the correspondence of the Tafel slope to the rate-limiting step in the OER mechanism [19,54–56]. However, in current research, Tafel slopes are increasingly used for comparative discussion of OER activities without in-depth consideration of the reaction mechanism. The complex mechanism involving many different intermediates complicates reduction of the overpotential necessary for the OER.
compared to the comparably simpler HER [57]. In order to do so, many catalyst systems were developed and investigated to reduce the activation barrier and by this the overpotential. Correlating different descriptors, such as the enthalpy of transition from a lower to a higher oxidation state of a metal or the difference between $\Delta G_{O^*}$ and $\Delta G_{OH^*}$, against the overpotential needed to achieve a certain current density results in volcano type relationships (Figure 4) [58]. The former correlation arises due to the fact that the OER activity can be expressed as being dependent on the transition between two different configurations of the surface coordination complex [59]. This means that transition metal centers of metal oxides which are easy to oxidize adsorb oxygenated reaction intermediates too strongly, while they adsorb them too weakly when the oxidation is difficult [14]. A highly active catalyst has to be in between, similar to the aforementioned HER catalysis.

![Figure 4. OER volcano plot for metal oxides (adapted from [58]).](image)

When $*\text{OH}$ and $*\text{OOH}$ are involved reaction intermediates, many investigated catalysts obey a non-optimal scaling relation hindering the development of highly efficient catalysts [58]. It was observed for various catalyst materials, that the free energy for intermediates formed in OER and ORR change similarly with change in material properties. This phenomenon, called the scaling relations, is especially observed for the $*\text{OH}$ and $*\text{OOH}$ intermediates, whereby, weakening or strengthening energy of adsorption of these intermediates leads to a similar effect for the other intermediate [13,60–65].

In the last decades, a tremendous amount of OER catalysts were developed, based on different type of materials. The precious metal oxides, RuO$_2$ and IrO$_2$, known to be the best OER catalysts in acidic media were also applied for the OER in alkaline media [66,67]. The two
precious metal oxides adopt the rutile structure with Ir and Ru in the center of an octahedron with oxygen at the corners \[53\]. Although at least IrO\(_2\) is the only relatively stable OER catalysts in acidic electrolytes, its instability in alkaline media at highly anodic potentials was demonstrated \[68\]. Under oxidizing potentials, both RuO\(_2\) and IrO\(_2\) get oxidized to high oxidation states, which are soluble in the electrolyte \[23,68–70\]. In addition to their instability, their scarcity prevents large scale application for the envisaged industrial water splitting. Thus, cheaper and more stable alternatives were developed for alkaline OER, among which also more active candidates can be found. The structural variety of non-precious metal OER catalysts range from metal oxides \[24\], e.g. spinel oxides \[71–73\] and perovskites \[74\], transition metal (TM) hydroxides \[75,76\], e.g. layered (double) hydroxides \[77–79\], to non-oxide heteroatom doped transition metal materials, e.g. TM chalcogenides \[80\], phosphides \[49\] and borides \[46,47\]. In the following, special focus will be set on the classes of layered double hydroxides (LDHs), metal borides and phosphides, because of their recently growing interest in catalyst research.

Inclusion of non-metal or metalloid atoms into the lattice of metals is known to alter the electronic structure of the host metals. It was shown that introduction of boron into the metal crystal structure changes the lattice strain, hence decreasing the thermodynamic and kinetic barrier of the hydroxylation reaction \[46\]. Thus, the formation of the $*$OOH intermediate, a key limiting step in OER, is enhanced. Transition metal borides were already reported for the OER in alkaline electrolytes in the 1980s by Osaka et al. and further explored recently \[46–48,81\]. Electronegative dopants, e.g. phosphorous, when in close vicinity to electrocatalytically active sites can induce two effects \[82\]. The localized negative charge at the heteroatom increases the 3p-2p repulsion, hence deactivating the catalyst for coordination with hydroxide ions \[82\]. Evidently, this effect alone would increase the necessary OER overpotential substantially. This effect is compensated by the growth of an (oxy)hydroxide layer around the heteroatom doped metal core during a pre-OER conditioning process (Figure 5a) \[82\]. The growth of the (oxy)hydroxide layer can clearly be observed by electrochemistry and surface sensitive physical characterization techniques, e.g. X-ray photoelectron spectroscopy (XPS) (Figure 5b&c).

Co/Co\(_2\)P shows an irreversible oxidation peak when exposed to anodic potentials representing the oxidation of metallic Co to Co\(^{3+}\). Subsequent potential cycling shows a reversible 2+/3+ couple, which grows in intensity until a steady state is reached. The increase in the peak currents indicate growth of the formed (oxy)hydroxide layer necessary for accelerated OER. XPS analysis of a fresh and conditioned Co/Co\(_2\)P exhibit an obvious shift of the Co 2p\(_{3/2}\) signal to higher binding energies accompanied by a clear change of the peak shape, thus confirming the
transition of metallic Co to oxidized Co species. This growth of an (oxy)hydroxide layer was also observed for transition metal borides [46,47] and is a necessary prerequisite prior to oxygen evolution.

After complete hydroxide coordination of the shell metal ions, the coupled oxidation and deprotonation during OER is supported by the increased electron population at metal centers having electron donating dopant atoms in close vicinity [82]. Furthermore, the 3p-2p repulsion between the *OOH intermediate and the heteroatom dopant, induced by the electronegativity of the dopant, accelerates dioxygen formation from *OOH [82]. Although the beneficial properties occur at active sites in close vicinity with the heteroatoms, the doping can only happen to certain limits, otherwise, the material might transform into a semiconductor or even an insulator, both of which are undesirable for electrocatalysis, because such a change would substantially increase the ohmic drop and hence the OER overpotential [83].

Another very promising class of materials for the OER in alkaline media with growing interest in the electrocatalysis community are LDHs. They are currently reported to be the most active OER catalysts in alkaline media. LDHs are layered materials with a brucite type structure. They

![Figure 5](image-url)

**Figure 5.** Schematic representation of the growth of the (oxy)hydroxide layer around a Co/Co$_2$P core (a). Conditioning cyclic voltammograms of Co/Co$_2$P (red arrows indicate the growth of the (oxy)hydroxide layer) (adapted from [49]) (b). XPS Co 2p$_{3/2}$ core-level spectra of fresh and conditioned Co/Co$_2$P (adapted from [49]) (c).
are typically described by the chemical formula \( \text{M}^{2+}_{1-x} \text{M}^{3+}_x (\text{A}^n_m)^x/n \cdot y \text{H}_2\text{O} \), with \( \text{M}^{2+} \) and \( \text{M}^{3+} \) representing di- and trivalent metal cations, respectively. \( \text{A}^n_m \) is an anion having the valence \( n \) and \( x \) represents the \( \text{M}^{2+}/(\text{M}^{2+}+\text{M}^{3+}) \) ratio with reported values between 0.2 - 0.33. The partial replacement of bivalent cations by trivalent metal cations introduces a net positive charge in the hydroxide layers, which is balanced by anions present in the LDH galleries. This class of materials was already intensively explored in different fields, e.g. heterogeneous catalysis, pharmaceutics, polymer science and photochemistry [84,85]. The interest in applying LDHs for the OER intensified just recently. After the photochemical oxygen evolution driven by LDHs in 2009 [86], Hu et al. made initial observations regarding the electrochemical OER by LDH [87]. Broad interest in LDH as OER catalysts just intensified after the presentation of a NiFe LDH/CNT composite by Gong et al. in 2013 [88]. The authors overcame the low conductivity, which is usually associated with metal hydroxides, by combining it with a conductive material (CNTs), hence making NiFe LDH/CNT one of the most active catalyst for the OER in alkaline media at that time. Not only a high intrinsic activity but also a promising stability under OER conditions was already demonstrated. Since that report, vast efforts on elucidating LDHs as OER electrocatalysts in the last years focused on enhancing the intrinsic OER activity. Three major approaches pursued to facilitate the OER at low overpotentials can be distinguished: \( i \) Variation of the transition metals and their composition [89–91]; \( ii \) Combination of LDHs with functional carbon materials, e.g. CNTs, graphene or reduced graphene oxide [92–101]; \( iii \) Exfoliation of bulk LDHs to form highly active and ultrathin nanosheets [77,102–104]. Among the reported LDHs as catalysts for OER, materials containing Ni and Fe appeared to form the most active catalysts making them exemplarily worth for studying the influence of the interlayer anion, crystallinity, sheet size and the proceeding OER mechanism. Systematic studies of the sheet size and crystallinity of NiFe LDH demonstrated decreasing OER activity with increasing crystallinity and sheet size [105]. It was shown that the OER activity closely correlates with the amount of defect sites, a prerequisite for high OER activity, which is also decreasing with increasing crystallinity. Increasing sheet size leads to a decrease of accessible active sites, which are supposed to be predominantly located at the sheet edges, thus the electrocatalytic activity declines [105]. The interlayer anion was found to have a significant influence on the initial OER activity of NiFe LDH. Hunter et al. correlated the overpotential necessary to achieve 1 mA cm\(^{-2}\) with the \( pK_a \) values of the conjugate acid of the interlayer anion, and reported decrease of the overpotential with increasing \( pK_a \) [106]. On the contrary, the interlayer anion defined basal spacing cannot be correlated to the initial OER activity, at least not in the investigated range of 7.5 to 8.6 Å [106]. However, Hunter et al. further demonstrated the
exchange of all investigated anions against carbonate, originating from dissolution of ambient CO$_2$, when measurements are not done in virtually carbonate free solution [106]. Thus, controlled sheet size and crystallinity are of utmost importance in designing highly active LDH based OER catalysts rather than the choice of the interlayer anion. Although tremendous effort was expended in order to increase the OER activity of this class of materials, a survey of the benchmark OER activity of LDH materials over a time span from 2013 to 2016, reveals no remarkable improvement of the intrinsic OER performance (Figure 6).

**Figure 6.** Box plot of the average overpotential required to reach a current density of 10 mA cm$^{-2}$ using LDH catalysts immobilized on flat and OER inert electrode surfaces for the years 2013, 2014, 2015 and 2016. Values taken from [88] (2013, grey); [77,103,102,107,108] (2014, black); [93–95,104,109,108,110] (2015, red); [90,91,96–98,100,111–114] (2016, purple) [adapted from [115]].

In order to overcome the apparent limitations in the enhancement of the OER activity of LDH based materials and also in the overall development of electrocatalysts, new strategies mostly based on the use of high surface area materials as supports for electrocatalysts were developed. In particular, nickel foam gained a lot of attention as a highly conductive and high surface area catalyst support [49,91,116–120]. The porous high surface area of nickel foam (NF) or generally foamy and three-dimensional electrode supports open the possibility of increasing the apparent intrinsic activity drastically, represented in achievement of high current densities at low overpotential. The difficulty to reliably determine the real surface area of 3D structures and the normalization of current by the geometric area of the electrode increase the apparent catalytic activity of catalysts supported on porous 3D structures with respect to the activity obtained employing flat inert electrodes. However, this apparent increase in activity might also be the result of a synergistic effect between real catalysts and metal cations originating from the support electrodes upon application of highly anodic potentials or simply a magnification effect due to false normalization of the current by the geometric area of the 3D support. The
latter case was demonstrated by Suen et al. by comparison of the anodic current of Co$_3$O$_4$ normalized by the geometric surface area of various types of electrodes against those obtained by normalization with the electrochemically active surface area (ECSA) (Figure 7) [53].

![Figure 7. Polarization curves of Co$_3$O$_4$ on various types of electrodes with currents normalized by the geometric area of the electrode (a), and the electrochemically active surface area (b) (adapted from [53]).]

Besides the tremendous effort conducted in order to design more active electrocatalysts, understanding the mechanism of oxygen evolution and the specific material properties continuously gained interest. For NiFe (oxy)hydroxide based OER catalysts, Friebel et al. [121] revealed iron to be a highly active site for the OER by employing operando X-ray absorption spectroscopy (XAS). Additionally, they observed a change in the oxidation state of Ni from the initial 2+ state to a formal 3.6+ state, while Fe remains in the 3+ state during active oxygen evolution. Surface interrogation scanning electrochemical microscopy further proved the Fe sites in NiFe (oxy)hydroxides to be faster in terms of catalytic turnover [122], thus further confirming the findings of Friebel et al.. Dionigi and Strasser published a comprehensive review article covering a wide range of influences on the OER activity of NiFe (oxy)hydroxides combined with advanced in-situ characterization techniques in order to understand the contribution of the various influences [123]. Density functional theory (DFT) calculations were employed by Fan et al. in order to get an insight into the origin of the superior OER activity of their NiV LDH with respect to a NiFe LDH [91]. They found that on both materials, two different OER mechanisms take place, with two different reactions being the rate limiting steps. Despite significant efforts in the last years, the OER mechanism on NiFe (oxy)hydroxides is still not fully revealed and still under debate [123].
Oxygen evolution catalysis is not only of high importance for the electrochemical water splitting process, but also a key reaction in rechargeable metal air batteries. Thus, the next section focuses on electrochemical energy storage in metal air batteries.

2.1.2 Metal-air batteries

In the search for new energy storage systems with high energy density, metal-air batteries have become the focus of attention. In theory, metal-air batteries have very high energy densities, which makes them appealing for applications in electromobility and energy storage for smart grids [7,124–127]. Surplus energy can be stored in metal-air batteries in the form of redox states due to redox reactions between anode metal and oxygen from air. They essentially consist of a metal anode and a cathode with an open structure. The objective of the open cathode structure is to maintain a continuous supply of oxygen from the air. The high energy density, which is theoretically comparable to that of gasoline [126,127], is governed by two key factors. On the one hand, oxygen, the cathode reactant, is not stored in the cell and on the other hand, the anode metals, e.g. Li, Zn, Mg and Al, posses a high ratio of valence electrons to atomic nuclei and therefore a high energy density [128]. A schematic representation of a metal-air battery is depicted in Figure 8. During discharging, the anode is oxidized releasing metal cations into the electrolyte and form oxides or hydroxides, the generated electrons are used at the cathode to reduce molecular oxygen to hydroxide ions. The electrochemical charging process involves the oxygen evolution at the oxygen electrode and reduction of the metal ions. However, mechanical replacement of the discharged metal anode and the electrolyte by a new metal anode and metal cation free electrolyte can also be used to regenerate the battery. The discharged anode can be electrochemically recycled together with the metal cation containing electrolyte. One of the major drawbacks of mechanical recharging is that it necessitates the transportation of additional equipment and resources, hence an electrochemical approach would be highly desirable.

Several critical issues have to be addressed in order to realize widespread application of rechargeable metal-air batteries. Both electrodes suffer from various limitations. On the one side, the low utilization efficiency of the anode has to be overcome. The efficiency of the metal anode can drop because of various reasons, e.g. corrosion due to the high alkaline electrolyte pH value, passivation by accumulation of metal oxides and hydroxides at the electrode surface and self-discharging. Even though the problems regarding the anode deterioration can be solved [129], the air electrode presents serious bottlenecks because of the sluggish reaction kinetics, the high overpotentials and the poor reversibility, governed by the inherently different nature of the OER and the ORR [130–132].
2.1 Electrochemical energy conversion and storage

2.1.2.1 Oxygen reduction reaction (ORR)

The oxygen reduction reaction (ORR) is the reverse of the OER, thus its kinetics can similarly be described by the Butler-Volmer equation (Eq. 4). The ORR either involves the transfer of 4 or 2 electrons [133]. The energetically more efficient 4 $e^-$ pathway (Eq. 17 – 19) is highly preferred for fuel cell and metal-air battery applications, while the 2 $e^-$ pathway can be used for cathodic hydrogen peroxide production [134]. The mechanisms proposed in alkaline media are the following [135,136]:

Dissociative mechanism:

\[ O_2 + 2* \rightarrow 2O^* \]  
\[ 2O^* + 2e^- + 2H_2O \rightarrow 2OH^* + 2OH \]  
\[ 2OH^* + 2e^- \rightarrow 2OH^- + 2* \]  

Figure 8. Schematic representation of the structure of a metal-air battery with the corresponding reactions during discharging and charging processes.

In the following sections, deeper insight in the ORR and bifunctional oxygen electrocatalysis is given.
This mechanism can be described as $O_2$ adsorption followed by $O-O$ bond dissociation and formation of two adsorbed $O^*$ species. $O^*$ further reacts with $2e^-$ and two protons directly to $OH^-$ without $OOH^-$ formation. Besides the dissociative mechanism, ORR can also proceed via an associative pathway (Eq. 20 – 27):

Associative 4 $e^-$ mechanism: $O_2 + * \rightarrow O_2^*$  

$$O_2^* + H_2O + e^- \rightarrow OOH^* + OH$$  (21)

$$OOH^* + e^- \rightarrow O^* + OH$$  (22)

$$O^* + H_2O + e^- \rightarrow OH^* + OH$$  (23)

$$OH^* + e^- \rightarrow OH^- + *$$  (24)

The 4 $e^-$ associative pathway (Eq. 20 – 24) can be described more precisely as a [2+2] $e^-$ oxygen reduction. After the adsorption of a dioxygen molecule at an active site, a peroxide intermediate is formed, which is further reduced to an adsorbed oxygen atom. Two subsequent proton coupled electron transfer steps finally lead to the formation of the hydroxide. Depending on the properties of the electrocatalytic material, reduction of the adsorbed peroxide intermediate can lead to the formation of hydrogen peroxide as final product. This pathway is generally described as the associative 2 $e^-$ pathway (Eq. 25 – 27).

Associative 2 $e^-$ mechanism: $O_2 + * \rightarrow O_2^*$  

$$O_2^* + H_2O + e^- \rightarrow OOH^* + OH$$  (25)

$$OOH^* + e^- \rightarrow OH^- + *$$  (26)

Whether the ORR follows the associative or dissociative mechanism essentially depends on the initial $O_2$ dissociation energy barrier on the catalytically active surface [135]. DFT calculations revealed that the dissociation energy barrier on carbon materials is normally very high, thus many of those materials tend to reduce oxygen according to the associative mechanism with the number of transferred electrons being less than four [137]. On the other hand, most of the metallic ORR catalysts show strong oxygen adsorption and hence follow the dissociative 4 $e^-$ reduction pathway [138,139]. It appears that knowledge about the selectivity of the ORR catalyst under investigation is of highest importance. Various electrochemical methods can be applied to determine the apparent number of transferred electrons and additionally, whether
hydrogen peroxide is produced or not. Typically, the selectivity of the investigated ORR catalyst is investigated by means of hydrodynamic voltammetry. Useful tools for this purpose are the rotating disk electrode (RDE) and rotating ring disk electrode (RRDE) (Figure 9). For reactions limited by diffusion of the reactant, rotation of the disk electrodes facilitates high mass transport of the reactant to the electrode surface. A RRDE additionally consists of a ring electrode (often platinum) surrounding and concentric with the disk electrode. Typically, the ring and disk electrode are electrically separated by an insulating material, often PTFE or PEEK, at a precisely defined distance.

Levich showed that under controlled hydrodynamic conditions, the diffusion limited current $I_d$ of a smooth electrode surface correlates with the number of transferred electrons and the angular velocity of the electrode. The correlations are expressed in the Levich equation (Eq. (28)):

$$I_d = 0.62nFAD_0^{2/3} \omega^{1/2}v^{-1/6}C_0$$

With $n$ being the number of transferred electrons, $A$ the surface area of the electrode, $\omega$ the angular velocity (rad s$^{-1}$), $F$ the Faraday constant, $D_0$ the diffusion coefficient of the reactant, $C_0$ the concentration of the reactant and $v$ the kinematic viscosity of the electrolyte.

Thus, at a given electrode rotation speed, the number of transferred electrons can be estimated by solving the Levich equation for $n$. When different rotation speeds are applied, $n$ can be obtained from a plot of the diffusion limited current $I_d$ versus the square root of the angular velocity.
velocity, which yields a linear plot with the slope \( \frac{1}{i} = \frac{1}{i_k} + \frac{1}{i_d} \) (29)

with \( I_k \) being the kinetic current and \( I_d \) the diffusion limited current. \( I_d \) can also be expressed as product of the Levich constant \( B (=0.62nFAD_0^{2/3}\omega^{1/2}v^{1/6}C_0) \) and \( \omega^{1/2} \). Plotting \( I^1 \) versus \( \omega^{-1/2} \) at a specific potential leads to a straight line with the slope \( B^{-1} \), from which the number of transferred electrons \( n \) may be determined.

The RRDE uses the ring as a sensor electrode designed to detect products from the reaction taking place at the disk electrode. In order to do so, the life time of the species produced at the disk has to be long enough to allow them to transverse the radius of the disk electrode and the insulating layer between the disk and the ring to reach the ring electrode. Generally, the ring is constantly kept at a suitable potential to oxidize or reduce the product of interest. For the case of the ORR, the ring is held at a potential sufficiently anodic to oxidize any formed hydrogen peroxide. The amount of hydrogen peroxide can then be calculated according to equation (30):

\[
X_{H_2O_2} = \frac{2i_R/N}{i_D + i_R/N}
\]

With \( i_R \) being the current measured at the ring, \( i_D \) the current measured at the disk electrode and \( N \) the collection efficiency. Typically, \( N \) is provided by the manufacturer of the RRDE, however, it is advisable to check the collection efficiency with each modified electrode using a simple redox mediator.

Obviously, RDE and RRDE voltammetry are useful techniques for investigation of the ORR mechanism and kinetics. However, it is worth to bear in mind that the theoretical considerations and the mathematical formulations behind the equation presuppose conditions of flat and smooth surfaces and laminar flow velocity profiles. Evidently, extended electrode surfaces with high surface area and porous materials cannot be considered as flat and smooth, thus the theoretical boundaries are not fulfilled and the derived \( n \) and \( X_{H_2O_2} \) are to be interpreted more as apparent values. Additionally, the detection of \( H_2O_2 \) by the RRDE and the resulting \( n \) are crucial since the formed \( H_2O_2 \) can further react either at the disk or ring electrode or chemically
decompose before it can be detected, hence leading to erroneous conclusions about the ORR selectivity of the investigated catalyst. Many catalytic systems have been developed and investigated for the ORR. Commercial fuel cell catalysts are based on platinum nanoparticles supported on carbon black. However, pure Pt nanoparticles are known to be instable under fuel cell operation, thus researchers tried to stabilize them by alloying with various transition metals [140]. In addition to enhanced stability, the alloying is able to improve also the catalytic activity. The enhanced activity of Pt-TM alloys (TM = transition metal) can be attributed to two aspects: ligand effects and strain effects [65]. Both effects may change the d-band center and chemisorption properties of the surface [65]. A change in the strength of \( \text{OH}^* \) adsorption on Pt surfaces can be correlated with a shift in the d-band center due to alloying [146]. Because of the well-known scarcity of Pt, non-precious metal catalysts (NPMCs) were also developed. In alkaline media, NPMCs are able to approach or even surpass the ORR activity of Pt based electrocatalysts [14,147]. Highly active NPMCs can generally be separated into two classes: i) TM-N4 macrocycles, either supported or unsupported, pyrolyzed and not pyrolyzed and ii) TMs coupled to or supported on nitrogen doped carbon. In the 1960s, Jasinski first reported cobalt phthalocyanines as a NPMC for the ORR [150]. Following his report, numerous studies were published regarding variation of the incorporated metal, the N4 macrocycle, e.g. phthalocyanine, porphyrin and tetraazaanulene, and their substituents [147,152–155]. It was shown that the electronic structure of the metal center has a beneficial influence on the \( \text{O=O} \) bond dissociation [158,159]. However, TM-N4 macrocycle based ORR catalysts suffer from various drawbacks, for example, they possess poor thermal and chemical stability in common electrolytes for ORR, and poor electrical conductivity, although they have delocalized \( \pi \) electrons. Thermal treatment at high temperatures in an inert gas atmosphere was demonstrated to improve the stability of TM-N4 active sites [147,161,162]. Rather than starting from N4-macrocycles, a simpler approach for preparation of TM-N4-type catalysts was developed and is based on thermal treatment of a mixture containing a metal salt, a suitable form of carbon and a nitrogen source. Recently, metal organic frameworks (MOFs) were presented as precursors of well-structured TM-N\(_4\) ORR catalysts [141–143]. During the formation of carbonaceous ORR catalysts, mainly three different types of active sites can be obtained [167–170]: \( i \) TM centers coordinated to nitrogen atoms embedded in a carbon matrix; \( ii \) TM centers inside nitrogen doped carbon species such as graphene, CNTs etc.; \( iii \) metal free hetero atom doped carbon species, where the metal might be leached out after the preparation or not present at all. Based on the variety of possible precursors and synthesis procedures, many different structures can be obtained, hence altering
the electronic and structural environment of the metal centers [174–176]. A key structure for a
high ORR activity of TM-N/C catalysts is the coordination of nitrogen to TM centers, in which
the coordinating nitrogen atoms have a pyridinic or pyrrolic conformation [145]. The high
activity of these moieties originates from Sabatier’s principle arising from a moderate
adsorption strength between the metal center and the ORR intermediates. If incorporated into
N-doped carbon and not actively involved as active sites, the TM center can evoke improved
ORR activity by modulation of the electronic structure and work function of the carbon support
[145]. The N-doping itself further improves the ORR activity by enhancing the $O_2$ adsorption
and its activation [174]. The activity of metal free ORR catalysts is based on their unique
electronic structure for the adsorption of $O_2$ and intermediates as well as a large number of
exposed active sites [145]. Metal free ORR catalysts can be divided into carbon and nitride
based materials, of which the carbon based subcategory is most developed. It is noteworthy that
pure carbon materials do not exhibit decent ORR catalytic activity [145]. The ORR activity is
introduced by doping the carbon material with heteroatoms such as N, B, P and S [14]. The
heteroatom doping may introduce two beneficial effects: $i$) changing the electronic structure of
the carbon framework, and $ii$) creating defect sites leading to a stronger (but not too strong)
oxygen adsorption [188,189]. The most developed and investigated metal free and carbon based
ORR catalysts are nitrogen doped CNTs and graphene or graphene type structures (e.g. reduced
graphene oxide) [14]. The nitrogen can be present in three different conformations, graphitic,
pyrrolic and pyridinic, within the carbon network (Figure 10) [14].

![Figure 10. Schematic representation of the different nitrogen conformations in nitrogen doped carbon.](image)
Of these, pyridinic carbon induces the highest ORR activity [60,144]. Guo et al. reported that the ORR active sites in nitrogen doped carbon are carbon atoms with Lewis basicity induced by adjacent pyridinic nitrogen [144]. Experimental and theoretical investigations demonstrated that double heteroatom doping can enhance the ORR activity of carbon based catalysts even further than single doping [196,197]. It was shown that this is evoked by a synergistic effect between the two heteroatom dopants. Although often claimed to be metal free, catalytically grown carbon materials as e.g. CNTs might contain residual growth catalyst in amounts not detectable by analytical methods. It was indeed shown that such trace metal residues are able to substantially enhance the ORR catalytic activity when exposed to the electrolyte or by altering the surface electronic properties of their host carbon framework [148,149].

2.1.2.2 Bifunctional oxygen electrocatalysts

For the development of electrochemically rechargeable metal-air batteries, bifunctional oxygen electrodes are essential. As mentioned previously, both the ORR and the OER suffer from their sluggish kinetics and high overpotentials, thus being individually challenging reactions by themselves. The task to develop materials, able to efficiently catalyze both reactions on the same electrode introduces even more difficulties. It was observed that highly active catalysts for the ORR, e.g. platinum based catalysts, are not reasonably active for the OER and vice versa. The origin of this phenomenon is the substantial dissimilarity of the two reactions. The activity of the ORR is restricted by the initial $O_2$ reduction, and $OH^*$ reduction steps, while the OER activity is governed by the $O^*$ and $OOH^*$ formation steps [164]. Since the binding energies of the catalysts cannot be optimal for all the limiting intermediates involved either in the ORR or in the OER, most of the electrocatalysts are either active for the OER or for the ORR. Hence, bifunctional oxygen electrocatalysts are often based on composites of OER and ORR active centers combined on one electrode surface. These composites might be built from the same precursor or are physical mixtures of two distinct materials [151], of which one is active for OER and the other for ORR. The former can be synthesized by a two-step thermal treatment of TM-N4 macrocycles, or a composite of TM-N4 macrocycles with a network of few layer graphene. The first step of the thermal treatment, pyrolysis under an inert atmosphere, leads to formation of the ORR active TM center coordinated by four pyridinic nitrogen atoms, while the second step, a mild calcination step, forms metal oxide moieties, which are active for the OER [156,157]. A similar two-step protocol was recently applied to a Co containing metal organic framework, with the difference that the first step was done under a reductive hydrogen
atmosphere. The resulting core-shell material comprising a cobalt oxide on cobalt nanoparticle (core) showed high bifunctional activity [141]. Zhong et al. presented a material consisting of a crystalline Co$_2$P and Co$_3$N core surrounded by a nitrogen doped carbon shell [160]. Although highly active bifunctional catalysts have apparently been developed, their stability and reversibility is still insufficient. The highly anodic potentials applied during the OER lead to oxidation of the materials, which although desirable for formation of the OER active sites, often results in irreversible destruction of the ORR active sites, thus leading to a poor ORR/OER cyclability [151,156,163]. Therefore, despite developing highly active bifunctional oxygen electrodes, more research has to be devoted toward high cyclability in order to achieve fully rechargeable metal-air batteries.

### 2.2 Polybenzoxazine resins

Polybenzoxazine (pBO) resins are highly crosslinked networks of benzoxazine (BO) monomers or oligomers. BOs are heterocyclic compounds consisting of a benzene ring condensed to an oxazine ring, a six-membered ring containing oxygen and nitrogen heteroatoms. Depending on the position of the heteroatoms in the ring, different BO structures are obtained [165]. 1,3-benzoxazines are particularly of high interest for the development of polymeric materials, because of their ability to undergo cationic ring-opening polymerization [165]. They are products of a Mannich-type reaction between phenol derivatives, primary amines, either aliphatic or aromatic, and formaldehyde. In the 1940s, Cope and Holly synthesized the first benzoxazines via reaction of aldehydes or ketones with o-aminobenzyl alcohol and the reaction of formaldehyde and o-hydroxybenzyl amine [166]. The first polymerization product, thus the first pBO, was obtained by Ning and Ishida upon thermal polymerization of bifunctional BO monomers in 1994 [171]. Thermal treatment of the monomers leads to a crosslinking process forming a phenolic polymer network (Figure 11).

![Figure 11. Schematic representation of thermally induced polymerization of 1,3-BO monomers.](image)

2.2 Polybenzoxazine resins
The large variety of suitable amine and phenol derivatives for the monomer synthesis provides the later formed resins with several unique properties:

i) Near-zero volumetric shrinkage upon polymerization.

ii) Low absorption of water.

iii) $T_g$ higher than the polymerization temperature.

iv) Polymerization in absence of strong acids and catalysts possible.

v) Large amount of commercially available monomer precursors.

vi) Polymerization without the formation of side products.

vii) High thermal stability and high residual char after carbonization.

These properties made pBO highly interesting for material sciences and the electronic and aerospace industry [172]. The development of new BO monomers and investigation of the polymerization mechanism are the two main pursuits in the field of polybenzoxazine research. A high stability of BO monomers towards ring-opening and by this the formation of a Mannich-bridge is of pivotal importance. The presence of acidic protons as in naphtols, indoles, carbazoles, imides and phenols might cause such unwanted ring opening at unstable BO monomers. The stability of the BO monomer can easily be enhanced by variation of the substituents at the oxazine ring and the use of basic amines and weak acidic phenols [173]. Slow reaction rates, large amounts of solvents and poor solubility of reactants are major disadvantages of conventional wet chemical synthesis strategies. BO monomers may contain solvent residues, which may cause failure during the polymerization process. To this end, Ishida et al. developed a solvent free approach, to overcome aforementioned issues by conducting the syntheses at temperatures higher than the melting points of the reactants. The low boiling point and thus the fast evaporation of formaldehyde makes it unsuitable for the new methodology, because its evaporation would change the stoichiometry, hence it was replaced by the thermally more stable paraformaldehyde. The virtually endless variety of conceivable BO monomers can be seen in the development in recent years, in which tremendous work was done to adjust specific BO monomer properties by varying their precursors. Implementation of second polymerizable functionalities, e.g. allyl, acetylene or epoxy, into the monomers generally leads
to a higher thermal stability [177–184], while introduction of an aliphatic chain forms more flexible monomers and polymers [185,186].

In benzoxazine research, the mechanism of polymerization is a highly investigated aspect. In order to understand the ability of BO to polymerize, it is necessary to understand their molecular structure. According to molecular modeling, a distorted half-chair conformation is energetically most favorable for the oxazine ring [187]. The resulting ring strain thus allows polymerization via opening of the oxazine ring. The high Lewis basicity of nitrogen and oxygen most probably promote a cationic ring opening mechanism in which either oxygen or nitrogen can act as polymerization initiator [187]. Usually, BO polymerization is thermally induced, starting with ring opening, followed by electrophilic attack and rearrangement in order to yield the most favored phenolic structure shown in Figure 11 [173,190,191]. Liu et al. carried out in-depth investigation of the polymerization mechanism in the presence of different catalysts [192,193]. They discovered various mechanisms which differ not only in the ring opening process but also in the subsequent electrophilic attack. The cationic ring opening of a 1,3-benzoxazine is dependent on the nature of the catalyst and occurs either via bond dissociation between the oxygen and the carbon atom at position 2 of the oxazine ring, or between the nitrogen and either the carbon atom at position 2 or 4 of the oxazine ring. The resulting cationic intermediates can subsequently react with another benzoxazine monomer via electrophilic attack at the oxygen, nitrogen or aryl ring [192,194,195]. Thus, the polymerization can proceed via nine different pathways depending on the used catalyst. Typically, phenoxy structures are obtained upon polymerization, which rearrange to the desired phenolic structure. One possible polymerization pathway is schematically described in Figure 12.

![Figure 12. Schematic representation of one possible polymerization pathway via bond dissociation between nitrogen and the C2 atom followed by an arylc electrophilic attack and a final rearrangement of the phenoxy to a phenolic structure (adapted from [192]).](image_url)
Besides their application in corrosion protection [198,199], as flame retardants [200,201] and as high performance thermosets [202,203], polybenzoxazine networks also found their way into application in electrochemistry [204–207].

2.2 Polybenzoxazines (pBO) in electrochemistry

Electrochemical polymerization of precursor materials yielding corrosion protective layers on metal substrates is already known for polymer coatings such as polyphenols [208], hence, it is interesting to understand the electropolymerization process of benzoxazine monomers on conductive surfaces. Audebert et al. investigated (1995) the electrochemical properties of methyl benzoxazines in different deposition electrolytes [208]. They found that polymeric films which could be used for corrosion protection were formed in basic electrolytes upon electrochemical oxidation of the monomers. The proposed mechanism is based on deprotonation of the monomer by the base, followed by electrochemical oxidation of the formed anion, leading to the formation of a neutral radical. The formed radical further reacts either with another monomer to initiate the polymerization, or with a hydroxide anion or another radical, both of which suppress the polymerization. In contrast to the thermal polymerization, no cationic ring-opening is expected upon polymerization. On the contrary, Li et al. proposed cationic ring-opening electropolymerization in the presence of a base several years later [209]. The authors observed a two-step oxidation process, in which the second oxidation at higher potentials results in polymerization. Physical characterization of the polymerization product revealed a phenolic structure of polybenzoxazine as described previously for thermal polymerization [209]. In 2009, Chen et al. confirmed the cationic mechanism leading to ring-opening polymerization by means of rotating ring disk electrode (RRDE) voltammetry [210]. They observed potential dependent formation of two cationic species formed upon electrochemical oxidation of the BO monomer, which is in good agreement with the two oxidation peaks observed by Li et al. [210]. Chen et al. proposed a [2+2] electron oxidation mechanism for the polymer formation. Thus, the preferred phenolic structure of the polymer can be achieved by simple electrochemical oxidation without the need for thermal treatment. The electrochemical polymerization opens new fields of application for pBOs, where a high temperature treatment cannot be applied. The development of the water soluble main-chain-type BO BA-tepa paved the way for the use of pBO in bioelectrochemical research. BA-tepa is the product of the Mannich-type reaction of bisphenol A, tetraethylenepentamine and formaldehyde [211]. BA-tepa was used by different groups, for example, as an electrodeposition polymer to entrap enzymes on an electrode surface in order to fabricate
amperometric biosensors [212,213]. Andronescu et al. prepared the first amperometric biosensor using an enzyme entrapped in a polymer layer based on pBO [213]. They entrapped glucose oxidase into a BA-tepa film by electrodeposition on glassy carbon electrode surfaces. The insulating nature of pBO can lead to complete blockage of electron transfer depending on the number of deposition cycles or pulses. Using a Fe$^{3+/4+}$ mediator system, the influence of the number of deposition pulses was investigated. The peak current of the redox couple decreased with every deposition pulse until the electrode was completely blocked after 60 pulses. Nonetheless, Andronescu et al. demonstrated the possibility of designing a glucose oxidase based biosensor based on pBO electrodeposition. A similar concept was also explored for fabrication of miniaturized glucose and adenosine triphosphate (ATP) biosensors [212]. Further development was achieved by codeposition of redox polymers and glucose oxidase into electrochemically cross-linked BA-tepa oligomers [204]. This approach allowed electron shuffling via the redox active Os centers bound to a methacrylate backbone from the enzyme’s active center to the electrode, while the large methacrylate backbone ensured tight fixation of the redox polymer inside the biocatalytically active layer. Thus, freely diffusing mediators were no longer necessary. Alsaoub et al. reported Os complex modified benzoxazine monomers for the first time [205], combining the high stability of cross-linked monomers and the redox activity of Os complexes for electron hopping between the enzyme and electrode, hence presenting a new class of redox polymers for bioelectrochemical applications based on benzoxazines. A schematic representation of the development of benzoxazine based biocatalytically active electrode films is presented in Figure 13.

![Figure 13. Schematic representation of the different types of pBO based bioelectrochemically active films; a) Enzyme entrapped in a pure pBO film; b) Enzyme entrapped in codeposited redox polymer and pBO film and c) Enzyme entrapped in redox active pBO film.](image)

Besides the application of polymeric pBO networks in electrochemical systems, interest towards the formation of porous carbon networks derived from pBO pyrolysis has increased. The unique property of a high post-pyrolysis char yield provided by highly crosslinked pBO allows using them for the design of carbon based networks with tunable properties. Three
dimensional porous carbon networks can be achieved following various approaches. Zhang et al. directly grew pBO on a three dimensional nickel foam support, ensuring a conducting scaffold as well as porosity [214]. After pyrolysis and thus transformation of the insulating organic polymer into a porous carbon structure, they used it as a binder-free electrode for supercapacitors. A different approach of tuning the porosity was applied by Katanyoota et al, who introduced a slow, low temperature polymerization step to create a benzoxazine aerogel. Complete crosslinking and subsequent pyrolysis of the benzoxazine aerogel led to the formation of carbon aerogel electrodes for supercapacitor applications [215]. Template assisted formation of benzoxazine networks with successive pyrolysis created carbon networks with different morphologies, e.g. coral-like or spheres, which found their way into application as electrodes for lithium ion batteries and supercapacitors [216–220].
3 Problem identification and motivation of the work

In the field of electrocatalysis research, tremendous effort is conducted to develop new catalytically active materials to reduce reaction overpotentials, and to unravel the fundamental factors which govern specific electrocatalytic reactions and the mechanism taking place. In the last decades, thousands of new materials appeared in electrocatalysis related literature, apparently outperforming simple Ni based electrodes, which are currently used in industrial alkaline water electrolysis [221]. However, until now, most of these novel catalysts, especially powder based materials, cannot be applied in electrolysis because of insufficient catalyst fixation approaches. Thus, besides activity, the intrinsic stability and the stability of catalyst/electrode assemblies are of pivotal importance for further development of electrochemical energy conversion and storage devices. The obtained materials have to be brought in intimate contact with the electrode surface and fast electron transfer pathways between the particles as well as between the particles and the electrode have to be established. Furthermore, a catalyst film has to withstand the harsh and corrosive conditions as well as the physical stress upon gas bubble formation and departure during gas evolving reactions. The lack of sufficient strategies for catalyst fixation has led to a widespread use of organic polymers, especially Nafion, as binder matrices. However, organic polymeric binders might be insulating if used in too high amounts, thus blocking catalytically active sites and decreasing the catalytic activity. Poor conductivity, either as an intrinsic material property or evoked by the binder, is often compensated by the addition of conductive auxiliary agents (mostly carbon materials). Nonetheless, the mixtures of catalytically active material and conductive additives are finally affixed on the electrode with the aid of an adhesive organic polymer. It appears, that the development of new and innovative catalyst fixation strategies is highly needed, not only for the envisaged technical application but also for the characterization of possible structural changes of the catalytic material in the long term. The latter becomes obvious in LDH based materials, which can be produced containing various anions in the interlayer galleries, thus bearing different intrinsic catalytic activities. Hunter et al. demonstrated an exchange of all the tested anions for carbonate originating from atmospheric CO$_2$ dissolved in the electrolyte [106]. This anion exchange was accompanied by a change in the OER activity of the investigated materials. For observation of phenomena occurring over a longer time scale, e.g. structural changes from LDH to spinel or partial metal dissolution, catalyst fixation has to be resolved so that activity changes can be solely addressed to intrinsic material changes rather than material losses. A part of this work is thus dedicated to the development of methodologies and
techniques for stable fixation of catalysts on electrode surface, an issue which has hitherto received little importance in electrocatalysis research. Since polymeric binders are already widely used for catalyst fixation, would it be possible to choose an organic compound which does not decrease the film conductivity, or is it possible to embed catalyst particles inside a conductive matrix to avoid the addition of conductive additives?

In this work, polybenzoxazines and their previously described unique properties are investigated as binder matrices for various electrocatalysts. Catalytically active materials are embedded into a pBO derived N-doped carbon matrix via a polymerization and subsequent carbonization two-step thermal treatment procedure directly on electrode surfaces. The influences of the immobilization treatment and change of the precursor structure on the catalytic activity are studied by means of physical characterization techniques directly after preparation of the catalytic films and after electrochemical investigations. The conditions for the carbonization treatment are adjusted according to the kind of precursor used in order to tailor the properties of the final catalyst, or to ensure regeneration of the initial structure in a post-thermal treatment procedure. Furthermore, the formation of N-doped carbon is known to enhance or create ORR active species, which can additional coordinate to TM ions to form TM/NC-type catalysts. Thus, the feasibility of incorporation of TM precursors into pBO derived N-doped carbon for the creation of a TM/NC ORR catalysts directly on the electrode is explored.

Finally, an innovative binder free immobilization method, based on nanoparticle collision events and electrostatic interactions, is developed. From single nanoparticle collision events, it is known that the interaction between particles and electrodes can follow two different behaviors, the particle hits the electrode surface and stays (“hit-and-stay”) or it leaves (“hit-and-run”). It was envisaged that the former behavior can be exploited for immobilization of catalytically active particles on electrodes surfaces without the aid of any binders. This was thus explored for various water splitting catalysts bearing either negative or positive zeta potentials. In order to understand the catalyst film formation, the underlying mechanism and the film properties are investigated.
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4.1 Polybenzoxazine-derived nitrogen-doped carbon as matrix for Prussian blue analogue based OER catalysts

Prussian blue analogues were synthesized by Dr. Stefan Klink, X-ray photoelectron spectroscopy and thermogravimetric analysis were done in close cooperation with Dr. Corina Andronescu, both of them based in the Department for Analytical Chemistry – Center for Electrochemical Sciences, Ruhr-Universität Bochum. Transmission electron microscopy analysis was performed by Dr. Aziz Genc and Prof. Dr. Jordi Arbiol, Institut Català de Nanociència i Nanotecnologia, ICN2. Parts of the following section are included in the publication: Barwe, S., Andronescu, C., Masa, J., Ventosa, E., Klink, S., Genc, A., Arbiol, J., Schuhmann, W., Polybenzoxazine-derived Nitrogen-Doped Carbon as Matrix for Powder-based Electrocatalysts, ChemSusChem (2017) 10, 2653 – 2659.

In this chapter, the stabilization of transition metal based OER catalysts in a pBO derived carbon matrix is investigated. The thermal treatment of pBO at high temperatures leads to its carbonization when executed in an inert atmosphere. In order to obtain catalytically active material embedded inside the formed carbon matrix, the employed materials have to fulfil specific properties. The materials, later representing the catalytically active material, either i) transform during the pBO carbonization process from a precursor form into OER active materials, or ii) do not undergo any significant changes at the temperatures employed to convert the pBO into carbon. In the following studies, Prussian blue analogues (PBA) were chosen as precursor materials.

Recently, PBAs gained broad interest in energy research covering batteries, supercapacitors and electrocatalysis [222–232,142,233]. PBAs are cubic metal organic frameworks with the general structure $A_m T_x[M(CN)_6]_y$, in which a central transition metallate (T) is bridged to other transition metals (M) such as Fe, Ni, Co or Mn over six cyano ligands. PBAs provide a facile route to synthesize an endless list of different mixed metal compounds by varying the starting metal salts and their concentrations. Moreover, thermal treatment of PBAs leads to the formation of mixed metal oxides (calcination) or carbides (pyrolysis), further expanding the range of their possible applications [234,235].
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4.1.1 PBA and pBO composite preparation and screening of various PBAs as precursor

In order to explore a wide range of different metal compositions, five different PBAs served as precursors for the preparation of pBO/PBA composites. Transition metal combinations of NiCo, NiCoMn, CoCo, MnCo and NiFe were deliberately chosen because they are known to be potentially active for the OER in alkaline media [236,163,71,237,88,238,239]. PBA based catalyst particles embedded in a porous nitrogen-doped carbon matrix were prepared according to a three-step procedure (Figure 14, section 6.4.1). Thermally induced polymerization of a mixed film of a bisphenol A and aniline based BO monomer and PBA powder drop-coated on a glassy carbon electrode surface led to a polymer layer with incorporated PBA particles. Subsequent pyrolysis transformed the deposited pBO/PBA film into a conducting N-doped carbon matrix incorporating PBA derived mixed metal particles.

![Figure 14. Schematic representation of the electrode preparation procedure and the transformation of precursor materials into the final catalyst, exemplarily shown for K$_{n}$Mn$_{x}$[Co(CN)$_{6}$]$_{y}$ x nH$_{2}$O PBA as the precursor.](image)

The unique near-zero shrinkage property of pBOs led to a homogeneously distributed carbon matrix over the electrode surface even after pyrolysis. The modified electrode is entirely covered with PBA-based nanoparticles with the relatively larger particles representing agglomerates of the nanoparticles (Figure 15).
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The prepared composite materials based on a PBA to pBO ratio of 1:1 were investigated toward their OER activity by means of hydrodynamic potential cycling. Consecutive cyclic voltammograms reveal an activation process for the materials (Figure 16a). The OER activity of a composite of a NiCo PBA and BO showed substantial increase in the activity during the initial 20 cycles, manifested by a 100 mV decrease of the overpotential to afford a current density of 10 mA cm\(^{-2}\). Evidently, the overall OER activity is solely due to the pyrolyzed PBA, because the carbon matrix itself exhibited negligible oxygen evolution in the investigated potential window (Figure 16a, red line). Comparison of hydrodynamic linear sweep voltammograms (LSVs) of the various activated composites revealed only 30 mV difference in the potential necessary to achieve a current density of 10 mA cm\(^{-2}\) between the most and the least active composites, that is MnCo PBA and NiFe PBA, respectively (Figure 16b). The composite material based on the pyrolysis of a mixture of a MnCo PBA and BO afforded a low overpotential of 0.38 V (@ 10 mA cm\(^{-2}\)) and was the most active OER material in the tested series. However, high activity alone cannot be used as conclusive catalyst evaluation criterion, especially bearing in mind the highly demanding circumstances at oxygen evolution conditions. Therefore, all the composite materials were investigated for their intrinsic stability and catalyst adhesion on the electrode following an advanced stability assessment protocol (short: GSS test) [240]. Briefly, the GSS procedure consisted of a repeating sequence of electrochemical impedance spectroscopy, cyclic voltammetry and galvanostatic polarization at 10 mA cm\(^{-2}\) for

Figure 15. SEM micrographs of a glassy carbon electrode covered with PBA derived particles embedded into a pBO derived carbon matrix, exemplarily shown for K\(_{\text{mMn}_{x}[\text{Co(CN)}_{6}]_{y}}\), x nH\(_2\)O PBA as the precursor.
a time span of 12 h and the obtained data were semi-automatically evaluated to compare the change in the OER potential at 1.4 and 10 mA cm⁻² (for detailed description see section 6.4.2.2). The GSS test showed for both the activity at low current density and the stability at higher current density the same trend. All composites underwent initial activation as described before, reflected in decrease of potential measured at the different current densities (Figure 16c&d). The composites based on NiCoMnCo and MnCo PBA appeared to be stable over the entire measurement period, while the other materials tended to slowly lose activity from the 10th cycle onwards. Nevertheless, the concept of embedding PBAs as catalyst precursors into a pBO matrix with subsequent pyrolysis formed, for all the tested materials, OER active composites with a decent life-time under oxygen evolution conditions, worth to be further explored. The overall better performance of the MnCo PBA based composite in terms of activity, and the negligible change in activity after the activation period during the GSS test made it particularly interesting for a further detailed investigation. Therefore, the underlying process during thermal electrode preparation, the BO to PBA ratio and the physical properties of the MnCo PBA based composite are investigated in depth.

Figure 16. a) Cyclic voltammograms of a NiCo PBA/pBO composite (black) and pyrolyzed pBO (red) at 1600 rpm and a scan rate of 5 mV s⁻¹. b) LSVs of different PBA/pBO composites at 1600 rpm and a scan rate of 5 mV s⁻¹. c) Potentials at a current density of 1.4 mA cm⁻² extracted from the CVs of the GSS test for the different PBA/pBO composites. d) Potentials corresponding to a current density of 10 mA cm⁻² extracted from the galvanostatic polarization of the GSS test for the different PBA/pBO composites. All the measurements were done in O₂-saturated 0.1 M KOH.
4.1.2 In-depth investigation of a MnCo PBA/pBO based composite as catalyst for the OER

Because of its comparatively higher OER activity as compared with other tested PBA-based composites, a MnCo and pBO based composite was investigated in depth for its behavior upon thermal treatment, as well as the influence of the PBA to pBO ratio on the final catalytic performance. Furthermore, the structure and the electrochemical properties were characterized in depth. Polymerization and pyrolysis were performed under Ar flow to prevent oxidation of pBO. However, although the thermal treatment was performed under an inert gas atmosphere, traces of manganese oxide were formed at higher temperatures, which might arise due to traces of oxygen entrapped in the composite film, or oxidation of manganese upon exposure of the pyrolyzed product to the atmosphere. This was also observed after pyrolysis of the pure PBA precursor. The Mn core-level XPS spectrum shows a Mn 2p_{3/2} peak with a binding energy of 641.48 eV, representing oxidized manganese (Mn^{2+}/Mn^{3+}) species (Figure 17a). Thermogravimetric analysis of the two precursors (PBA and BO) was employed to gain further insight into the influence of the temperature during the polymerization and pyrolysis processes on the decomposition behavior (Figure 17b). In a first step, the temperature was increased stepwise from room temperature to 240 °C to induce BO polymerization, resulting only in a minor weight loss of the pure pBO due to evaporation of residual solvent. A further increase of the temperature to 600 °C during pyrolysis led to an additional drastic weight loss of 68 % caused by loss of volatile fragments from the degradation of the polymer chain (e.g. aniline). The pBO gave a residual char yield of 27 % after the complete thermal treatment. The behavior of the pure PBA is dominated by three major weight changes during the thermal treatment. First, a weight loss of 23 % occurred during the first heating step, caused by evaporation of crystal water of the PBA. A second weight loss of 35 % after reaching 350 °C is due to the release of cyanide groups of the PBA as toxic cyanogen. The observed behavior conforms well to the pyrolysis of PBAs as previously reported [235]. A weight increase of 5 % further indicates the formation of metal oxides as supported by the previously mentioned XPS results. A mixture of the pBO and PBA with a ratio of 1:1 (wt%) followed a similar behavior as the two starting materials, but the decomposition at high temperature is hampered compared to the pure PBA leading to a residual char yield of 30 %.
4.1 Polybenzoxazine-derived nitrogen-doped carbon as matrix for Prussian blue analogue based OER catalysts

The influence of the BO content on the OER activity of the MnCo PBA-derived electrocatalyst was investigated by means of rotating disk electrode (RDE) voltammetry using electrodes prepared with 0 wt%, 2 wt%, 10 wt%, 17 wt%, 28 wt%, or 50 wt% BO with respect to the overall solid content in the drop-coated ink (Figure 18a&b). The voltammograms of as-prepared samples indicate a clear decline of the catalytic activity with increasing pBO:PBA ratio (Figure 18a). These observations suggest that during the pyrolysis step a catalytically inactive carbon matrix is formed from pBO masking the catalytically active sites on the embedded metal oxide particles. However, consecutive potential cycling (50 cycles, scan rate 50 mV s⁻¹) substantially activates the catalytic activity of the modified electrodes prepared with 28 wt% and 50 wt% pBO while all other electrodes lost activity because of insufficient catalyst fixation on the electrode surface due to an insufficient amount of pBO during film formation (Figure 18b). Samples before and after electrochemical cycling are referred to as “as-prepared” and “activated”, respectively. The activation process apparently eliminates amorphous carbon layers thus exposing more highly active sites to the electrolyte, concomitantly reducing the overpotential for the OER. The carbon removal can be considered as self-limiting. After activation, the catalysts with a pBO content of 50 wt% showed the highest activity. The activation effect explains the different surface morphologies as seen in the SEM micrographs of the as prepared and activated electrodes with 50 wt% pBO (Figure 18d&e). The SEM micrograph of the as-prepared electrode shows the Mn₃Co₃O₉ nanocubes covered with an additional layer, while the image of the activated electrode reveals uncovered and porous Mn₃Co₃O₉ nanocubes. Furthermore, SEM revealed preservation of the cubic structure of the precursor material during the heat-treatment processes (Figure 18c-e).
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Figure 18. RDE cyclic voltammograms (scan rate 5 mV s\(^{-1}\), 0.1 M KOH, O\(_2\)-saturated, 1600 rpm) of glassy carbon electrodes modified with different amounts of BO in the drop-coating solutions (0 wt%, 2 wt%, 10 wt%, 17 wt%, 28 wt%, and 50 wt% of solid content in solution) before (a) and after potential cycling (b). SEM micrographs of (c) as-prepared \( \text{K}_x\text{Mn}_x\text{[Co(CN)}_6\text{]}_x \text{H}_2\text{O}, (d) \text{carbon-Mn}_x\text{Co}_y\text{O}_z \text{before and e) after potentiodynamic activation.}

\( \text{Mn}_x\text{Co}_y\text{O}_z \) nanocubes obtained without any addition of pBO showed an initial high activity during the first voltammogram, however, the catalyst detaches easily from the electrode surface leading to drastic activity loss (Figure 18a&b). Stabilization of the \( \text{Mn}_x\text{Co}_y\text{O}_z \) nanocubes with Nafion as a binder led to a substantially less active and less stable films (Figure 19) as compared to the activated sample containing a PBA/pBO ratio of 1:1, thus clearly confirming the benefit of using pBO derived carbon networks for incorporating catalyst particles compared to the most commonly used binder.
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A sample containing 50 wt% pBO was investigated by means of SEM, X-ray diffraction (XRD), X-ray photoelectron spectroscopy (XPS) and TEM related techniques, such as high resolution TEM (HRTEM), scanning TEM (STEM) in the high angle annular dark field mode (HAADF) and STEM-electron energy loss spectroscopy (EELS). The edge length of the cubic catalyst particles varied between 120 nm to 270 nm and was independent of the preparation step (Figure 20a&b). Energy dispersive X-ray spectroscopy (EDX) (Figure 20c&d) and XPS (Figure 22) revealed the presence of the expected components Mn, Co, O and C in the catalyst layer.

HAADF STEM micrographs show the presence of small nanoparticles and the presence of flake like regions embedded in a graphitic carbon matrix (Figure 21a-b, section 8.1). The nanoparticles with sizes between 10 and 40 nm are well distributed in the carbon matrix. The HRTEM micrographs revealed a mixed amorphous/graphitic carbon layer covering the whole structure, confirming the results from the SEM micrographs (Figure 18c). The typical (0002) planes of the graphitic C phase (space group = P63/mmc) with lattice parameters of a = 0.246 nm and c = 0.671 nm can be clearly observed (section 8.1). The existence of mixed amorphous/graphitic carbon was further confirmed by Raman spectroscopy (Figure 20e), showing the typical carbon D and G bands at wavenumbers of 1349.7 cm\(^{-1}\) and 1588.8 cm\(^{-1}\), respectively. Moreover, Co is shown to partly remain as metallic Co (Figure 21e, section 8.1), whereas Mn is only present in its oxidized forms and could not be observed in its metallic state, supporting

![Figure 19. Cyclic voltammograms of a glassy carbon electrode modified with a Mn\(_x\)Co\(_y\)O\(_z\) film with Nafion as a binder before (black) and after (red) potential cycling.](image-url)
the earlier statement of its affinity to be oxidized. Furthermore, a Mn, Co and C containing region seems to exist (Figure 21e). Additional STEM EELS maps also show partial segregation of Mn and Co, Mn oxide rich and Co/MnCoO core-shell particles (section 8.1). Furthermore, XPS (Figure 22) and XRD (Figure 23) revealed the existence of metal carbide phases, which is in good agreement with the literature about pyrolysis of PBA in an inert atmosphere at 600 °C [235].

Figure 20. SEM micrographs of MnCo nanocubes embedded in a N-doped graphitic-type carbon matrix before (a) and after (b) potentiodynamic activation. EDX elemental maps (c) and corresponding EDX spectrum (d) of a glassy carbon electrode modified with carbon-MnₓCoᵧOᵣ. Raman spectrum of the carbon-MnₓCoᵧOᵣ composite showing its D and G bands (e).
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The C 1s spectrum (Figure 22b) was deconvoluted into five peaks with binding energies at 283.52 eV, 284.22 eV, 285.36 eV, 288 eV, and 291.57 eV corresponding to metallic carbides, sp2 C-C, C-O-C/C-N, O=C-O and a shake-up feature, respectively [241]. The peak at 283.52 eV can be safely assigned to carbides of Co and Mn owing to its good conformance to the C 1s binding energies of other transition metal carbides, and is therefore in accordance with the MnCoC region in Figure 21e [242–244]. Deconvolution of the N 1s spectrum revealed the presence of pyridinic N (399.09 eV) and pyrrolic N (401.06 eV) groups (Figure 22c), and hence the formation of N-doped carbon as described previously by Zhang et al. for the pyrolysis of pBO [245]. The presence of Co$^{2+}$ is difficult to assign from the binding energies of the Co 2p$_{1/2}$ and Co 2p$_{3/2}$ peaks (Figure 22d) [246]. However, both Co 2p peaks have characteristic satellite features at higher binding energies, supporting the presence of Co$^{2+}$ ions [247]. The absence of satellite features in the Mn 2p (Figure 22e) spectrum and the peak splitting of 5.5 eV in the binding energy of the Mn 3s spectrum (Figure 22f) confirms the presence of oxidized Mn species [246,248]. The not symmetric Mn 2p$_{3/2}$ peak indicates an overlapping of Mn$^{2+}$ and Mn$^{3+}$ contributions. The binding energy of 529.18 eV in the O 1s spectrum further confirms the existence of transition metal oxides (Figure 22g).

Figure 21. TEM analysis of as-prepared carbon-Mn$_x$Co$_y$O$_z$. HAADF STEM (a, b) and HRTEM (c, d) micrographs of the carbon-Mn$_x$Co$_y$O$_z$ composite showing several nanoparticles with a flake-like structure and the C matrix. EELS mapping was obtained from the white square area. Individual EELS composition maps of Mn (red), Co (green), O (blue) and C (turquoise) along with composite maps of Mn–Co–O, Mn–Co, Mn–O and Co–O (e).
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Figure 22. XPS analysis of the as prepared carbon-Mn$_x$Co$_y$O$_z$ composite. XPS survey spectrum (a), high-resolution XPS spectra of C 1s (b), N 1s (c), Co 2p (d), Mn 2p (e), Mn 3s (f) and O 1s (g).

XRD revealed the existence of three crystalline phases with different compositions (Figure 23). The reflection at 25.8° is assigned to both graphitic and amorphous carbon. The second dominant reflection for graphitic carbon at 44° cannot be observed because it is hidden underneath other signals. Therefore, a clear assignment of the nature of the carbon is not possible based on the XRD data, however, comprehensive analysis of TEM, XRD and XPS reveal a high degree of graphitization. The reflections at 35.12° and 58.85° originate from the (111) and (220) planes, respectively, of cubic MnO (JCPDS 75-0625) with the space group Fm-3m, whereas the most intense reflection at 41.20° and the additional two at 47.93° and 70.16° correspond to the (111), (002) (200) and (220) (202) planes of tetragonal Mn$_2$Co$_2$C (JCPDS 89-3688) with the space group P4/mmm. The remaining intense reflection at 44.28° was assigned to the (511) plane of the cubic Mn$_{23}$C$_6$ phase (JCPDS 80-1701) with the space group Fm-3m. The cubic crystal structure of two of the phases is reflected in the highly cubic particle shape. The formation of carbides is in good agreement with previous reports on the heat treatment of PBA up to
600 °C in an inert gas atmosphere [235]. The presence of MnO confirms the results of the TGA data regarding the observed weight increase during the cooling step. Although the XRD pattern was difficult to analyze and does therefore not preponderate, it confirms the results obtained by TEM and XPS, despite the CoMn₂O₄ spinel structure observed by TEM is not detectable in the XRD pattern, likely due to their very small particle size (~10 nm).

Figure 23. XRD patterns of carbon-MnₓCoₜOₖ and reference patterns of Mn₂Co₂C, MnO and Mn₂₃C₆.

A PBA/pBO ratio of 1:1 revealed the highest activity (Figure 18). Therefore, this ratio was chosen for a detailed study of the electrochemical performance of MnCo nanocubes embedded in a pBO derived N-doped carbon matrix with respect to activity and stability towards the OER. Carbon-MnₓCoₜOₖ showed high oxygen evolution activity affording a current density of 1 mA cm⁻² at 1.54 V and a current density of 10 mA cm⁻² at 1.60 V (Figure 24b). The overpotential of 0.37 V required to reach a current density of 10 mA cm⁻² is significantly lower as compared to CoₓMnᵧOₖ based catalysts, which had values in the range of 0.39 V to 0.63 V [72,237,249,250,251]. The Tafel slope of carbon-MnₓCoₜOₖ is 59 mV dec⁻¹ (Figure 24c) which indicates very fast kinetics and a transfer coefficient (α) very close to 1 ((2.303RT)/αF). On the basis of the Tafel slope, discharge of OH⁻ is assumed to be the rate determining step [54]. In-situ Raman spectroscopy (Figure 24a) in KOH (0.01 M) at different potentials before and during oxygen evolution gave signals of both Mn²⁺ and Mn³⁺ species. The intensities of the peaks with Raman shifts between 487 cm⁻¹ and 496 cm⁻¹ were dependent on the applied potential and correlate with the theoretically predicted values (484 cm⁻¹ and 500 cm⁻¹) of the LO mode of Mn²⁺ [252,253]. Two signals arise at 371 cm⁻¹ and 644 cm⁻¹, both coming from Mn³⁺.
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Furthermore, the latter signal increased when oxygen evolution began indicating further hydroxylation.

A recently developed stability assessment methodology [240] was applied to evaluate the carbon-Mn$_x$Co$_y$O$_z$ catalyst and showed a negligible change in activity at current densities of 1.4 mA cm$^{-2}$ and 10 mA cm$^{-2}$, respectively (Figure 24d). Additional stability measurements were conducted using carbon-Mn$_x$Co$_y$O$_z$ modified Ni foam in a custom-built flow-through cell [240]. During the accelerated galvanostatic stability test at an applied current density of 10 mA cm$^{-2}$ (with respect to the exposed surface of $\varnothing = 8$ mm), the corresponding potential increased from an initial value of 1.61 V to 1.68 V vs. RHE after 67 h (Figure 24e). After the first 19 h, the potential remained constant without any visible change until the end of the measurement indicating a stable state of the catalyst layer. Taking into account that Ni foam is by itself active for catalyzing the OER, analogous measurements were performed with pure Ni foam as control. The activity of pure Ni foam increased at the beginning of the measurement due to the formation of NiO$_x$/NiOOH, however, it later remained constant at an overpotential of about 0.17 V higher than the carbon-Mn$_x$Co$_y$O$_z$ modified Ni foam electrode (Figure 24e). The observed activity and stability can hence safely be attributed to the carbon-Mn$_x$Co$_y$O$_z$ catalyst.

Figure 24. a) Raman spectra recorded at different applied potentials ($E$ / V vs. RHE, 661 nm, 11 mW, acquisition time 10 s, 5 repetitions, 60x magnification immersable objective). b) LSV (5 mV s$^{-1}$, 0.1 M KOH, O$_2$ saturated, 1600 rpm) of an activated carbon-Mn$_x$Co$_y$O$_z$ electrode prepared with a pBO/PBA ratio of 1:1. c) Tafel plot derived from the LSV in b). d) $E$ vs. $t$ curves at current densities of 1.4 and 10 mA cm$^{-2}$, respectively, extracted from stability measurement cycles. e) $E$ vs. $t$ curves of carbon-Mn$_x$Co$_y$O$_z$ on Ni foam (white), and pure Ni foam (black) recorded in 0.1 M KOH, O$_2$-saturated at a current density of 10 mA cm$^{-2}$ extracted from the stability measurement cycles.
4.2 Cobalt-cobalt phosphide nanoparticles and the influence of nickel inclusions on the OER activity

XRD analysis was performed in cooperation with Dr. Corina Andronescu, Analytical Chemistry – Center for Electrochemical Sciences, Ruhr-Universität Bochum, and Dr. Eugeniu Vasile, Department of Oxide Materials Science and Engineering, University “Politehnica” of Bucharest. Parts of this section are included in the publication: Masa, J., Barwe, S., Andronescu, C., Sinev, I., Ruff, A., Jayaramulu, K., Elumeeva, K., Konkena, B., Rolstan Cuenya, B., Schuhmann, W., Low overpotential water splitting using cobalt-cobalt phosphide nanoparticles supported on nickel foam, ACS Energy Lett. (2016) 1, 1192-1198; and the publication: Barwe, S., Andronescu, C., Vasile, E., Masa, J., Schuhmann, W., Influence of Ni to Co ratio in mixed Co and Ni phosphides on their oxygen evolution activity, Electrochem. Commun. (2017) 79, 41 – 45.

Inclusions of non-metal or metalloid moieties are known to alter the surface electronic structure of their host metals, metal oxides or metal oxyhydroxides, hence improving their electrocatalytic activity [46,48,51,83,160,255]. However, the synthesis of especially transition metal phosphides is challenging because of the difficulties in handling hazardous phosphorus. Thus, a safe and facile procedure for synthesis of transition metal phosphides is vitally needed. In this section, a novel synthesis of cobalt-cobalt phosphide nanoparticles is described and furthermore the effect of nickel inclusions on the OER activity of the cobalt-cobalt phosphide nanoparticles is investigated.

The developed cobalt-cobalt phosphide (Co/Co₂P) nanoparticle synthesis procedure is based on reductive thermal degradation of dichlorobis(triphenylphosphine) cobalt(II) [Co(PPh₃)₂]Cl₂. Upon thermal treatment of [Co(PPh₃)₂]Cl₂ in the presence of hydrogen, the complex decomposes yielding Co/Co₂P (Figure 25) with a substantial activity towards the OER (Figure 25), while HCl is formed, and triphenylphosphine condensates at the cooler edges of the reaction tube inside the tube furnace. Pyrolysis of the precursor complex in the absence of hydrogen or at lower temperature led to substantially less active materials (Figure 25). Without the reductive atmosphere, chloride ions remain in the obtained product, most likely as CoCl₂, and the formation of the Co/Co₂P nanoparticles is hampered. A weight loss of close to 90 % indicates a complete degradation of the precursor complex. The obtained pure triphenylphosphine could be recycled for new dichlorobis(triphenylphosphine) cobalt(II) by reaction with cobalt(II) chloride in alcohols or glacial acid.
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4.2 Cobalt-cobalt phosphide nanoparticles and the influence of nickel inclusions on the OER activity

Electrochemical and structural investigations were discussed in depth by Masa et al. [49]. Interestingly, supporting Co/Co$_2$P on nickel substrates invoked a synergistic effect between the catalyst and the supporting electrode, noticeable in a substantially decreased overpotential for the OER. When supported on flat Ni RDE, the overpotential needed to achieve a current density of 10 mA cm$^{-2}$ decreased by about 30 mV compared to similarly modified glassy carbon RDEs. The apparent synergistic effect became predominant as soon as Co/Co$_2$P was supported on nickel foam. Its activity towards the OER was exceptionally increased, reflected in the low overpotential of 0.19 V to provide a current density of 50 mA cm$^{-2}$. In addition to the enhanced OER activity, a change in the oxidation of Co in Co/Co$_2$P and Ni of the electrode occurred, further indicating the formation of new active species. The high anodic potential necessary to be applied during the OER forces the surface Ni of the electrode to transition to higher oxidation states. The formed Ni ions may then migrate into the catalyst structure. Thus, a study concerning the influence of nickel inclusions in Co/Co$_2$P appeared to be highly relevant. From literature, it is already known that different metal cations can alter the redox behavior and the OER activity of nickel (oxy)hydroxide [256]. Zhao et al. discovered that a coupling effect between Ni and Co can change the initial OER activity [257]. Podesta et al. investigated the behavior of binary and ternary Co/Ni phosphides for alkaline water splitting already in the early 1990s, however, their results for the OER do not lead to a clear conclusion of the stoichiometry dependent trend in activity [258].

Therefore, the effect of nickel inclusions on the OER activity of Co/Co$_2$P nanoparticles was investigated on inert electrodes, to exclude possible synergistic effects due to interaction of the
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4.2 Cobalt-cobalt phosphide nanoparticles and the influence of nickel inclusions on the OER activity

catalyst with an OER active support. The materials for this study were prepared according to the aforementioned procedure as described in [49]. Partial substitution of [Co(PPh\textsubscript{3})\textsubscript{2}]Cl\textsubscript{2} with dichlorobis(triphenylphosphine)nickel(II) [Ni(PPh\textsubscript{3})\textsubscript{2}]Cl\textsubscript{2} in the range from 0 to 100 n/n%, where the materials with 0 n/n% and 100 n/n% are the pure cobalt and the pure nickel phosphides, respectively, prior to reductive thermal treatment led to the formation of different Co, Ni, Co\textsubscript{x}Ni\textsubscript{y}P, Co\textsubscript{2}P, Ni\textsubscript{x}P based materials showing different OER electrocatalytic activities in 1 M KOH. The successful transformation of the precursors into phosphides was confirmed by XRD for all the 6 samples (Figure 26). The X-ray diffraction pattern of the material prepared with 0 n/n% Ni is in good agreement with the published Co/Co\textsubscript{2}P [49], showing only characteristic reflections of Co at 47.48° and 75.9° and Co\textsubscript{2}P at 40.9°, 42°, 44.4°, 43.4°, and 51.6° (Figure 26). The addition of 5 n/n% Ni led to the formation of Co (47.48° and 75.9°) (Figure 26b&c) together with CoNiP (40.94°, 47.58°) and Ni\textsubscript{2}P (44.53°, 47.36°). 10 n/n% nickel led to the formation of only Co (47.48° and 75.9°) and CoNiP (41.02°, 44.89°, 47.55°). No Co reflections were observed for materials with a Ni content higher than 10 n/n%. Increasing the content of Ni to 50 n/n% Ni led to formation of a material containing different mixed CoNiP (38.57°, 41.04°, 41.85°, 47.23°, 47.62°, 49.21°) and Ni\textsubscript{2}P (41.85°, 43.75°, 46.64°) while 90 n/n% Ni led predominantly to Ni\textsubscript{2}P (36.44°, 41.85°, 42.89°, 43.78°, 45.31°) and Ni (44.5°, 51.89°) with minor Co\textsubscript{2}P (52.85°, 55.45°) and mixed CoNiP (41.85°, 44.5°). Different Ni and P containing alloys, mainly Ni\textsubscript{2}P (40.68°, 44.5°), Ni\textsubscript{3}P (36.42°, 41.83°, 51.86°), Ni\textsubscript{12}P\textsubscript{5} (38.5°, 41.83°, 44.5°) and Ni (44.5°, 51.86°), were formed during reductive thermal degradation of pure [Ni(PPh\textsubscript{3})\textsubscript{2}]Cl\textsubscript{2}.

![Figure 26. Structural analysis of the prepared Co/Ni phosphides. XRD patterns of the materials based on Co/Co\textsubscript{2}P and its Ni containing alloys (n/n% Ni in the range of 0 – 100) (a); magnified view of the patterns between 45° and 50° (b); magnified view of the region between 70° and 80° (c). b) and c) show the characteristic region for Co reflections.](image-url)
The influence of the different structures and compositions of the catalysts on their electrochemical response is reflected in the cyclic voltammograms of the materials (Figure 27a). The last scan of the conditioning cycles indicates a change in the pre-OER redox wave, especially for the materials with a Ni content of 50 n/n% and higher. Increase of the Co content shifted the Ni$^{2+}$ to Ni$^{3+/4+}$ oxidation peak to more cathodic potentials with respect to the peak for the Ni-only phosphide. This peak shift, induced by Co is in good agreement with the work of Wang et al. for electroless cobalt plated nickel hydroxide [259]. Not only the pre-OER wave but also the OER activity itself is influenced by the Ni content (Figure 27b). The overpotential needed to achieve a current density of 10 mA cm$^{-2}$ decreased from 0.41 V to 0.36 V with the Ni content, with the Ni-only phosphide showing the highest activity. The increase in OER overpotential when cobalt is added to nickel was also previously described by Wang et al. [259]. The Tafel slopes follow the same trend as the overpotential, that is, the Tafel slope decreased with increase of the n/n% Ni content. The lowest slope for Ni/Ni$_x$P$_y$ (59 mV dec$^{-1}$) is substantially lower than the highest for Co/Co$_2$P, with 105 mV dec$^{-1}$ (Figure 27c). Tafel analysis confirms, as suggested by XRD, different active centers, thus leading to different preferred OER mechanisms as described by Shinagawa et al. [19]. Introducing a Ni content of 10 n/n% formed Co/CoNiP particles with improved OER activity with respect to the initial Co/Co$_2$P. The overpotential of the OER on Co/CoNiP is 30 mV lower than on Co/Co$_2$P, a similar result to what was observed for the change from Co/Co$_2$P on GC-RDE to a Ni-RDE [49]. This result clearly confirms the synergistic effect resulting from Ni incorporation into Co/Co$_2$P forming new active materials, which could be part of the explanation for the higher OER activity of Co/Co$_2$P when supported on Ni substrates. Interestingly, the described influence of the Ni content on the observed trend in OER activity can only be observed in the low current density regime (Figure 27d). At current densities higher than 100 mA cm$^{-2}$, the trend in activity changed and the materials with 0, 5 and 10 n/n% Ni are more active than their counterparts with a higher Ni content (Figure 27d). Comparing the overpotential at an industrially interesting current density of 200 mA cm$^{-2}$ [221], the differences between the three materials with a low Ni content and the three with a higher Ni content is notably substantial. In numbers, 100 mV higher overpotential was needed for Ni/Ni$_x$P$_y$ to achieve 200 mA cm$^{-2}$ compared to Co/Co$_2$P, and 120 mV compared to the material with 5 n/n% Ni (Figure 27f). Composition-activity correlations reveal the impact of Co nanoparticles being present in the prepared catalysts. According to the XRD data, the three most active phosphides at high current densities contained a significant amount of Co. In the materials prepared with 50 n/n% Ni and higher, cobalt is present as phosphides or in the case of 100 n/n% Ni not present at all (Figure 26).
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Figure 27. Electrochemical investigation of the prepared Co/Ni phosphide alloys. Last scan of electrode conditioning cyclic voltammetry (a); Linear sweep voltammograms for the OER activity in the low current density region (b); Tafel plots for the different materials (c); linear sweep voltammograms for the OER activity (d); Nyquist plots of the electrochemical impedance of the prepared phosphides ($I_{\text{app}} = 1$ mA cm$^{-2}$) (e). Comparison between the overpotential at 10 mA cm$^{-2}$ and 200 mA cm$^{-2}$ in relation to the Ni content during material synthesis (f).
EIS during oxygen evolution revealed a relatively lower charge transfer resistance for the three materials containing Co (Figure 27e). Thus, the higher activity is presumably governed by the cobalt induced higher conductivity of the prepared catalyst film. Increased conductivity of Ni based electrodes by introduction of Co moieties is well known in literature [260–264]. Thus, two phenomena could be observed in the present study, that is, Ni enhanced the OER activity of Co based phosphides in the low current density regime while Co enhanced the OER activity at higher current densities due to conductivity improvement. The particularly high activity of the catalyst with 5 n/n% Ni at high current densities is presumably due to the unusual combination of Co nanoparticles, mixed CoNiP and Ni3P as revealed by XRD (Figure 26a). The results demonstrate not only the effect of nickel inclusions into Co/Co2P but also that not only the potential at the mostly compared current density of 10 mA cm−2 and the Tafel slopes should be taken into account when catalysts are evaluated for their activity. Furthermore, the comparison of electrocatalysts for oxygen as well as hydrogen evolution at high current densities can be very interesting, especially considering the envisaged technical application of such materials at industrial scale water splitting.
4.3 Metal-metal metalloids and pBO based composites as bifunctional oxygen electrocatalysts

Some of the experiments in this section were performed by Bert Schlütler and Ruben Engels, both at Ruhr-Universität Bochum, in the framework of their master theses. Scanning electrochemical microscopy (SECM) experiments were done in cooperation with Dr. Felipe Conzuelo and XPS analysis was done in cooperation with Dr. Corina Andronescu, both at Analytical Chemistry – Center for Electrochemical Sciences, Ruhr-Universität Bochum. Parts of the text in this section are included in the submitted manuscript: Barwe, S., Andronescu, C., Engels, R., Conzuelo, F., Masa, J., Schuhmann, W., Cobalt/Cobaltmetalloid and polybenzoxazine derived composites for bifunctional oxygen electrocatalysis.

In this chapter, the aforementioned property of pBOs to form N-doped graphitic carbon matrices is used in order to activate metal-metal metalloid (M/MₓY) based bifunctional water splitting catalysts for the ORR. Heteroatom doped transition metal compounds known to be bifunctional water splitting catalysts were already activated for the ORR by supporting them on functionalized carbon structures [265,266]. Embedding transition metal oxide nanoparticles in N-doped carbon improves their electric conductivity thus facilitating enhanced charge transfer and ultimately the catalytic activity [95,176]. Additionally, the carbon shell could prevent corrosion and agglomeration of the metallic nanoparticles [176,267].

4.3.1 Evaluation of precursor influences on the ORR and OER activity

Electrodes modified with bifunctional oxygen electrocatalysts were prepared by thermal treatment in a similar way to the PBA-based OER electrodes (Section 4.1). The electrodes were first modified with a film of M/MₓY homogeneously suspended in a solution of the BO (Figure 28). For the presented approach, two different BO precursors were chosen. BA-a, the product of the Mannich type reaction of bisphenol A (BA) and aniline (a), and BA-tepa, a product of the reaction between BA and tetraethylenepentaamine (tepa). BA-a was already used in section 4.1. BA-tepa was deliberately chosen as the second BO precursor because of its high thermal stability of up to 800 °C in inert atmosphere, while the five amino groups in tepa introduce nitrogen into the formed pyrolytic carbon. The M/MₓY particles and BO modified electrodes then underwent thermal treatment in inert atmosphere, consisting of polymerisation steps followed by the final pyrolysis step. The first steps lead to formation of a highly crosslinked organic network essential for the thermal stability, while the second (pyrolysis) step transforms the organic
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4.3 Metal-metalloid and pBO based composites as bifunctional oxygen electrocatalysts

network formed in step one into a N-doped pyrolytic carbon matrix embedding the active catalyst particles. The introduction of nitrogen into the carbon matrix is essential since either nitrogen functionalized carbon or nitrogen coordinated transition metals act as ORR active sites.

Hydrodynamic voltammetry reveals different activities for all tested materials towards the ORR and OER (Figure 29). The materials were based on pBO composites of nickel-nickel boride and cobalt-cobalt boride, two already known bifunctional water splitting catalysts [48,46]. The pyrolyzed pBOs without any catalyst particles did not show satisfactory ORR and OER activity. The OER can be considered as not catalyzed whereas the overpotential for the ORR to reach a current density of -1 mA cm\(^{-2}\) (defined as \(E_{\text{ORR}}\)) was as high as 0.56 V and 0.64 V for pyrolyzed BA-a and BA-tepa, respectively. A summary of the ORR and the OER activity of the various catalysts, expressed as the potentials corresponding to current densities of -1 mA cm\(^{-2}\) and 10 mA cm\(^{-2}\) (defined as \(E_{\text{OER}}\)), respectively, and the corresponding bifunctional ORR/OER activity expressed as the difference of the potential between the ORR at -1 mA cm\(^{-2}\) and the OER at 10 mA cm\(^{-2}\) (defined as \(E_{\text{OER}-\text{ORR}}\)) is presented in Table 1.

![Figure 28. Schematic representation of the electrode preparation procedure. A: Drop-coated electrode modified with catalyst in the BO oligomer film. B: Nitrogen doped carbon matrix embedding bifunctional oxygen catalyst particles.](image)
4.3 Metal-metal metalloids and pBO based composites as bifunctional oxygen electrocatalysts

Table 1. Summary of the ORR activity ($E_{\text{ORR}}$ vs. RHE), OER ($E_{\text{OER}}$ vs. RHE), and the bifunctional activity $E_{\text{OER}}-E_{\text{ORR}}$.

<table>
<thead>
<tr>
<th></th>
<th>$E_{\text{ORR}}$ vs. RHE (V)</th>
<th>$E_{\text{OER}}$ vs. RHE (V)</th>
<th>$E_{\text{OER}}-E_{\text{ORR}}$ (V)</th>
</tr>
</thead>
<tbody>
<tr>
<td>BA-a</td>
<td>0.67</td>
<td>----</td>
<td>----</td>
</tr>
<tr>
<td>BA-tepa</td>
<td>0.59</td>
<td>1.93</td>
<td>1.34</td>
</tr>
<tr>
<td>Co/Co$_x$B/BA-a</td>
<td>0.8</td>
<td>1.62</td>
<td>0.82</td>
</tr>
<tr>
<td>Co/Co$_x$B/BA-tepa</td>
<td>0.84</td>
<td>1.61</td>
<td>0.77</td>
</tr>
<tr>
<td>Ni/Ni$_x$B/BA-a</td>
<td>0.74</td>
<td>1.60</td>
<td>0.86</td>
</tr>
<tr>
<td>Ni/Ni$_x$B/BA-tepa</td>
<td>0.76</td>
<td>1.63</td>
<td>0.87</td>
</tr>
</tbody>
</table>

Evidently, a distinction in the electrochemical performance can be seen by comparing either the influence of the pBO precursor or the different metal borides. BA-tepa enhanced the ORR activity due to the comparably higher amount of nitrogen with respect to BA-a. The overpotential necessary to drive the ORR at a current density of -1 mA cm$^{-2}$ for the BA-tepa based composites is 40 and 20 mV lower for the cobalt and nickel based borides, respectively. Whereas BA-tepa also improved the OER activity of Co/Co$_x$B/BA-tepa slightly compared to Co/Co$_x$B/BA-a, the OER activity of Ni/Ni$_x$B/BA-tepa decreased in relation to that of Ni/Ni$_x$B/BA-a. Comparing the influence of the transition metals, it can be observed that the cobalt based composites were strikingly more active towards the ORR than their nickel based counterparts while the latter were more active towards the OER when embedded in a BA-a derived carbon matrix. However, for the envisaged application of bifunctional oxygen catalysts, the roundtrip potential, the potential difference between ORR and OER, is a very important measure. The lower the roundtrip potential, the lower the reversible overpotential for the two reactions. For the nickel based composites, the potential difference between -1 mA cm$^{-2}$ and 10 mA cm$^{-2}$ for both composites was almost similar with 0.86 and 0.87 V, respectively. The BA-tepa and cobalt boride based composites were the most active bifunctional materials with a roundtrip overpotential of 0.77 V. The high activity of Co/Co$_x$B/BA-tepa towards both reactions is not surprising, since Co/Co$_x$B is already known to be a highly active OER catalyst [46] and additionally, the pyrolysis of the nitrogen-rich BA-tepa leads to a N-doped carbon matrix embedding Co/Co$_x$B. Embedding cobalt based materials in nitrogen rich carbon is already known to facilitate the ORR [163,141]. Because of its outstanding bifunctional activity, Co/Co$_x$B/BA-tepa was chosen for further investigation of the influence of the Co/Co$_x$B to BA-tepa ratio and the pyrolysis temperature.
4.3.2 Influence of the Co/CoₓB to BA-tepa ratio on the bifunctional activity of the formed composites

The pre-pyrolysis ratio of the BO monomer and the catalyst precursor was shown to have a significant influence on the OER activity of PBA and pBO based catalysts (Section 4.1). Thus, the influence of the pre-pyrolysis amount of Co/CoₓB (wt%) in the composite film on the ORR, OER and OR/OER bifunctional catalytic activity was investigated for Co/CoₓB/BA-tepa composites with 0, 16.7, 50, 66.7, and 100 wt% Co/CoₓB. RDE measurements revealed that the ratio of 1:1 yielded not only the most active ORR but also the most active OER catalyst. A pre-pyrolysis 50 wt% content of Co/CoₓB yielded a Co/CoₓB/BA-tepa derived catalyst with the lowest roundtrip overpotential (Figure 30e). The pure pyrolyzed BA-tepa showed only marginal OER activity while Co/CoₓB alone showed reasonable OER activity (Figure 30a&b). A Co/CoₓB content of 50 wt% did not change the OER activity substantially, however, it increased the ORR activity and drastically decreased the roundtrip overpotential with respect to as prepared Co/CoₓB. The difference between the as prepared and the pyrolyzed pure Co/CoₓB is attributed to sintering effects instigated by the thermal treatment as described in [46]. The pBO based matrix presumably protected the embedded particles from sintering, leading to only minor differences in the OER overpotential for composites with 16.7, 50, and 66.7 Co/CoₓB wt%.

**Figure 29.** LSVs of electrodes modified with different pyrolyzed polymers or different M/MₓY pBO composites for the ORR (a) and the OER (b) (O₂-saturated 0.1 M KOH, 5 mV s⁻¹ scan rate, and 1600 rpm electrode rotation).
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Figure 30. LSVs of electrodes modified with Co/Co,B/BA-tepa composites having different Co/Co,B content before pyrolysis (b.p.) for the ORR (a) and the OER (b) (O₂-saturated 0.1 M KOH, 1600 rpm). Averaged potentials $E_{\text{ORR}}$ (c), $E_{\text{OER}}$ (d), $E_{\text{OER}}-E_{\text{ORR}}$ potential difference (e) ($N = 3$ for all and standard deviation) for electrodes modified with the different composites.

4.3.3 Investigation and optimization of the oxygen reduction measurements with pyrolyzable electrodes

Interestingly, it strikes that the LSVs for the oxygen reduction do not depict a mass transport limitation, which would appear as a current plateau. Moreover, the currents reached exceed the theoretical mass transport limited current achievable according to the Levich equation (31).

$$I_d = 0.62nFAD_0^{2/3} \omega^{1/2} v^{-1/6}C_0$$  \(31\)

With $I_d$ being the diffusion limited current, $n$ the number of transferred electrons per oxygen molecule, $A$ the surface area of the electrode, $\omega$ the angular velocity (rad s$^{-1}$), $F$ the Faraday
constant (96 485 C mol⁻¹), $D_0$ the diffusion coefficient of O₂ in 0.1 M KOH (1.9 × 10⁻⁵ cm² s⁻¹), $C_0$ the concentration of O₂ in 0.1 M KOH (1.2 × 10⁻⁶ mol cm⁻³), $v$ the kinematic viscosity of 0.1 M KOH (0.01 cm² s⁻¹).

At a rotation speed of 1600 rpm and an assumed 4 electron oxygen reduction, the limited current is supposed to be -5.7 mA cm⁻² in 0.1 M KOH, but the ORR currents measured exceeded 6 mA cm⁻² by far. This unexpected anomaly can be caused by the type of electrode used for growth of the composite film directly on the electrode. Conventional Teflon sealed electrodes (Figure 31 Type C) would not sustain the high temperature necessary for the pBO pyrolysis, hence they could not be used. Therefore, bare glassy carbon rods without any insulating shroud were prepared with the desired films and underwent the heat treatment. Afterwards, the glassy carbon rods were tightly insulated with Teflon tape in a manner that only the disk shaped electrode surface is exposed to the electrolyte (Figure 31 Type A). The chosen type of electrodes did not affect the OER activity since the rotation only facilitates gas bubble departure. However, for the ORR, a laminar electrolyte flow during forced oxygen delivery towards the electrode surface is mandatory. The electrolyte flow invoked by the rotation is influenced by the thickness of the insulating shroud (d_iso) around the electrode. At the edges of the electrode, turbulences may occur leading to the creation of a non-defined mass transport situation. Such turbulences can deliver more oxygen towards the active electrode exceeding the amount defined under the laminar flow conditions, hence leading to a higher current than expected, and the absence of a well-defined mass transport limited current. In order to evaluate the used type of electrodes, a highly efficient ORR catalyst based on a composite of cobalt, nitrogen and carbon, i.e. Co-NC catalyst [141] was used to compare LSVs of the ORR on conventional RDE electrodes and the custom-made RDE electrodes used in this work. Figure 31 shows the three different types of electrodes and the corresponding ORR LSVs of the Co-NC catalyst. Electrode type A represents the electrodes used until now and type C the conventional RDE, also used in the original publication [141]. Obviously, the LSVs of type A and type C differ substantially. LSVs obtained with type A electrodes show similar behavior as the previously reported curves, while the LSVs measured with the type C electrodes evidently reveal mass transport limitation and equidistantly distributed $E / I$ transients at the various rotation speeds, as expected for highly active ORR catalysts. The obtained results manifest that the type of electrodes chosen for the previous ORR measurements is not beneficial for achieving a reasonable insight into the ORR activity of the studied catalysts. Although the shapes of the LVSs differ, particularly, in the region where diffusion limiting currents would be expected, the potential at a current density
of -1 mA cm\(^{-2}\) (0.87 V vs. RHE) was identical for both the conventional electrode and the custom-made electrode, implying that within the kinetic region of the LSVs the figure of merit for the ORR can still be reliably obtained using the custom-made type A electrodes. Nonetheless, in order to improve the reliability the ORR data obtained on pyrolyzed the initially non-insulated carbon rod electrodes, a strategy was developed to increase the thickness of the insulating shroud around the carbon rod. After the thermal electrode preparation, during which the electrodes have to be free of any insulation, the composite modified electrodes were carefully shoved into a Teflon tube with an inner diameter as small as the diameter of the glassy carbon rod (Figure 31 Type B).

**Figure 31.** Schematic representation of different types of electrodes used for RDE measurements. The electrodes were insulated with a Teflon tape after thermal treatment leaving the disk shaped part bearing the catalyst film exposed (type A), or insulated by covering with a piece of Teflon tube (type B). Type C represents a conventional Teflon sealed RDE fabricated in the mechanical workshop. The bottom row shows the corresponding RDE voltammograms.
Using a tube with smaller inner diameter than the electrode’s outer diameter prevents the electrolyte from wetting the outer part of the carbon rod electrode, thus leaving only the disk end of the electrode exposed to the electrolyte. The hydrophobicity of Teflon further inhibits electrolyte leakage. Co-NC modified electrodes sealed with the newly developed Teflon tube methodology gave an oxygen reduction response very close to the one obtained by the conventional type C electrodes. The LSVs recorded with the type B electrodes show a diffusion limited current plateau not exceeding the theoretical limited current. The potential at a current density of -1 mA cm$^{-2}$ was with 0.87 V similar to both type A and type C electrodes. Evidently, the new approach for post-thermal treatment insulation can be used for further investigation of ORR active electrodes necessitating a pyrolysis or calcination step. It is noteworthy that the Teflon tube, because of its soft structure, changes its inner diameter with time after a number of applications on the electrode, hence being too loose for further use with different electrodes. Thus, it was of high importance to replace the Teflon tube sealing regularly to prevent electrolyte leakage between the carbon rod electrode and the insulation.

4.3.4 Influence of the pyrolysis temperature on the ORR and OER activity of Co/Co$_x$B/BA-tepa

Besides the Co/Co$_x$B to BA-tepa ratio, the pyrolysis temperature of the Co/Co$_x$B/BA-tepa composites can have a significant influence on the activity of the resulting catalysts. Co/Co$_x$B embedded in a BA-tepa film was therefore pyrolyzed at various temperatures between 500 °C and 700 °C to find the optimal conditions for the highest bifunctional activity. LSVs reveal a substantial difference in the ORR activity in the temperature range between 500 °C and 700 °C (Figure 32a). The potential needed to attain a current density of -1 mA cm$^{-2}$ during ORR was 0.54 V vs. RHE at 500 °C and 0.81 V vs. RHE at 650 °C (Figure 32c). Similar differences are also projected in the current densities at 0.2 V vs. RHE, indicating different preferential ORR pathways. The composite pyrolyzed at 500 °C showed very sluggish reaction kinetics and a diffusion limited current of around -2 mA cm$^{-2}$ pointing toward hydrogen peroxide as the preferentially formed product, on the basis of the estimated number of transferred electrons ($n$) determined from the Levich equation (Eq. 31). Increasing the pyrolysis temperature led to enhancement of the ORR activity in terms of reduced overpotential and higher mass transport limited current until 650 °C (Figure 32a). After pyrolysis at 700 °C, the activity towards the ORR decreased again and was comparable to the activity of composites pyrolyzed at 600 °C. Pyrolysis at 650 °C appeared to be optimal in order to obtain a highly active ORR catalyst based on
Co/Co$_x$B/BA-tepa, manifested by the lowest ORR overpotential at -1 mA cm$^{-2}$ among the tested temperature series (Figure 32c).

Figure 32. LSVs of Co/Co$_x$B/BA-tepa modified electrodes prepared at different pyrolysis temperatures for ORR (a) and OER (b) (1600 rpm, O$_2$-saturated 0.1 M KOH, 5 mV s$^{-1}$). Averaged potentials $E_{\text{ORR}}$ (c), $E_{\text{OER}}$ (d), $E_{\text{OER}}$-$E_{\text{ORR}}$ overpotential (e) ($N = 3$ for all and standard deviation) for electrodes pyrolyzed at various temperatures.

However, in contrast to the ORR, the pyrolysis temperature only had a minor influence on the OER activity. For example, at a current density of 10 mA cm$^{-2}$, a difference of only 60 mV was observed, between the least and most active material formed at 500 °C and 650 °C, respectively (Figure 32b&d). The OER activity followed the same temperature dependence as the ORR. Hence, pyrolysis at 650 °C formed the most active bifunctional electrode, represented by the lowest round-trip voltage of 0.8 V between the ORR at -1 mA cm$^{-2}$ and the OER at 10 mA cm$^{-2}$ (Figure 32e).
Interrogation of the surface state of the Co/Co$_x$B/BA-tepa catalysts prepared at different temperatures using XPS revealed substantial differences between the samples. However, all samples had dominant boron, nitrogen and cobalt signals although their surface oxidation states varied substantially (Figure 33). Elemental boron and Co$_x$B can be observed in all samples prepared at the different temperatures at binding energies of 187.35 eV and 778.35 eV (Figure 33a&c), respectively [46]. The observed binding energy of 778.35 eV for Co$_2$B is in good agreement with the literature [46,268]. A pyrolysis temperature of 500 °C led to a material with a high degree of surface oxidation evidenced by the dominant peaks of boron-oxo species at 191.85 eV (Figure 33a) and the Co 2p$_{3/2}$ and Co 2p$_{1/2}$ peaks at 781.5 eV and 797.3 eV, respectively, indicating the formation of oxidized Co species (Figure 33c). As already mentioned in section 4.1, determination of the exact oxidation state of cobalt from the binding energies of the Co 2p$_{1/2}$ and Co 2p$_{3/2}$ signals is difficult, but the characteristic satellite peaks at higher binding energies indicate the presence of Co$^{2+}$ ions [246,247]. The oxidized surface led to comparatively poorer ORR performance as shown by the LSV of the 500 °C sample (Figure 32a). Furthermore, it is possible that pyrolysis at 500 °C is too low to transform the insulating organic pBO completely into conductive N-doped graphitic carbon, hence reducing the catalytic activity. For the pyrolysis temperatures 600 °C, 650 °C and 700 °C, not only the peak for boron-oxo species is significantly less intense, but also the Co 2p signals for oxidized Co species at 781.5 eV and 797.3 eV, indicating a drastic diminishment of the contribution of oxidized boron and cobalt. The minor oxidation of the 650 °C sample led to much higher activity towards the ORR, in relation to the samples prepared at 600 °C and 700 °C (Figure 32a&c). On the other hand, the pyrolysis temperature does not similarly influence the OER because the composition and nature of the OER active sites differs substantially from the ORR active sites. A Co(OH)$_2$/Co$_2$B core-shell configuration which is formed prior to the OER represents the active form of the OER catalyst as described in the work of Masa et al. [46]. This Co(OH)$_2$ shell is formed during the OER conditioning if the the electrode potential is anodic enough to irreversibly oxidize Co$^0$ to Co$^{3+}$. Further potential cycling led to the growth of the oxyhydroxide shell until a steady state was reached. Based on these and previous results, Co/Co$_x$B/BA-tepa with the ratio of 1:1 and pyrolyzed at 650 °C was further investigated in depth for its activity as a bifunctional oxygen catalyst. Furthermore, because of its structural similarities [46,49] and its high bifunctional water splitting activity, a Co/Co$_x$P based composite was similarly prepared and investigated.
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4.3.5 In-depth electrocatalytic investigations of Co/CoₓY (Y = B, P)/BA-tepa composites

Co/CoₓB/BA-tepa and Co/CoₓP/BA-tepa were prepared at 650 °C with a cobalt-cobaltmetalloid to BA-tepa ratio of 1:1 and electrochemically investigated in depth towards their bifunctional oxygen activity. RDE voltammograms at various rotation speeds indicate a mass transport limited current response with nearly equidistant current/potential transients at 100, 400, 900 and 1600 rpm for both materials (Figure 34a&b). The potentials needed to afford a current density of -1 mA cm⁻² were as low as 0.83 V and 0.82 V vs. RHE for Co/CoₓB/BA-tepa and Co/CoₓP/BA-tepa, respectively, placing them among the lowest reported for cobalt based ORR catalysts [141,157,265,266,269,270]. In general, the ORR can proceed via different mechanisms, resulting in different numbers of transferred electrons per oxygen molecule [271,272]. Briefly, a dioxygen molecule can be reduced either in a 4 e⁻ transfer pathway to hydroxide ions or via a 2 e⁻ transfer pathway to hydrogen peroxide. The formed hydrogen peroxide can either disproportionate in solution or undergo a further 2 e⁻ reduction to hydroxide. The formation of hydrogen peroxide is undesired because of its corrosive and oxidizing nature, which is potentially destructive to device components. In order to determine the mechanism of the ORR of the two catalysts, the number of electrons transferred per oxygen molecule was determined using the Koutecky-Levich (KL) equation (Eq. 32). (Figure 34c&d) The slopes of the linear fits of the KL plots at various potentials were used to calculate the number of transferred electrons.

\[
\frac{1}{J} = \frac{1}{J_k} + \frac{1}{B \omega \sqrt{2}}
\]

\[
B = 0.62nFC_0(D_0)^2\nu^{1/6}
\]
With $J$ being the measured current, $J_k$ the kinetic current, $\omega$ the angular velocity (rad s$^{-1}$), $B$ the Levich constant, $n$ the number of transferred electrons, $F$ the Faraday constant (96 485 C mol$^{-1}$), $D_0$ the diffusion coefficient of O$_2$ in 0.1 M KOH (1.9 x 10$^{-5}$ cm$^2$ s$^{-1}$), $C_0$ the concentration of O$_2$ in 0.1 M KOH (1.2 x 10$^{-6}$ mol cm$^{-3}$), $\nu$ the kinematic viscosity of 0.1 M KOH (0.01 cm$^2$ s$^{-1}$).

According to the KL analysis, Co/Co$_x$B/BA-tepa transferred about 3.2 electrons per oxygen molecule while Co/Co$_x$P/BA-tepa preferentially reduced oxygen via the 4 electron transfer mechanism. However, KL analysis of the ORR on electrodes modified with catalyst powders can only give an apparent number of transferred electrons since the theory and mathematical derivation of the equations were developed for flat and thin rather than porous and inhomogeneous films. Therefore, scanning electrochemical microscopy (SECM) was additionally applied to validate the number of transferred electrons derived by the KL analysis and to detect and quantify the amount of hydrogen peroxide formed (Figure 35a). The catalyst modified sample electrode was polarized at potentials at which the ORR occurred while a microelectrode was used as SECM tip to detect possibly formed hydrogen peroxide (Figure 35a). A platinum
microelectrode tip was positioned above the catalyst modified electrode at a working distance of 12.5 µm. The potential of the catalyst modified sample electrode was swept from 1.0 to 0.0 V vs RHE, similar to the potential window used for RDE voltammetry, while the tip potential was kept constant at 0.5 V vs. Ag/AgCl/3 M KCl (1.47 V vs. RHE), a potential sufficiently high to oxidize any formed hydrogen peroxide at a mass transport limited rate. The reductive current measured at the sample electrode increased upon oxygen reduction. The oxidative current at the tip electrode only increased when hydrogen peroxide was formed at the sample and then oxidized at the tip (Figure 35b&c).

The recorded tip and sample currents were used to calculate the number of transferred ($n$) electrons according to the literature [273] (Eq. 33):

$$n = \frac{4i_{\text{sample}}}{i_{\text{tip}}^{\text{CE}}}$$  \hspace{1cm} (33)
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With $i_{sample}$ being the measured current at the sample, $i_{tip}$ the measured current at the tip electrode and $CE$ the collection efficiency ($3.7 \times 10^{-4}$).

The amount of hydrogen peroxide produced was then calculated based on the derived value of $n$ (Eq. 34):

$$x_{H_2O_2} = \frac{4-n}{2} \times 100\%$$  \hspace{1cm} (34)

Contrary to the results from the KL analysis, Co/Co$_x$B/BA-tepa reduced oxygen over the entire potential window via the 4 electron mechanism without hydrogen peroxide production (Figure 35d), while between 3.7 and 4.0 electrons were transferred during the ORR on Co/Co$_x$P/BA-tepa with at most 15 % hydrogen peroxide production at potentials around 0.15 V vs. RHE (Figure 35d). The good agreement of the results obtained from SECM and RDE voltammetry therefore confirms that both catalysts reduce O$_2$ preferentially via the 4-electron transfer pathway.

Besides the ORR activity, the OER activity represents a very important parameter for a bifunctional oxygen catalyst and is therefore investigated in the following. Hydrodynamic voltammetry revealed higher OER activity by the carbon containing composites, Co/Co$_x$B/BA-tepa and Co/Co$_x$P/BA-tepa, both of which required 0.05 V less overpotential to drive a current density of 10 mA cm$^{-2}$ compared to their pristine Co/Co$_x$B and Co/Co$_x$P counterparts (Figure 36a). After the thermal treatment process, which resulted in embedment of the cobalt-cobalt metalloids inside the resulting N-doped carbon matrix, the Tafel slope changed substantially from 103 mV dec$^{-1}$ for the pristine material (Co/Co$_x$B) to 80 mV dec$^{-1}$ for Co/Co$_x$B/BA-tepa. For the phosphide based materials, a Tafel slope of 81 mV dec$^{-1}$ was determined for both the composite and the pristine material (Figure 36b). A change in the Tafel slope generally indicates a change in the nature of the OER active sites, and thus the reaction mechanism [19]. Different active sites would also explain the substantial change in overpotential. Therefore, the thermal treatment that transforms the insulating polybenzoxazine matrix into the conductive nitrogen-doped carbon matrix also simultaneously enhances the OER activity of the composite. The high ORR and OER activity of Co/Co$_x$B/BA-tepa and Co/Co$_x$P/BA-tepa makes them interesting to be investigated for bifunctional oxygen electrocatalysis. The practicability of the prepared boride and phosphide based materials embedded in a stabilizing nitrogen-doped carbon matrix for their possible application as catalysts for bifunctional oxygen electrodes in rechargeable metal-air batteries was investigated by alternating pulse chronopotentiometry (Figure 37) between the OER and the ORR.
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In rechargeable metal-air batteries, the OER takes place during the charging process while the ORR occurs upon discharging. These processes were simulated by current steps of 10 mA cm$^{-2}$ and -1 mA cm$^{-2}$ for the OER and ORR, respectively, for 15 minutes each (Figure 37), repeating 10 cycles. For both Co/Co$_x$B/BA-tepa and Co/Co$_x$P/BA-tepa, the OER response did not show any change in the measured potential, indicating highly stable OER active centers as well as stable immobilization of the powder materials on the electrode surfaces as already presented for PBA based OER catalysts (Section 4.1). However, the round-trip overpotential, expressed as the difference between the potentials measured at current densities of 10 mA cm$^{-2}$ and -1 mA cm$^{-2}$, increased from 0.84 V to 1.1 V for Co/Co$_x$B/NC and from 0.8 V to 1.03 V for Co/Co$_x$P/NC. The initial bifunctional activities of the presented materials are comparable to the activities of the bifunctional metal-metalloid catalysts recently published [265,274]. The increase in the round-trip voltage arises upon subjection of the ORR active sites to high anodic potentials during OER, which results in their irreversible oxidation, a notable problem of bifunctional oxygen catalysts [156,151]. Here, in the specific case of Co$_x$B and Co$_x$P based materials, the anodic potentials irreversibly oxidize the metallic cobalt species, forming a Co(OH)$_2$/CoOOH shell around a metal-metalloid core as described in the literature [46,49,275]. Nevertheless, the potential responses for both the ORR and the OER pulses reached a steady state after the fifth alternating ORR/OER cycle. The processes for deactivation of the ORR active sites have to be thoroughly investigated and addressed in order to achieve better cycling stability of bifunctional ORR/OER electrocatalysts.

Figure 36. LSVs for the OER on Co/Co$_x$B/BA-tepa, Co/Co$_x$P/BA-tepa, Co/Co$_x$B and Co/Co$_x$P (1600 rpm, O$_2$-saturated 0.1 M KOH, 5 mV s$^{-1}$) (a) and the corresponding tafel plots (b).
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Figure 37. Alternating pulse chronopotentiometry for bifunctional ORR/OER stability evaluation. Each cycle consists of 15 min OER at 10 mA cm$^{-2}$ and 15 min ORR at -1 mA cm$^{-2}$ (1600 rpm, O$_2$-saturated 0.1 M KOH). For each cycle, the potential at 7.5 min during each pulse for both reactions are presented.
4.4 LDH and pBO based composites as electrocatalysts

Some of the experiments in this section were performed by Bert Schlüter, Ruhr-Universität Bochum, in the framework of his master thesis. Physical characterization was done in cooperation with Dr. Corina Andronescu, Analytical Chemistry – Center for Electrochemical Sciences, Ruhr-Universität Bochum, and Dr. Eugeniu Vasile, Department of Oxide Materials Science and Engineering, University “Politehnica” of Bucharest. Differential electrochemical mass spectrometry was done in cooperation with Sandra Möller, Analytical Chemistry – Center for Electrochemical Sciences, Ruhr-Universität Bochum. Parts of the work are included in the manuscript: Andronescu, C.*, Barwe, S.*, Ventosa, E., Masa, J., Vasile, E., Konkena, B., Möller, S., Schuhmann, W., Powder Catalyst Fixation for Post-Electrolysis Structural Characterisation of NiFe Layered Double Hydroxide Based Oxygen Evolution Reaction Electrocatalysts, Angew. Chem. Int. Ed. (2017) 10.1002/anie.201705385, Angew. Chem (2017) 10.1002/ange.201705385.

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Layered double hydroxides (LDHs) are layered solid and ionic materials with the general formula $\text{M}^{2+}_{1-x}\text{M}^{3+}_x(\text{OH})_2(\text{A}^{n-})_{\frac{x}{n}}y\text{H}_2\text{O}$, where $\text{M}^{2+}$ and $\text{M}^{3+}$ are divalent and trivalent metal cations, respectively, $\text{A}^{n-}$ is an anion having the valence $n$ and $x$ represents the $\text{M}^{2+}/(\text{M}^{2+}+\text{M}^{3+})$ ratio, with reported values commonly between 0.2 - 0.33. The hydroxide layers are typically of the brucite structure. Partial exchange of bivalent cations with trivalent metal cations introduces a net positive charge in the hydroxide layers, which is balanced by anions present in the LDH galleries. These materials are already widely used in the fields of heterogeneous catalysis [84], pharmaceutics, polymer science, electrochemistry and photochemistry [85]. Recently, LDHs, especially as exfoliated nanosheets [77,102,104] or supported on carbon nanotubes [88], graphene [92,93] or containing different metals [89,90] were reported to be among the most active OER catalysts in alkaline media, outperforming current state-of-the-art OER catalysts in terms of activity [276,84]. In the following section, the previously described beneficial properties of pBO/electrocatalyst composites are explored for their use in combination with NiFe LDH, the state-of-the-art OER catalyst in alkaline media.

4.4.1 NiFe LDH and pBO composite as highly active OER electrocatalyst with enhanced stability

LDH materials naturally exhibit a high charge density at the hydroxide layers due to the partial exchange of bivalent transition metal motifs by trivalent metal ions. Since this charge is usually
balanced by nitrate, carbonate or halide ions, LDHs are predominantly of hydrophilic nature. Evidently, LDHs seem to be incompatible with the pure organic BO monomers, thus preventing intimate incorporation of BO in the interlayer galleries. However, the interaction of BO with the LDH and its propagation into the interlayer space is necessary in order to form highly dispersed LDH sheets embedded in the later formed carbon matrix. To overcome these limitations, firstly a NiFe LDH with nitrate (NiFe-NO$_3$ LDH) as charge balancing anion was prepared adapting a method from Song and Hu [77]. During synthesis of the LDH, it was of pivotal importance to have a carbonate free environment. A carbonate free environment is highly important for the strategy of exchanging the nitrate anion against an organic anion in order to increase the LDH and BO compatibility. Carbonate ions are known to exhibit the strongest affinity to the interlayer galleries of LDHs, hence they are shown to replace other interlayer ions, like nitrate, thereby hindering further anion exchange reactions [106]. After the synthesis of the NiFe-NO$_3$ LDH, the nitrate ions were replaced by the organic anion sodium dodecyl sulfate (SDS) to form NiFe-SDS LDH. The long hydrophobic organic tails of SDS do not only increase the interlayer spacing but also create a more hydrophobic environment inside the LDH galleries, hence facilitating the insertion of BO monomers inside the LDH motifs. XRD analysis revealed an increased interlayer distance for the LDH after anion exchange (Figure 38). The (003) reflection, which is a measure for the basal plane spacing of NiFe-SDS LDH (3.43 °) is shifted to lower angles with respect to NiFe-NO$_3$ LDH (8.63 °). A lower angle suggests an increase in the basal spacing and indeed the basal spacing changed from 1.02 nm to 2.57 nm upon intercalation of the long chain SDS molecules.

**Figure 38. XRD patterns of NiFe-NO$_3$ LDH and NiFe-SDS LDH.**

NiFe LDH and pBO nanocomposites were prepared by *in-situ* thermal polymerization of BO molecules in the presence of homogeneously dispersed LDH by thermal treatment of their
mixtures directly on electrode surfaces as described in sections 4.1 & 4.3. After polymerization, a second heating step converted the insulating organic pBO into a conductive carbon matrix. Different LDH to pBO ratios, temperatures and carbonization atmospheres were investigated in order to find the most suitable conditions for the LDH based materials. Evidently, calcination of a 3 to 1 LDH to pBO ratio at 450 °C led to formation of a nanocomposite with the highest activity towards the OER for the shortest calcination time (Figure 39). As expected, composites based on NiFe-NO₃ LDH show lower activity presumably due to agglomeration of the LDHs inside the organic polymer film (Figure 39). Interestingly, suspensions of the LDHs in dissolved BO monomers where homogeneous and stable for the NiFe-SDS LDH while in the case of NiFe-NO₃ LDH, agglomerates where readily formed and observed to sediment within a few minutes.

![Diagram](image)

**Figure 39.** Comparison of differently prepared NiFe/C nanocomposites and their corresponding OER activities shown in the form of LSVs recorded at a scan rate of 5 mV s⁻¹ in oxygen saturated 0.1 KOH and 1600 rpm of electrode rotation.
Although one would expect calcination of pBO in the presence of oxygen to completely degrade the polymer film and transform it into CO\textsubscript{2} or other volatile species, it is known that LDH-based pBO nanocomposites favor the formation of a high residual char yield by dispersion of LDH nanolayers in the pBO network [277]. TGA of the pristine BO showed that at temperatures higher than 300 °C, pBO decomposed to form a residual char of 4 % (Figure 40). Calcination of the pristine NiFe-SDS LDH started with loss of adsorbed water up to a temperature of 225 °C. Higher temperatures led to the loss of OH\textsuperscript{−} followed by decomposition of the SDS anions and loss of aliphatic carbons at T > 300 °C. A further temperature increase up to 425 °C resulted in a total loss of OH\textsuperscript{−} and a plateau without any further weight changes. The pure NiFe-SDS LDH yielded a residual weight of 62 %. As expected, NiFe SDS/pBO behaved similarly to the pure NiFe-SDS LDH but with increased weight loss due to the presence of pBO and a residual char of 44 % was obtained.

The comparatively higher activity of the composite based on the mild calcination of the pBO and LDH nanocomposite is not surprising. LDHs are known to possess an intrinsic memory effect when calcined mildly [278]. The memory effect describes the ability of LDHs to regenerate their layered structure after thermal treatment in the presence of solutions containing anions and a high concentrations of OH\textsuperscript{−}. At the same time, pyrolysis in an inert atmosphere leads to a loss of this very special property [279,280]. For this reason, and the demonstrated high OER activity of LDHs, further investigations were done with NiFe-SDS/pBO ratio 3:1 samples calcined at 450 °C. The aforementioned memory effect becomes obvious by comparing XRD
patterns of a calcined NiFe-SDS/pBO (from now on denoted as NiFe/C) sample directly after calcination (denoted as BC, representing the material before potential cycling in KOH) and after electrochemical cycling in the presence of a high OH⁻ ion concentration, i.e. 0.1 M KOH (denoted as AC, representing the material after potential cycling in KOH) (Figure 41). The XRD pattern of NiFe/C BC shows four major reflections at $2\theta = 35.9^\circ$, $37.4^\circ$, $43.5^\circ$, and $63.4^\circ$ which can be correlated to the NiFe$_2$O$_4$ and NiO reference diffraction patterns. NiO and NiFe$_2$O$_4$ are the expected products of mildly calcined NiFe LDH, thus the findings correlate well with the literature [281]. The reflection at $2\theta = 35.9^\circ$ is assigned to the (311) reflections of NiFe$_2$O$_4$, the one at $37.4^\circ$ to reflections of both (222) of NiFe$_2$O$_4$ and (111) of NiO, the one at $43.5^\circ$ to the (400) reflection of NiFe$_2$O$_4$ and (200) reflections of NiO, respectively, while the reflection at $63.4^\circ$ is a convolution of the (440) reflection of NiFe$_2$O$_4$ and the (220) reflection of NiO. No characteristic LDH peaks were observable in the diffraction pattern of the NiFe/C BC sample. However, after 30 min of potential cycling in 0.1 M KOH, the NiFe motifs partially recover their layered structure, which was lost during the calcination step with OH⁻ and carbonate as the interlayer anions. The XRD pattern of NiFe/C AC shows again the characteristic LDH reflections at $2\theta$ values of $11.3^\circ$, $22.9^\circ$ and $34.5^\circ$, representing the (003), (006) and (012) reflections, respectively (Figure 41). The basal plane spacing of the recovered NiFe LDH was 0.75 nm, clearly smaller than that of NiFe-NO$_3$ LDH (1.02 nm). This observation is in good agreement with the size difference between NO$_3^-$ and OH⁻ ions. In addition to OH⁻, CO$_3^{2-}$ from dissolved atmospheric CO$_2$ can intercalate into the LDH galleries. CO$_2$ is known to be one of the main contaminants of LDHs [106]. After regeneration of the LDH, different amounts of the M$^{II}$/M$^{III}$ oxide, here NiO, are still observed depending of the initial M$^{II}$/M$^{III}$ ratio. Usually, the regenerated LDHs have a M$^{II}$/M$^{III}$ ratio $= 2$ independent of the initial ratio [282]. Although NiO might still be present, the OER activity of the resulting composite can clearly be attributed to the restructured LDH since NiO itself is known to exhibit a comparatively low OER activity [283].

Transformation of the pBO network into carbon is a crucial step. Without this step the pBO would act as an insulator. Unfortunately, it is not possible to conclusively determine the nature of the formed carbon from the XRD. Carbon species are usually evaluated according to their (002) and (100) diffraction of graphitic carbon. In the XRD pattern of the BC sample, a small peak at around $24^\circ$ can be observed (Figure 41), which is difficult to definitively assign. In addition, the diffraction peak at $44^\circ$ (100) is also difficult to ascribe since it overlaps with the diffraction from NiFe$_2$O$_4$ (400) and NiO (200). In the NiFe/C AC sample, the reflection at $24^\circ$
possibly originating from carbon (002) is masked by the (006) reflection of NiFe LDH in the region of 20-24°.

![XRD patterns](image)

**Figure 41.** XRD patterns of a calcined NiFe-SDS/pBO composite (NiFe/C) before (BC) and after (AC) potential cycling in 0.1 M KOH, and of NiO and NiFe$_2$O$_4$ reference patterns.

According to reports presented in literature, graphitic carbon can be obtained by pyrolysis of polybenzoxazine in the presence of different metals (including Ni) at temperatures higher than 600 °C [284,285]. Since the thermal treatment temperature used in this study was 450 °C, the carbon presented in the catalyst layer is presumably of amorphous nature. Furthermore, transformation of the insulating organic polymer into amorphous carbon is manifested by the typical D and G bands of carbon at Raman shifts of 1350 cm$^{-1}$ and 1590 cm$^{-1}$, respectively [284] (**Figure 42**).

TEM images show that upon calcination (NiFe/C BC) nanometric particles of different sizes embedded in a carbon matrix are formed (**Figure 43a**). The nanometric particles are found to represent either NiO or NiFe$_2$O$_4$ (**Figure 43b**). After potential cycling in 0.1 M KOH, the material adopted a clearly different structure. TEM analysis revealed the presence of layers, confirming regeneration of the layered structure after introducing the mixed oxides into the OH$^-$ containing solution (**Figure 43d&e**). Besides the LDH layers, discrete NiO nanoparticles were also
observed within the carbon matrix (Figure 43f), indicating that only NiFe$_2$O$_4$ and not the discrete NiO particles are transformed into NiFe LDH.

Figure 42. Raman spectrum of the calcined NiFe SDS/pBO nanocomposite before potentiodynamic cycling (NiFe/C BC sample).

Figure 43. a) and b) HR-TEM images of a calcined NiFe-SDS LDH/pBO nanocomposite (NiFe/C BC sample), c) FFT of the marked area in b). d)-f) HR-TEM images of the calcined NiFe-SDS LDH/pBO nanocomposite after fast electrochemical cycling (NiFe/C AC sample).
XPS survey spectra confirm the presence of carbon in NiFe/C both before and after cycling (Figure 44a) in good agreement with the Raman results. Furthermore, the main components nickel, iron and oxygen were also detected. The high resolution XP spectrum of Ni 2p$_{3/2}$ of the calcined composite NiFe/C BC (Figure 44b) was deconvoluted into 4 peaks, one at 855.5 eV corresponding to Ni species from NiO, one at 857.7 eV attributed to Ni from a NiFe$_2$O$_4$ spinel type structure [286] and two shake-up satellites at binding energies higher than 860 eV. The Fe 2p high resolution spectrum of the calcined composite BC and AC (Figure 44d) show the Fe 2p$_{3/2}$ peak at ~712 eV and Fe 2p$_{1/2}$ peak at ~724 eV, proving Fe to be present as Fe$^{3+}$. Deconvolution of the Fe 2p region of mixed NiFe compounds is problematic due to the presence of Ni LMM Auger peaks in the same region. The high resolution spectrum of the Ni 2p$_{3/2}$ region of NiFe/C AC revealed a change in the chemical state of of Ni, indicated by a shift of the Ni$^{2+}$ binding energies (Figure 44c). The nature of the carbon does not change upon potential cycling. The high resolution C 1s spectra of the BC and AC samples can both be deconvoluted into C-C, C-S, C-O and O=C-O components (Figure 44e&f). A new potassium signal appeared in the AC sample, which obviously originated from the electrolyte (KOH).

Figure 44. Survey spectra of NiFe-SDS LDH and calcined NiFe/C before (BC) and after (AC) potentiodynamic cycling (a). High-resolution Ni 2p$_{3/2}$ spectra for the calcined NiFe-SDS LDH/pBO nanocomposite b) before (NiFe/C BC) and c) after (NiFe/C AC) the potential cycling. High resolution Fe 2p spectra for the calcined NiFe-SDS LDH/pBO nanocomposite before (NiFe/C BC) and b) after (NiFe/C AC) potentiodynamic cycling (d). High-resolution C 1s spectra of the calcined NiFe-SDS LDH/pBO nanocomposite e) before (NiFe/C BC) and f) after (NiFe/C AC) the potential cycling.
Therefore, XRD, TEM and XPS comprehensively confirm the partial regeneration of the LDH structure upon electrochemical cycling of the calcined sample. Hydrodynamic voltammetry revealed the outstanding electrochemical properties of NiFe-NO₃ LDH towards OER as already known from published literature [77,287,288]. It delivered a current density of 10 mA cm⁻² at an overpotential as low as 0.27 V with a Tafel slope of 56 mV dec⁻¹ (Figure 45a&amp;b). Organophilization of NiFe-NO₃ LDH via anion exchange of NO₃⁻ against SDS led to NiFe-SDS LDH. LSV in O₂-saturated KOH (0.1 M) revealed a lower activity of NiFe-SDS LDH as compared to NiFe-NO₃ LDH with an overpotential of 0.29 V to reach a current density of 10 mA cm⁻² (Figure 45a). The Tafel slope of NiFe-SDS LDH changed from 59 mV dec⁻¹ in the lower current density region to 150 mV dec⁻¹ at higher current densities, indicating a change in the OER mechanism (Figure 45b). The lower activity of NiFe-SDS LDH can be explained by the larger interlayer spacing induced by the larger organic anion, decreasing the electronic conductivity between the single layers [77]. The initial OER activity of the prepared composite NiFe/C (ratio NiFe SDS: BO monomer = 3:1) before cycling (NiFe/C BC) decreased with respect to NiFe-NO₃ LDH (Figure 45a), represented by an overpotential of 0.35 V at 10 mA cm⁻², which is 0.06 V higher than the one obtained by NiFe-SDS LDH (0.29 V) at the same current density. The initial Tafel slope of NiFe/C BC (Figure 45b) was similar to that of NiFe-NO₃ LDH and NiFe-SDS LDH (around 59 mV dec⁻¹).

A simple stability test using consecutive voltammetric scans revealed poor stability of both NiFe-NO₃ LDH as well as NiFe-SDS LDH (Figure 45c&amp;d). In the course of 50 CVs of fast potentiodynamic cycling, the activity of both pristine LDHs decreased drastically while it was essentially unchanged for the NiFe/C nanocomposite (Figure 45c-e). NiFe-NO₃ LDH still had an early OER “onset”, but the overpotential needed to afford 10 mA cm⁻² increased to 0.32 V. The drastic decrease in the current density suggests a decline in the electronic conductivity of the catalyst layer. The decline in the OER activity of NiFe-SDS LDH was even more pronounced and the overpotential to reach the same current density increased to 0.4 V, while NiFe/C AC required an overpotential of 0.33 V to reach 10 mA cm⁻² (Figure 45e). Additionally, the Tafel slopes increased significantly after potential cycling to 158 mV dec⁻¹ and 131 mV dec⁻¹ for NiFe-NO₃ LDH and NiFe-SDS LDH, respectively (Figure 45g). The Tafel slope of NiFe/C remained constant (57 mV dec⁻¹) upon potential cycling (Figure 45g). The lower Tafel slope of NiFe/C compared to the pristine LDHs after potential cycling can be attributed to an enhanced stability as well as the favorable electronic conductivity of the catalyst film provided by the formed carbon matrix. Carbon supports and carbon matrices are well known to enhance inter-particle electron transfer, hence they increase the electric conductivity [95].

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**Figure 45.** LSVs in O$_2$-saturated KOH (0.1 M) recorded at a scan rate of 5 mV s$^{-1}$ and 1600 rpm electrode rotation showing OER electrocatalysis by NiFe-NO$_3$ LDH (black), NiFe-SDS LDH (red) and NiFe/C (green), before (a) and after (f) potentiodynamic cycling. Tafel slopes of NiFe-NO$_3$ LDH (black squares), NiFe-SDS LDH (red cycles) and NiFe/C (green triangles) before (b) and after (g) potentiodynamic cycling. Cyclic voltammograms of NiFe-NO$_3$ LDH (c), NiFe-SDS LDH (d) and NiFe/C (e) before (black) and after (red) potentiodynamic cycling (50 cycles, 50 mV s$^{-1}$, grey).

A combination of differential electrochemical mass spectrometry (DEMS) and rotating ring disk electrode (RRDE) Faradaic efficiency determination revealed oxygen as the only reaction product in the potential window of interest. The Faradaic efficiency of NiFe/C AC towards the OER, determined by means of RRDE voltammetry as described in section 6.4.2.3 and elsewhere [236,289] was close to 100 % (98.3 %). Galvanostatic and potentiostatic DEMS
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measurements proved the formation of oxygen. By applying a current density of 2.1 mA cm\(^{-2}\), the ion current corresponding to the M/z = 32 (O\(_2\)) increased (Figure 46a) and stayed constant over the measurement time span of 5 min. The potentiostatic measurements clearly demonstrate the correlation of the ion current to the O\(_2\) evolution at potentials higher than 1.4 V vs. RHE, confirming that the electrochemical response observed in Figure 45 is solely generated by the OER (Figure 46b-d).

![Figure 46](image)

**Figure 46.** a) Chronopotentiometric measurement performed at a current density of 2.1 mA cm\(^{-2}\) and an electrolyte flow rate of 6.5 mL min\(^{-1}\), b, d) variation of the ion current m = 32 and c) current density recorded during a CV scan between 0.98 V and 1.58 V vs. RHE at 5 mV s\(^{-1}\) with an electrolyte flow rate of 6.5 mL min\(^{-1}\).

In case of the RDE measurements, adequate catalyst adhesion is hindered by the very smooth nature of the finely polished glassy carbon surface, hence hampering meaningful long-term stability assessments. In order to overcome this limitation, further stability investigations were conducted with the catalyst supported on graphite paper, which has a well-defined two dimensionally structured surface and offers improved catalyst adhesion. Furthermore, graphite paper is by itself inherently catalytically inert towards the OER at the applied potentials. NiFe-NO\(_3\) LDH was chosen as a reference material for stability studies, because it exhibited the highest
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Initial activity. For evaluation of the catalyst stability at OER conditions, a modified version of
the procedure as used in section 4.1 was applied to the catalyst modified graphite paper elec-

trodes in a specially designed flow-through cell [240] with O₂-saturated 0.1 M KOH as electro-

lyte. Briefly, the procedure consists of repeating cycles of EIS, CV and galvanostatic polariza-

tion. The EIS is used in order to determine the resistance of the electrolyte. After recording a
CV in the OER potential window, galvanostatic polarization followed at 50 mA cm⁻² for a time
span of 15 min. This current density was chosen, because it is significantly higher than those
conventionally applied for catalyst durability evaluation [77,88,93,107,117,290–293] and thus
exerts higher stress to the catalyst by imposition of more vigorous gas bubble formation. A
comparison of the first and last CVs of NiFe-NO₃ LDH and NiFe/C (Figure 47a) further under-
lines the contrastingly enhanced stability of NiFe/C compared to NiFe-NO₃ LDH. The poten-
tials at the commonly used current density of 10 mA cm⁻² taken from the 48 CVs increased
gradually for pristine NiFe-NO₃ while it fluctuated around 1.60 V for NiFe/C after an initial
activation phase (Figure 47b). During 48 consecutive cycles of the galvanostatic polarization,
the potential required to provide a current density of 50 mA cm⁻² for NiFe-NO₃ LDH fluctuated
but increased from 1.69 V vs. RHE in the first cycle to 1.84 V vs. RHE in the last cycle (Figure
47c). The potential of NiFe/C was 1.76 V vs. RHE in the first cycle and remained unchanged
through the 48th cycle (Figure 47c), with only minor potential fluctuations. Those fluctuations
of the potential in both cases were due to the dynamics of bubble formation, growth and depar-
ture. Evidently, these results demonstrate that despite the impressive OER activity of NiFe-NO₃
LDH, its durability would not suffice for potential applications. The comparatively poor stabili-
ty of NiFe-NO₃ LDH may be caused either by (electro)chemical deactivation or by detachment
of the catalyst from the electrode surface. The enhanced long-term stability of NiFe/C is due to
its improved immobilization on the electrode surface indicating that in the case of NiFe-NO₃
LDH, detachment of the catalyst from the electrode was presumably the major cause of its
relatively faster activity loss. In conclusion, the stability and consequently the long-term
durability of the NiFe/C nanocomposite catalyst introduced in this work clearly outshine that
of the pristine LDH.

Because of its promising stability, a home-made, non-zero gap water electrolyzer (section 6.4.3)
was employed for alkaline (3 M KOH) water electrolysis at room temperature with NiFe/C
modified graphite paper as anode and nickel foil as cathode. The current density was increased
incrementally from 0 to 30 mA cm⁻² and then kept constant to investigate variation of the overall
cell voltage with time.
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Figure 47. a) Voltammograms recorded during the first (solid line) and last (dotted line) of stability assessment (scan rate 5 mV s\(^{-1}\)) of NiFe-NO\(_3\) LDH and NiFe/C. (b) Potential versus cycle number for NiFe-NO\(_3\) LDH and NiFe/C, with each point representing the potential at 10 mA cm\(^{-2}\) taken from the CVs. (c) Potential versus cycle number for NiFe-NO\(_3\) LDH and NiFe/C, with each point representing the potential at 450 s during galvanostatic polarization at 50 mA cm\(^{-2}\).

There was a negligible loss in the efficiency of the cell over a period of 14 days with the cell continuously polarized at 30 mA cm\(^{-2}\) (Figure 48a) which clearly demonstrates the potential of the catalyst to endure long-term performance under harsh conditions. The cell voltage remained essentially unchanged around 2.25 V for the entire test duration of 14 days. Although the NiFe/C nanocomposite showed impressive stability, the overall cell voltage was relatively higher than one would expect on the merit of the high OER activity of an optimized electrolyzer and cathode electrocatalyst. Generally, the overall cell resistance and, consequently, the cell voltage in an electrolyzer setup employing electrolyte flow and a membrane, especially when operated in the non-zero gap configuration, is influenced by many parameters. The total resistance of the cell, the resistances of the electrochemical reactions, the electrical resistance of the circuit, the resistances of formed gas bubbles, and the membrane and the electrolyte
resistances [11]. The overall electrolyzer cell resistance plays a crucial role for the efficiency and stability of the catalyst, as immense gas bubble formation may virtually decrease the electroactive electrode area available for the reaction. The NiFe/C modified electrode did not show any visible signs of degradation after the stability test (Figure 48a inset). On the other hand, an electrolyzer with a bare graphite paper serving as the anode and operated at the same current density (30 mA cm\(^{-2}\)) had an initial cell voltage of 3.25 V, and the electrode rapidly degraded within a few minutes of water electrolysis (Figure 48b&c).

![Figure 48](image)

**Figure 48.** Cell voltage versus time transients of a home-made, non-zero gap, precious metal free electrolyzer operating at room temperature (anode: NiFe/C composite (a) or graphite paper (b), cathode: Ni; 3 M KOH). Inset a) Optical image of the NiFe/C modified graphite paper after the measurement. The white lines indicate the electrolyte flow channel. c) Optical image of the graphite paper anode after the measurement shown in b). White lines indicate the electrolyte flow channel.

Since the NiFe/C nanocomposite showed already very promising stability under the aforementioned conditions, it was subjected to further stability tests under even harsher conditions, i.e. in 5 M KOH at 60 °C by applying a current density of 200 mA cm\(^{-2}\). To avoid limitations caused by corrosion of the electrode support, NiFe/C was prepared on nickel foam, since Ni is known...
to be resistant and is one of the most used electrode materials in alkaline electrolysis [221]. Furthermore, Ni foam is known to be a highly suitable and often used substrate especially for NiFe based OER catalysts [117,290,294,295]. Bearing in mind that Ni foam itself might have intrinsic OER activity, the NiFe/C modified Ni foam was compared with bare Ni foam (Figure 49a). Obviously, Ni foam itself is already active under the used conditions, however, NiFe/C modified Ni foam clearly outperformed the bare substrate, manifested in a potential difference of 0.23 V after 15 min at an applied current density of 200 mA cm\(^{-2}\) in 5 M KOH at 60\(^{\circ}\) C. Thus, the shown catalytic activity can be safely attributed to the NiFe/C nanocomposite. The potential to afford the current density of 200 mA cm\(^{-2}\) fluctuates constantly around a value of 0.5 V vs. Ag/AgCl/3M KCl for a time span of 100 h (Figure 49b). The observed fluctuations in the potential are caused by the high amount of O\(_2\) formed during the measurement. The growth and departure of gas bubbles as well as changes in the electrolyte volume overnight also contributed to such fluctuations in the potential. Due to temperature induced faster electrolyte evaporation at 60 \(^{\circ}\)C and no electrolyte maintenance overnight, the potential slightly increased during the night while it decreased upon refilling of the electrolyte during the day.

The NiFe/C modified NF was investigated in-depth for structural and morphological changes after it was subjected to the stability assessment. SEM images at different magnification scale revealed no obvious changes in the catalyst morphology after applying 200 mA cm\(^{-2}\) in 5 M KOH at 60 \(^{\circ}\)C for 100 h (Figure 50a&b). Furthermore, EDX confirms the presence of all the expected components, nickel, iron and especially carbon, which would be suspected to corrode...

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**Figure 49:** a) Galvanostatic polarization of NiFe/C on nickel foam and bare nickel foam (NF). b) Potential versus cycle number for NiFe/C with each point representing the potential at 450 s during galvanostatic polarization at a current density of 200 mA cm\(^{-2}\) in 5 M KOH, at 60 \(^{\circ}\)C.
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fastest (**Figure 50c**). Also, sulfur originating from thermal decomposition of SDS was detectable, further proving that the NF was still covered with the original NiFe/C catalyst resulting from calcination of NiFe-SDS LDH/pBO.

![Figure 50. SEM images of NiFe/C at different magnifications: 100 x, 500 x, 5000 x and 100000 x (from left to the right), prepared on Ni foam before (a) and after (b) operating for 100 h at a current density of 200 mA cm\(^{-2}\) in 5 M KOH and at 60 °C. c) SEM of the catalyst deposited on Ni foam after operating for 100 h at a current density of 200 mA cm\(^{-2}\) in 5 M KOH and at 60 °C, magnification 200000 x and the associated EDAX spectrum.](image)

Interrogation of the high resolution C 1s XP spectra of the NiFe/C catalyst before and after the 100 h electrolysis revealed a mixture of C-C carbon and oxidized carbon in both cases (**Figure 51a**). No significant difference can be observed between the two samples indicating that the nature of the carbon did not change during the OER. The XRD pattern of the NiFe/C modified Ni foam after the 100 h durability test shows the characteristic diffraction pattern of Ni and NiO.
from the Ni foam support and additionally three very small peaks are observed at 30 °, 35.7 ° and 57.2 ° which are characteristic of NiFe$_2$O$_4$ (Figure 51b). However, no LDH characteristic reflection can be observed. Moreover, TEM images show that after the 100 h, the NiFe/C is a mixture of NiO and NiFe$_2$O$_4$ nanoparticles (Figure 51c-e). Thus, the catalyst is evidently transformed into a spinel structure during the 100 h of oxygen evolution. Transformation of LDH into a spinel at temperatures between 60 – 95 °C in aqueous media was already described in literature for other types of LDH [296].

**Figure 51.** a) XPS High resolution C 1s spectra of the NiFe/C catalyst before and after testing for 100 h at 200 mA cm$^{-2}$ in 5 M KOH and 60 °C. b) XRD pattern of the NiFe/C catalyst deposited on Ni foam after 100 h of OER in 5 M KOH, 60 °C at 200 mA cm$^{-2}$. HR-TEM (c, e) images of the NiFe/C catalyst deposited on Ni foam after 100 h of OER in 5 M KOH, 60 °C at 200 mA cm$^{-2}$. d) SAED pattern of c).

Furthermore, it is already known that the NiFe catalyst structure is usually changed when high anodic potentials, as required for the OER, are applied [123]. Although the structure of the NiFe LDH catalyst changed during OER, the catalyst was still immobilized on the electrode after the measurement at such a high current density (200 mA cm$^{-2}$) in 5 M KOH at 60 °C, showing that the proposed approach used to immobilize powder catalysts is not only highly efficient but also makes it possible to observe such structural changes.
4.4.2 Variation of the pBO precursor of NiFe/C

Based on the very promising results obtained with the BO monomer BA-a, the previously presented and deeply investigated methodology of fixing LDH-based OER catalysts was further explored for three different types of pBO precursors. The BOs were chosen according to their possible influence on the final ORR activity of the composite material. BA-tepa was already shown in section 4.3 to enhance the ORR activity of cobalt-cobalt metalloid catalysts. Based on those results, BA-tepa and two other BOs with higher and lower nitrogen content (Figure 52), i.e. Cp-mel and BA-1.6dah, respectively, were chosen to be investigated. While BA-1.6dah has obvious structural similarities with BA-tepa, Cp-mel differs substantially. The first two are oligomers with aliphatic chains between the BA building blocks while the latter forms defined monomers comprising three BO functionalities around a triazine ring. Furthermore, Cp-mel has secondary polymerizable moieties with its cyanide groups and might therefore form denser networks, thus leading to a higher stability. However, the comparatively larger size of Cp-mel has to be compatible with the LDH galleries.

![Figure 52. Schematic representation of the used pBO precursors BA-1.6dah, BA-tepa and Cp-mel.](image)

The electrodes were modified as discussed in section 4.4.1 with composites of NiFe-SDS LDH and the different pBOs. Taking into account the beneficial influence of the nitrogen content of the BO, BA-tepa and Cp-mel based composites were investigated towards their ORR activity. However, only poor ORR activity was obtained for the various composite materials. The potential necessary to drive the ORR at \(-1\) mA cm\(^{-2}\) was for all the tested materials around 0.71 V vs. RHE and 0.66 V vs. RHE for BA-tepa and Cp-mel based composites, respectively (Figure 53).
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All LSVs recorded at a scan rate of 5 mV s\(^{-1}\) and with an electrode rotation speed of 1600 rpm in O\(_2\)-saturated KOH (0.1 M) show a two-step ORR process, resulting in the formation of two distinct mass transport limited regions. The described curve shapes clearly indicate that the ORR proceeds via a hydrogen peroxide forming mechanism. The obtained results do not indicate the prospect of a substantial ORR activity for the formed materials to be achievable. Therefore, the NiFe-SDS LDH/pBO based composites were not further investigated for the ORR. Thus, the studies that follow hereafter focus only on the OER activity.

![Figure 53. LSVs of nanocomposites based on NiFe-SDS LDH / BA-tepa (a) and NiFe-SDS LDH / Cp-mel (b) (1600 rpm, O\(_2\)-saturated 0.1 M KOH, 5 mV s\(^{-1}\)), with different ratios between the LDH and the BO.](image)

The oxygen evolution activity of nanocomposites of NiFe-SDS LDH and the different pBOs was investigated based on similar methods described before. Freshly prepared electrodes were investigated by means of LSV in KOH (0.1 M) and then underwent a fast potential cycling for approximately 30 min in order to regenerate the LDH structure. A second LSV at a slower scan rate revealed the OER activity of the nanocomposites. A calcination procedure of 2 h at 450 °C was applied to the LDH/BA-a composites. A systematic study of the influence of the LDH to BO ratio revealed that higher amounts of LDH during electrode preparation are beneficial for the obtained OER activity. For all three tested BOs, the nanocomposites with ratios of 5 or 3 to 1 showed the highest activities (Figure 54a-c). As expected, all prepared composites showed an activity increase upon potential cycling. This phenomenon was already discussed in detail in the previous section and is based on restructuring of the layered structure of the dehydrated LDH directly after calcination. A NiFe-SDS LDH to BA-tepa ratio of 3:1 showed a potential of 1.60 V vs. RHE to achieve a current density of 10 mA cm\(^{-2}\) before the potential cycling.
which decreased after the cycling procedure to 1.58 V vs. RHE. Similar observations were obtained for Cp-mel and BA-1.6dah based materials. A ratio of LDH to BO of 5:1 for Cp-mel had a BC potential at 10 mA cm\(^{-2}\) of 1.59 V vs. RHE, similar to a BA-1.6dah based material with a 3:1 ratio. The potential cycling process decreased the necessary potential by about 20 and 30 mV for the Cp-mel and BA-1.6dah based nanocomposites, respectively. Comparable to the results obtained for the BA-a based LDH composites, the Tafel slopes of the composites with the highest OER activity did not change substantially upon potential cycling (Figure 54e&g). Both BA-tepa and Cp-mel, BC and AC, show Tafel slopes close to 59 mV dec\(^{-1}\). The 3:1 ratio of NiFe-SDS LDH and BA-1.6dah gave a Tafel slope of 53 mV dec\(^{-1}\) regardless of whether it was cycled or not.

**Figure 54.** LSVs of nanocomposites based on NiFe-SDS LDH with BA-tepa (a), Cp-mel (b) and BA-1.6dah (c) with different ratios of the LDH to BO. LSVs of the best ratios of the different composites before (d) and after (f) potential cycling, with the corresponding Tafel plots (e, g) (1600 rpm, O\(_2\)-saturated 0.1 M KOH, 5 mV s\(^{-1}\)).

In general, the OER activities obtained by the different BOs are similar or slightly lower than those reported for BA-a based NiFe/C from the previous section.

The AC activities of the most active composites of the different BOs are very similar and also close to the activity obtained by BA-a and NiFe-SDS LDH investigated in section 4.4.1. Nevertheless, the stability of the prepared nanocomposites was further investigated with respect to the different BOs and the LDH:BO ratio. Stability assessments were done over a period of 12 h following the advanced stability test procedure comprising a repeating sequence of EIS, CV
and galvanostatic polarization at 10 mA cm$^{-2}$ with the catalyst modified glassy carbon RDEs. The LDH to BO ratio does not only influence the BC and AC activity in terms of the overpotential required to reach a certain current density, but it obviously also affects the stability of the obtained nanocomposite catalysts (Figure 55). BA-tepa based materials showed a strong dependence on the LDH to BO ratio, manifested by a poor ability to keep the potential constant at a current density of 10 mA cm$^{-2}$ when the BO content increased to 50 % and higher. The LDH:BO ratios of 5:1 and 3:1, which were demonstrated earlier to yield the most stable films are also similarly stable for the new family of the BO precursors. After an activation period of 2 h, both ratios maintained a low overpotential of around 0.35 V at the applied current density. In contrast, the supposedly more stable Cp-mel showed the lowest stability regardless of the LDH to BO ratio. All ratios underwent an activation within the first 2 h of the stability measurement, but afterwards the activity constantly decayed. Presumably, the bigger Cp-mel molecules do not interact intimately with the LDH, thus decreasing their potential benefit. Contrary to the case of the two preceding examples, BA-1.6dah and LDH based materials showed high stability for all the tested ratios. Although the composite with a ratio of 1:1 showed an increase in the overpotential during the first hours of the stability test, it reached a stable state within the 12 h of measurement time. Not only the dependence of the stability on the nature and content of the BO precursor, but also the activity over a period of 12 h was monitored. A comparison of the highest OER activity of all three tested BOs covering all the investigated LDH:BO ratios revealed NiFe-SDS LDH/BA-1.6dah (5:1) to be substantially more active than its BA-tepa and Cp-mel based counterparts (Figure 55d). The higher activity of BA-1.6dah might presumably be evoked by a better compatibility due its highly uncharged character. The aliphatic chains of BA-1.6dah are compatible with the aliphatic chains of SDS, thus the interlayer galleries provide a suitable environment for the BA-1.6dah. However, compared to the in-depth studied NiFe/C based on NiFe-SDS LDH and BA-a, the activity and stability did not increase. Nevertheless, based on the obtained results, BO monomers with higher compatibility or specific properties could be designed in future work.
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4.4.3 LDH and pBO composites for bifunctional ORR and OER electrocatalysis

In the following section, LDHs were modified in order to make them active for the OER and the ORR. In the previous section, it was not possible to activate the materials which are already highly active towards the OER also for the ORR by just increasing the nitrogen content of the used BOs analogue following the approach used in section 4.3. Therefore, transition metal-N4 macrocycles were used to modify the well-known NiFe-NO$_3$ LDH from section 4.4.1. Such macrocycles and their N4-coordinated transition metal centers are well established active materials for the ORR [154,156,157]. Two different strategies of combining transition metal-N4 macrocycles with LDHs were applied. On the one hand, an attempt was made to introduce transition metal phthalocyanine sulfonates into the interlayer galleries of NiFe-NO$_3$ LDH by anion exchange similar to the previous SDS anion exchange, and on the other hand,
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coprecipitation of a LDH in the presence of the transition metal phthalocyanine sulfonate was applied, adapted from Halma et al. [297], in order to directly use the sulfonate as the charge balancing anion during LDH synthesis.

Figure 56. Schematic representation of the two different procedures for incorporation of TM-N4 in NiFe LDH and the corresponding XRD patterns.

XRD analysis revealed a change of the (003) reflection for all samples (Figure 56). The (003) reflection appeared at lower 2θ angles with respect to the (003) reflection of pristine NiFe-NO₃ LDH, for all samples, indicating a larger basal spacing and thus a modification of the interlayer anion. For the samples prepared by the classical anion exchange reaction, the shift for NiFe LDH modified with cobalt phthalocyanine sulfonate (NiFe-CoN₄ LDH_{ae}) and nickel phthalocyanine sulfonate (NiFe-NiN₄ LDH_{ae}) was from 9.66 ° to 7.88 ° and 8.36 °, respectively. Preparation of the new LDH by coprecipitation led to the appearance of the (003) reflection at 7.64 ° and 7.61 ° for NiFe-NiN₄ LDH_{cp} and NiFe-CoN₄ LDH_{cp}, respectively. The differences in the 2θ angle of the (003) reflection are not surprising, since the TM-N4 macrocycles can arrange in different orientations inside the interlayer galleries [297]. However, for all samples
shoulders at the peak of the (003) reflection indicate partial presence of NiFe-NO₃ LDH remaining in the sample. It is worth to point out that anion replacement by carbonate impurities would have shifted the (003) reflection to higher 2θ angles compared to the nitrate [106]. Rotating disk electrode voltammetry revealed substantial differences between the pristine LDHs with N4 macrocycles in the interlayer galleries and their calcined counterparts (Figure 57). The potentials at -1 mA cm⁻² and 10 mA cm⁻² and the corresponding E_{OER}-E_{ORR} potential differences are summarized in Table 2. For all four LDHs, the calcined BA-a composite materials showed the highest OER activity. Furthermore, at least the calcination step enhanced the ORR activity for the new LDHs, except for NiFe-CoN4 LDH_{ae} for which the pristine material showed the highest ORR activity. In this particular case, a calcination step rather than pyrolysis was chosen to preserve the LDH specific memory effect and its ability of restructuring to a highly active OER layered material, which is lost after pyrolysis in inert atmosphere. However, the lowest roundtrip overpotential of 0.93 V obtained for a calcined BA-a and NiFe-NiN4 LDH_{ae} composite is comparatively high with respect to the state of the art bifunctional oxygen catalysts, thus necessitating further development of the TM-N4 macrocycle and LDH composites for bifunctional oxygen electrocatalysis.

**Figure 57.** LSVs/CVs of pristine, calcined and composite films of of NiFe-Ni4N LDH_{ae} with BA-a (a), NiFe-NiN4 LDH_{cp} (b), NiFe-CoN4 LDH_{ae} (c) and NiFe-CoN4 LDH_{cp} (d) (O₂-saturated 0.1 M KOH, 1600 rpm, 5 mV s⁻¹).
Nevertheless, it was shown that active bifunctional oxygen electrocatalysts could be realized and might be improved by systematic studies of various parameters, especially the starting LDH, the BO, LDH to BO ratio, thermal treatment (particularly the atmosphere, temperature and duration), and the transition metal of the N4 macrocycle. The difficulty might be to preserve the LDH’s memory effect upon calcination, while the calcination leads to oxidized and hence less active ORR transition metal centers of the TMN4 macrocycle. A possibility to overcome this problem could be to use the well-structured LDHs as precursors for highly active OER spinel type catalysts derived by pyrolysis. Pyrolysis conditions, i.e. the inert atmosphere, facilitate the formation of the highly active ORR N4 coordinated transition metal active sites, possibly leading to more active bifunctional oxygen electrocatalysts with a low roundtrip overpotential.

Table 2. Summary of the potential vs. RHE at -1 and 10 mA cm\(^{-2}\) and its difference (p = pristine; cal = calcined; comp = BA-a composite calcined; ae = anion exchange; cp = coprecipitated).

<table>
<thead>
<tr>
<th>Catalyst Type</th>
<th>(E_{\text{RHE}}) -1 mA cm(^{-2}) (V)</th>
<th>(E_{\text{RHE}}) 10 mA cm(^{-2}) (V)</th>
<th>(\Delta E_{(-1)-10\text{mA cm}^{-2}}) (V)</th>
</tr>
</thead>
<tbody>
<tr>
<td>NiFe-NiN4 LDHae (p)</td>
<td>0.56</td>
<td>1.66</td>
<td>1.10</td>
</tr>
<tr>
<td>NiFe-NiN4 LDHae (cal)</td>
<td>0.73</td>
<td>---</td>
<td>---</td>
</tr>
<tr>
<td>NiFe-NiN4 LDHae (comp)</td>
<td>0.71</td>
<td>1.64</td>
<td>0.93</td>
</tr>
<tr>
<td>NiFe-NiN4 LDHcp (p)</td>
<td>0.60</td>
<td>1.72</td>
<td>1.12</td>
</tr>
<tr>
<td>NiFe-NiN4 LDHcp (cal)</td>
<td>0.72</td>
<td>---</td>
<td>---</td>
</tr>
<tr>
<td>NiFe-NiN4 LDHcp (comp)</td>
<td>0.70</td>
<td>1.67</td>
<td>0.97</td>
</tr>
<tr>
<td>NiFe-CoN4 LDHae (p)</td>
<td>0.59</td>
<td>1.68</td>
<td>1.09</td>
</tr>
<tr>
<td>NiFe-CoN4 LDHae (cal)</td>
<td>0.53</td>
<td>1.61</td>
<td>1.08</td>
</tr>
<tr>
<td>NiFe-CoN4 LDHae (comp)</td>
<td>0.64</td>
<td>1.61</td>
<td>0.97</td>
</tr>
<tr>
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<tr>
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<td>1.84</td>
<td>1.13</td>
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<tr>
<td>NiFe-CoN4 LDHcp (comp)</td>
<td>0.71</td>
<td>1.72</td>
<td>1.01</td>
</tr>
</tbody>
</table>
4.5 Self-assembling and self-healing electrocatalyst films


Typically, already modified electrodes are used for their application in electrochemical measurements or utilization. Electrocatalytically active films on electrode surfaces often have to be thin to maintain a good electrical conductivity. This thin film methodology leads to low catalyst loadings per area and, more importantly, per electrolyte volume. Catalyst particles detached from the surface immediately spread into the bulk of the electrolyte. Loss of the catalyst directly results in a change in the catalytic activity of the prepared electrode. There are two general approaches of preparing catalyst films. The catalyst can directly be grown on a current collector by electroless [238], electrochemical [229,298], or vapor deposition methods [299,300]. Alternatively, a pre-synthesized catalyst nanopowder can be immobilized on a current collector [107,301]. The deposition methods may result in more stable catalyst films, however, immobilization allows for exploring an immense number of powders of tunable properties, particle sizes and shapes. Unfortunately, it is still highly challenging to securely immobilize catalyst powders, e.g. nanoparticles, to form appreciably stable gas-evolving electrodes.

From the electrochemistry of single nanoparticle collision events, it is known that the interaction between particles suspended in solution and the electrode can follow two types of behavior, namely hit-and-run (elastic impact) and hit-and-stay (inelastic impact) [302]. The former phenomenon is the basis of emergent electrochemical devices such as semi-solid flow batteries and electrochemical flow capacitors [303,304], while the latter offers the possibility of modifying electrode surfaces. Liu et al. [305] made use of the hit-and-stay behavior to immobilize nanoparticles from a suspension onto a transparent electrode for electrochromic applications. It was envisioned that the hit-and-stay phenomenon could be exploited to immobilize catalyst particles suspended in an electrolyte onto an electrode to form stable catalyst films with self-healing capability.
4.5.1 Proof of concept for alkaline water splitting

The aforementioned concept was exploited by adding catalyst particles into the electrolyte reservoir(s) of a running electrolyzer (section 6.4.3). The electrolysis cell can briefly be described as anode and cathode compartments separated by a flow channel/membrane/flow channel non-zero gap assembly and the electrolyte being pumped through the cell in two independent electrolyte circuits. Ni foil was chosen as the model current collector for both the cathode and anode because of the use of Ni based electrodes in commercial alkaline water electrolyzers [221]. The formation of self-assembling catalyst films was separately evaluated for four highly active catalyst powders: NiFe LDH [77] and CoMn LDH [102] for the anode, and Ni₅B [47,48] and CoₓP [49] for the cathode.

![Figure 58. Electrochemical and visual evidence of the formation of self-assembled catalyst films. Drop in the cell voltage ($U_{cell}$) observed in a Ni//Ni electrolyzer operating at 50 mA cm⁻² after addition of a catalyst powder into the electrolyte (3 M KOH) for (a) NiFe LDH, (b) CoMn LDH, (c) Ni₅B, and (d) CoₓP. The insets in the graphs are photographs of the corresponding electrode after disassembling of the electrolyzer. Concentration of the catalyst was ca. 1.3 mg mL⁻¹.](image-url)
The successful formation of catalyst films was confirmed by a drop in cell voltage immediately after addition of the catalyst particles into the electrolyte reservoir, and *ex-situ*, by visual inspection and microscopic characterization of the electrodes after disassembling the electrolyzer ([Figure 58](#)). Optical images obviously show the formation of a particle film on the electrodes along the area of the electrolyte flow channel. The average voltage drops for NiFe LDH, CoMn LDH, Ni\(_x\)B and Co\(_x\)P were 446 mV, 270 mV, 135 mV and 515 mV, respectively ([Figure 60b](#)). It should be noted that a constant catalyst concentration in the suspension of 1.3 mg mL\(^{-1}\) was used in this work. Interestingly, higher concentrations, e.g. 2.6 mg mL\(^{-1}\), did not result in improved performance as no further drop in cell voltage was observed ([Figure 59](#)). However, the steady cell voltage was reached in a shorter time for higher particle concentrations, which indicates faster formation of the self-assembling catalyst film.

![Figure 59](#) Evolution of the cell voltage with time after addition of 1.3 mg mL\(^{-1}\) and 2.67 mg mL\(^{-1}\) of NiFe LDH into the anolyte (3 M KOH) of a Ni//Ni alkaline electrolyzer (I\(_{appl.}\) = 50 mA cm\(^{-2}\)).

In the study of single nanoparticle collision events, the surface charge was suggested to play an important role on the nature of interaction between suspended particles and the electrode [306]. In this study, the surface charge of the tested materials was determined by zeta potential measurements, which revealed that in the used electrolyte (3 M KOH), the surfaces of NiFe LDH and CoMn LDH were negatively charged ([Figure 60a](#)), which seems to be surprising because of the net positive charge at the hydroxide layers due to partial exchange of divalent metal cations by trivalent ones. However, at highly alkaline pH values such as in 3 M KOH in this case, the omnipresent hydroxyl ions screen the net positive charge of the metal ion layers. Additionally, deprotonation of surface hydroxide groups of the LDH takes place, producing a
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negative zeta potential [307]. The surfaces of Ni$_x$B and Co$_x$P were positively charged (Figure 60a). Considering that under polarization, the surface of the anode is positively charged while that of the cathode is negatively charged with respect to the potential of zero charge of the electrode (+80 mV vs. Ag/AgCl/3 M KCl in the case of a Ni electrode in alkaline media [308,309]), the immobilization of NiFe LDH and CoMn LDH on the anode as well as Ni$_x$B and Co$_x$P on the cathode and the associated drop in cell voltage (Figure 58) can be explained on the basis of electrostatic interaction between the particles and the respective electrodes upon statistical intimate contact. The mechanism for the formation of self-assembled catalyst films is illustrated in Figure 60c.

Figure 60. Electrostatic nature of the formation of self-assembling catalyst films: (a) Zeta potential of NiFe LDH, CoMn LDH, Ni$_x$B and Co$_x$P in 3 M KOH (N = 3 for each one). (b) Drop in the cell voltage after addition of NiFe LDH (anode), CoMn LDH (anode), Ni$_x$B (cathode) and Co$_x$P (cathode) into the electrolyte (3 M KOH) (N = 3 for each one). The applied current density and final concentration of the catalyst were 50 mA cm$^{-2}$ and ca. 1.3 mg mL$^{-1}$, respectively. (c) Schematic representation of an alkaline electrolyzer with self-assembled catalyst films in the presence of suspended catalysts in the electrolyte.

To explore this hypothesis, Ni$_x$B an extremely active catalyst for HER and OER [47,48] was added to the catholyte and anolyte compartments. A clear drop in cell voltage was only observed when Ni$_x$B was added to the catholyte (Figure 58c), whereas no change in cell voltage was observed when Ni$_x$B was added to the anolyte (Figure 61). A dense particle film was observed on the cathode after disassembling of the electrolyzer while no film formation was observed on the anode. These results support an electrostatic interaction between charged particles and an
oppositely charged electrode surface as driving force for the formation of the film. The self-assembled film formation also requires an intimate contact between particle and electrode surface. Electrophoretic movement of the particle towards the electrode can be excluded as possibility at the applied voltage due to the very short Debye length in electrolytes with high ionic strength. The Debye length of the particles in a monovalent aqueous electrolyte at room temperature, 3 M KOH in this case, can be calculated according to equation 35 [310].

$$\kappa^{-1} = \frac{0.304}{\sqrt{I}}$$

With $\kappa^{-1}$ being the Debye length in nm and $I$ the ionic strength in mol L$^{-1}$.

Thus, a Debye length of 0.157 nm was calculated, which reveals that particles cannot be attracted just by applying a potential without any further forced migration. Further investigation and discussion about the film formation mechanism is given in section 4.5.3.

![Figure 61. Evolution of the cell voltage with time for a Ni//Ni electrolyzer at 50 mA cm$^{-2}$. Two additions of Ni$_x$B in the anolyte reservoir are indicated with arrows.](image)

**4.5.2 Characterization of the self-assembled films**

Electrodes modified using the described approach showed the obvious formation of a film along the area defined by the electrolyte flow channel (Figure 58). SEM images further confirmed the formation of catalyst films (Figure 62). Cross-section SEM images showed that the films were composed of aggregates of particles and had a thickness of several micrometers.
electrochemical activity of the deposited films towards either the HER or the OER was investigated in a three-electrode configuration. Linear sweep voltammetry revealed a higher activity for NiFe LDH and CoMn LDH for the OER and for Ni$_x$B and Co$_x$P towards the HER with respect to an unmodified nickel electrode (Figure 63a&b). Hence the LSVs were in good accordance with the trend given by the electrolyzer in terms of activity of the different catalysts for their specific reactions. The activity of the different catalyst films was in accordance with the trend observed in the electrolyzers: activity of NiFe LDH > CoMn LDH > Ni and Co$_x$P > Ni$_x$B > Ni. Hence, the films deposited on the electrolyzer current collectors are shown to be catalytically active, although they are not in contact with the particle suspension during LSV characterization.

![Image of SEM images](image)

**Figure 62.** SEM images of the various catalyst films formed by the self-assembling process. Cross-section SEM micrographs of (a) NiFe LDH (anode), (b) CoMn LDH (anode), (c) Ni$_x$B (cathode) and (d) Co$_x$P (cathode) films on Ni current collectors.
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Direct comparison between the results obtained with the electrolyzer and LSV measurements reveal slight differences between absolute voltage and potential, which are attributed to the methodology. The electrolyzer measurements were performed with a flowing electrolyte, while the LSVs were carried out under static conditions in a small volume cell. In any case, the discrepancies were only minor and the voltage drop in the electrolyzer and overpotential in LSV measurements followed the same trend. After the LSV measurements, a change in the film became obvious. Since the particle/electrode interaction is based on electrostatics the tremendous bubble departure appeared to have detached particles from the electrode (Figure 63c-f). The weak adhesion of the films confirmed electrostatics as attracting interaction rather than covalent electrochemical modification of the electrode.

![Graphs and photographs](image)

**Figure 63.** Linear sweep voltammograms (3 M KOH, 5 mV s⁻¹, surface area of 0.126 cm²) for (a) OER and (b) HER of electrodes modified with catalyst films that were prepared using the electrolyzer. (Blue) bare Ni foil, (black) NiFe LDH@Ni, (red) CoMn LDH@Ni, (green) NiₓB@Ni and (pink) CoₓP@Ni. Photographs of the self-assembled NiFe LDH and NiₓB films before and after LSV measurements. Red circles indicate the area where the electrochemical cell was placed for LSV.
The successful deposition of the different highly active OER and HER catalysts on the Ni anode and Ni cathode, respectively, by electrostatic interactions was additionally confirmed by XPS (Figure 64). For Ni cathodes the deposition of Ni$_x$B and Co$_x$P was also studied by XPS. The confirmation of the successful deposition of Ni$_x$B, which in its as prepared form consists of metallic and partially oxidized Ni [48], by means of XPS is rather difficult (Figure 64a) and can only be assumed by comparing the peak shapes of the Ni 2p region spectra (Figure 64c). The deposition of Co for the Co$_x$P was clearly observed by XPS (Figure 64b&d). Interestingly, no Ni signal was detectable for the Co$_x$P modified Ni foil suggesting that a thick compact film was formed during electrolysis, which is consistent with the SEM micrographs (Figure 62d). Due to spontaneous surface oxidation, the initial metallic character of Co$_x$P had only weak signals in the as prepared sample while it was not observable at all after electrolysis.

![Figure 64](image.png)

**Figure 64.** XP survey spectra of deposited and as prepared Ni$_x$B (a) and Co$_x$P (b). High resolution Ni 2p spectra of bare Ni foil, Ni(OH)$_2$ as reference, deposited and as prepared Ni$_x$B (c). High resolution Co 2p spectra of deposited and as prepared Co$_x$P (d).

For the Ni foil anode modified by CoMn LDH (Figure 65b), both the Co signal originating from the CoMn LDH OER catalyst and the Ni 2p signal from the Ni foil were still detectable.
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Figure 65. XP survey spectra of deposited and as prepared NiFe LDH (a) and CoMn LDH (b). High resolution Ni 2p spectra of Ni(OH)$_2$ as reference and deposited NiFe LDH (c). High resolution spectra Co 2p of deposited and as prepared CoMn LDH (d). High resolution Fe 2p spectra of Fe$_2$O$_3$ as reference and deposited NiFe LDH (e). High resolution Fe 3p spectra of Fe$_2$O$_3$ and Ni(OH)$_2$ as reference and deposited and as prepared NiFe LDH (f).

Interestingly, Mn was not detected in the CoMn LDH modified Ni anode in contrast to the CoMn LDH reference material. Furthermore, the characteristic peak shape of Co 2p core level region spectra (Figure 65d) suggesting that mainly Co$^{2+}$ was present in the as-prepared the CoMn LDH changed significantly. While the peak position of the main component barely changed, the absence of the satellite feature in the CoMn LDH modified Ni anode indicates the presence of Co$^{3+}$ as in Co$_3$O$_4$ [246,311]. Similarly, the deposition of NiFe LDH on Ni foil
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Anodes was confirmed by XPS. From the XPS survey spectra (Figure 65a) the characteristic signal of Fe 2p was clearly observed. High resolution Fe 2p region spectra confirm that Fe was mainly present as Fe$^{3+}$ as in Fe$_2$O$_3$. In contrast to the CoMn LDH OER catalysts, no changes in the oxidation states of Ni (Figure 65c) and Fe (Figure 65e) were detected after the immobilization, though Fe 3p (Figure 65f) was more intense after deposition of NiFe LDH on the Ni foil anode. The increase in signal intensity suggests a restructuring of the NiFe LDH and an exchange of intercalated NO$_3^-$ by OH$^-$ and CO$_3^{2-}$, which is known to occur in alkaline electrolyte [106]. Thus, surface modification was confirmed by XPS for both OER and both HER catalysts.

4.5.3 Mechanism of the formation of self-assembling catalyst films

The mechanism for the formation of self-assembled catalyst films is proposed to be governed by electrostatic interaction between the surface of the current collector and the suspended particles, which is schematically illustrated in Figure 66 for a cathode catalyst film. Particles with positively charged surfaces come in contact with the negatively polarized (vs. pzc$_{\text{Ni}}$) cathode by forced migration (Figure 66a), and electrostatic attraction between the oppositely charged elements leads to particle adhesion. Upon contact between electrode and particle, the particle adapts the electrode potential and, thus, polarization (Figure 66b). Since the immobilized particle changes its polarization, other suspended particles are not repelled and further immobilization of suspended particles may take place (Figure 66c). Immobilization of several particles leads to the formation of insoluble particle agglomerates bestowing higher stability to the particle film (Figure 66d). According to DLVO theory, the high ionic strength of the electrolyte resulting in short Debye-length favors the formation of particle agglomerates due to reduction of the inter-particle repulsion. However, aggregates in the solution phase are continuously broken down by the induced forced convection (stirring and pumping through the tubes). The surface charge of the electrode is dependent on the applied polarization with respect to its potential of zero charge. The potential of zero charge of Ni electrodes (pzc$_{\text{Ni}}$) in alkaline media was reported to be $+80$ mV vs. Ag/AgCl/3 M KCl [308,309]. Therefore, the surface of Ni is positively charged when the electrode is polarized at potentials higher than $+80$ mV vs. Ag/AgCl/3 M KCl and vice versa. As a consequence, the anode and cathode are positively and negatively charged, respectively, during electrolysis. The surface charge of suspended particles can be determined by measuring the zeta potential. Zeta potential values of $-26.3 \pm 3.5$ mV (NiFe LDH), $-55 \pm 4.5$ mV (CoMn LDH), $+104.3 \pm 3.1$ mV (Ni$_x$B) and $+110.7 \pm 3.8$ mV (Co$_x$P) were obtained in 3 M KOH (Figure 60a).
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Fig. 66. Schematic representation of the catalyst film formation starting with single particle collisions induced by forced convection under non-ideal laminar flow leading to the formation of insoluble particle agglomerates which bestow higher stability to the film.

According to the proposed immobilization mechanism, the polarization of the electrode with respect to its potential of zero charge (pzc) enables tuning the surface from positively to negatively charged and vice versa. As a result, the immobilization of particles with positively or negatively charged surfaces can be controlled, to a certain extent, by the applied electrode potential. Bearing in mind that pzc$_{\text{Ni}}$ is +80 mV vs. Ag/AgCl/3 M KCl the mechanism of the self-assembled film formation was investigated in a bulk electrochemical cell with a three electrode configuration (section 6.4.2.6) at a constant potential of ±200 mV vs. pzc$_{\text{Ni}}$, i.e. -0.120 V and +0.280 V vs. Ag/AgCl/3 M KCl for materials with positive (Ni$_x$B and Co$_x$P) and negative (NiFe LDH and CoMn LDH) zeta potential, respectively. After applying the immobilization potential for 60 min, during which no Faraday current was observed (Fig. 67) and thoroughly rinsing of the electrodes with water, visual inspection of the electrodes revealed the formation of films which covered the entire area immersed in the suspension (Fig. 68a&b).

LSVs of the electrodes modified with the self-assembled catalyst films revealed a substantially higher activity towards the OER and HER with respect to a bare nickel electrode (Fig. 68). NiFe LDH deposited at room temperature in 3 M KOH decreased the overpotential necessary to achieve a current density of 10 mA cm$^{-2}$ by around 150 mV compared to a bare nickel electrode (Fig. 68a). CoMn LDH reduced the overpotential for the OER by around 110 mV. The overpotential necessary to drive the HER at 10 mA cm$^{-2}$ was lowered by around 100 mV and 120 mV by the depositions of both Ni$_x$B and Co$_x$P, respectively, compared to a bare nickel electrode (Fig. 68b).
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Figure 67. Current transients ($I$ vs. $t$) of the chronoamperometric electrostatic deposition of NiFe LDH, CoMn LDH, Ni, $B$ and Co, $P$ on Ni foil at -0.120 V and +0.280 V vs. Ag/AgCl/3 M KCl for cathode and anode, respectively. The particle concentration was 1.3 mg mL$^{-1}$ in 3 M KOH for each catalyst. The solution was continuously stirred with a magnetic stirrer during deposition.

The formation of self-assembling catalyst films was further demonstrated to occur at higher temperature in an electrolyte with higher ionic strength, since these conditions are closer to the envisaged technical application of water electrolysis and might influence the electrostatic interaction. Immobilization was carried out exemplarily for one catalyst for each reaction under the aforementioned conditions with the only difference that the ionic strength and temperature of the electrolyte were increased to 5 M KOH and 60 °C, respectively. After the immobilization step in 5 M KOH at 60 °C, the formation of a catalyst film was evident by direct visual inspection of the electrodes (Figure 68c&d). Besides visual inspection, the electrochemical activities towards HER and OER of the deposited films were investigated. NiFe LDH deposited at 60 °C in 5 M KOH decreased the overpotential necessary to achieve a current density of 10 mA cm$^{-2}$ by around 110 mV (Figure 68c) compared to a bare nickel electrode. The Ni,B film, prepared at 60°C in 5 M KOH, decreased the overpotential necessary to drive the HER at 10 mA cm$^{-2}$ by 120 mV (Figure 68d) compared to a bare nickel electrode.

The trends in activity for the OER and HER clearly follow the same as observed for the self-assembled films in the electrolyzer cell and their three electrode LSV response. Evidently, the mechanism of the formation of self-assembled films is solely based on electrostatic interaction of the particles upon evoked intimate contact with the oppositely polarized electrode by forced migration.
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4.5.4 Operation of a self-assembled catalyst film based electrolyzer

The proof-of-concept for an electrolyzer based on the formation of self-assembling catalyst films was demonstrated using NiFe LDH and Ni,B as catalysts for OER and HER, respectively. A home-made, non-zero gap alkaline electrolyzer operating at room-temperature using Ni foil electrodes for both anode and cathode was employed as a model system. Catalyst powders were directly added to the electrolyte reservoirs during operation of the electrolyzer. Figure 69a shows the evolution of the cell voltage ($U_{\text{cell}}$) over 22 days. $U_{\text{cell}}$ dropped by 450 mV and 120 mV, respectively, as marked in Figure 69a as I and II, upon the addition of NiFe LDH and
Ni$_x$B powders to the anolyte and catholyte compartment, respectively. After the addition of both catalysts, $U_{\text{cell}}$ reached a steady value of 2.0 V which was maintained for over five days. The small fluctuations in $U_{\text{cell}}$ were due to changes in the pH value of the catholyte, which was manually controlled only during the day without maintenance overnight.

The presence of particles in the electrolyte after formation of the catalyst film was speculated to induce a self-healing process. Mark III in Figure 69a indicates the moment when the electrolyte suspensions in both the anodic and cathodic compartments were replaced by fresh particle-free electrolyte. $U_{\text{cell}}$ increased immediately by about 70 mV and kept increasing slowly with a slope of 18 mV d$^{-1}$ over a period of 7 days (between mark III and VI in Figure 69a). Note that the electrolyte was periodically replaced over this period to remove particles released from the film. This confirmed that the presence of particles in the suspension induces a self-healing process. Certainly, when some particles detached, others that were suspended in the electrolyte immobilized were replacing the detached ones. On the other hand, the catalyst films were not washed away immediately in the absence of suspended particles. After operating in the absence of suspended particles for 7 days, catalyst powders were again added to the electrolyte reservoirs. Mark VI and VII indicate the drop in $U_{\text{cell}}$ associated with this second addition of NiFe LDH and Ni$_x$B (130 and 60 mV, respectively). This decrease in $U_{\text{cell}}$ confirmed the self-healing process that occurs in the presence of catalyst in the electrolyte. Figure 69c shows the differences in $U_{\text{cell}}$ in the presence and absence of suspended particles, underscoring the clear benefit of the presence of particles in the electrolyte ($U_{\text{cell}}$ in the absence of a catalyst film is also provided for comparison). In the last 7 days of the test, the current density was increased to 0.1 A cm$^{-2}$ in the presence of the catalyst particles and $U_{\text{cell}}$ remained about 2.25 V over the entire time. Overall, the electrolyzer operated for 22 days over which time the catalyst films remained active.

Notably, when the current was interrupted, which is to be expected for practical applications, $U_{\text{cell}}$ did not increase significantly (mark IV in Figure 69a and Figure 70), indicating that the catalyst films were not severely deteriorated. The current was interrupted ($I_{\text{appl.}} = 0$ mA) for short periods of time (15 min) during operation of a NiFe LDH@Ni//Ni$_x$B@Ni electrolyzer to evaluate the stability of the catalyst films during start/stop sequences. Figure 70 shows that the catalyst films remained stable even in the absence of particles suspended in the electrolyte since the cell voltage did not change significantly (indicated by the red line).
Figure 69. Operation of a self-assembled NiFe LDH@Ni//Ni,B@Ni electrolyzer. (a) Evolution of the cell voltage over time (3 M KOH, room temperature) at current densities of 50 mA cm\(^{-2}\) and 0.1 A cm\(^{-2}\) in the presence (yellow background) and absence (white background) of suspended catalyst particles. (b) Cell voltage of the self-assembled NiFe LDH@Ni//Ni,B@Ni electrolyzer at 50 mA cm\(^{-2}\) (black squares) and 0.1 A cm\(^{-2}\) (red triangles) over a period of several days. (c) Cell voltage in the presence (black circles) and absence (blue triangles) of suspended particles of a NiFe LDH @ Ni//Ni,B @ Ni self-assembled film alkaline electrolyzer (for comparison the cell voltage of a Ni//Ni alkaline electrolyzer is also shown (green squares) at 50 mA cm\(^{-2}\) over a period of several h. (d) Schematic representation of the different stages during the formation of a self-assembled catalyst film and the corresponding cell voltage. The concentration of catalyst powder in the suspension was ca. 1.3 mg mL\(^{-1}\).
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The different stages during formation of the self-assembled catalyst films are illustrated in Figure 69d. In stage 1, $U_{\text{cell}}$ is defined by the HER and OER activity of the initial Ni\textsubscript{anode}/Ni\textsubscript{cathode} electrolyzer at a constant current density. In stage 2, the catalyst powder is added into the electrolyte forming a suspension that is pumped through the cell. Driven by electrostatic interaction, catalyst particles from the suspension self-assemble on the electrode surface forming the catalyst film. $U_{\text{cell}}$ drops as the catalyst films are being formed (stage 2) until it reaches a steady state. In stage 3, $U_{\text{cell}}$ remains constant enabled by the self-healing process as long as a sufficient concentration of the catalyst particles is present in the electrolyte. When a particle detaches from the electrode surface, another one that is suspended in the electrolyte instantaneously replaces the detached one. Stage 4 occurs when the suspension is replaced by a catalyst-free electrolyte resulting in the catalyst film losing its self-healing feature. In this case, catalyst particles are slowly removed from the catalyst film leading to an increase in $U_{\text{cell}}$. As in stage 2, $U_{\text{cell}}$ decreases when the catalyst is again added to the electrolyte reaching a steady value which is maintained as long as a sufficient catalyst concentration is in the electrolyte (stage 3).

The stable performance exhibited over the three weeks test period allows to rule out any major corrosion issue. The theoretical corrosion rate of the anode current collector at the applied current density was calculated for different Faraday efficiencies revealing that the Faradaic efficiency of the anode was above 99.5 %. In a galvanostatic measurement as in the presented electrolyzer, the current originates from the most favorable electrochemical reaction. In the case of the anode, the oxidation of transition metals in the collector, nickel in this case, takes place.
at lower potentials than the OER (see Ni$^{2+}$/Ni$^{3+}$ oxidation in Figure 63a & Figure 68a). As a consequence, the corrosion of the current collector may simultaneously occur in parallel with OER during the electrolysis of water. The Faraday efficiency quantifies how much of the applied current goes to the oxidation of the current collector instead of oxygen evolution. Thus, the Faraday efficiency can help estimating the durability of an electrode. In the presented case, a 100 $\mu$m thick Ni foil was used as current collector. Metallic Ni can be oxidized to Ni$^{3+}$ under the oxidizing conditions at the anode. Using the Faraday constant (96485 C), molecular mass (58.69 g mol$^{-1}$) and density (8.91 g cm$^{-3}$) of Ni, it can be calculated that 1.22 mA h are necessary to oxidize a depth of 1 $\mu$m over an area of 1 cm$^2$ (1.22 (mA h)/(cm$^2$ $\mu$m)) assuming an oxidation from Ni$^0$ to Ni$^{3+}$ at the anodic potentials. Based on that the corrosion rate of the current collector at 50 mA cm$^{-2}$ for different Faraday efficiencies can be estimated (Figure 71). For a Faraday efficiency of 99.5 %, 0.25 mA cm$^{-2}$ out of 50 mA cm$^{-2}$ are consumed in the oxidation of the current collector leading to an oxidation rate of 4.88 h $\mu$m$^{-1}$. Therefore, the full depth of the current collector would be oxidized within 20 days. However, the presented measurement lasted for at least 22 days, which means that the Faraday efficiency is higher than 99.5 %. This value is not surprising since Ni current collectors are used in commercial electrolyzers due to the high corrosion resistance of Ni in alkaline media [221]. It should be noted that the oxidation of the catalyst itself (20 mg of NiFe LDH) takes place in 1 minute at 50 mA cm$^{-2}$ (net current of 200 mA).

![Figure 71. Theoretical corrosion rate of the anode Ni foil current collector at an applied current density of 50 mA cm$^{-2}$. The graph shows the corrosion depth over the time at which the current is applied. The vertical green lines indicate the time needed until the whole Ni foil (thickness = 100 $\mu$m) is corroded for Faradaic efficiencies of 98 %, 99 % and 99.5 %.

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The electrolyzer cell voltage can be further improved by employing a more active catalyst film for HER. A stable cell voltage of 2.05 V over 48 h was obtained at a current density of 0.1 A cm\(^{-2}\) when using NiFe LDH and Co\(_x\)P on the anode and cathode, respectively (Figure 72). This value represents an improvement of 200 mV and 750 mV versus NiFe LDH@Ni//Ni\(_x\)B@Ni and Ni//Ni electrolyzers, respectively. Since the proof-of-concept was demonstrated using a home-made non-zero gap electrolyzer operating at room temperature, further improvements are expected by optimizing the engineering of the system.

![Graph showing cell voltage over time](image)

**Figure 72.** Comparison of cell voltage in Ni//Ni electrolyzer (without suspension, orange), NiFe LDH @Ni//Ni\(_x\)B@Ni electrolyzer (in the presence of particles in the electrolyte, purple) and NiFe LDH @Ni//Co\(_x\)P@Ni electrolyzer (in the presence of particles in the electrolyte, black) operating at 0.1 A cm\(^{-2}\) at room temperature. The particle concentration in suspension was ca. 1.3 mg mL\(^{-1}\).

### 4.5.5 Overcoming cathode impurities in alkaline electrolysis

Nickel has been the state of the art electrode and catalytically active non-precious material for alkaline electrolysis since decades due to its acceptable catalytic activity and, especially, the lack of proper approaches to permanently fix catalytically active powder materials on current collector’s. However, among others the continuous decay of hydrogen evolution activity of especially nickel based cathodes represents a serious issue hampering a faster development and application of alkaline water electrolysis [31,32]. Four major reasons for the loss in hydrogen evolution activity are generally proposed [31,32]:
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i) The omnipresent high concentration of molecular hydrogen can lead to an absorption of hydrogen at the catalyst, in this specific case, in the nickel structure, hence changing the intrinsic HER activity.

ii) A loss of catalytically active material can lead to a reduced HER activity.

iii) The adsorption of organic molecules originating from possible membrane degradation onto the catalyst or current collector’s surface can reduce the initial HER activity with time.

iv) The deposition of metal cations, predominantly electrolyte impurities, can form catalytically less active surface coatings, hence decreasing the HER activity.

In this section, the intrinsic properties of self-assembling films are exploited to prevent the deactivation of cathodes by the formation of passivating layers on the HER active electrode. The feasibility of this approach is explored for the case of detrimental deposition of trace metal impurities. These impurities can originate from several sources, e.g. impurities in the commercial electrolyte salt (KOH) or corrosion products of cell parts which do not resist the highly corrosive environment, i.e. highly alkaline electrolyte and presence of molecular oxygen. The deposition of such impurities can either occur upon reduction of the ions to metallic species at the cathodic potentials, needed to produce hydrogen, or by simple precipitation of their salts, i.e. their hydroxides in alkaline electrolysis [11]. The former is determined by the redox potential of the dissolved ions and their corresponding metallic forms, while the latter is related to the solubility product constant of the metal ions and their salts.

The previously described formation of self-assembling and self-healing catalytically active films (section 4.5.1) was used to overcome cathode deactivation triggered by impurities. Trace metal impurities in solution, regardless the source, slowly deposit on the electrode surface due to either precipitation or electrochemical reduction, hence passivating the catalytically active sites and concomitantly increasing the cell voltage at the applied current density (Figure 73 I&II). The addition of catalytically active material in the electrolyte reservoir leads to the formation of a catalyst suspension as described in the sections 4.5.1 and 4.5.3. This newly formed and self-assembled catalyst film covers the deactivated electrode leading to a decrease of the cell voltage even below the initial one (Figure 73 III). Additionally, the self-healing capabilities, demonstrated in section 4.5.4, of the self-assembled film would ensure no further deactivation by continuous renewal of the catalytically active layer.
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Figure 73. Schematic representation of the cathode deactivation due to deposition of trace metal impurities and the corresponding change in the overall cell voltage of the electrolysis cell. I) Bare nickel cathode electrolyte impurities. Slow deposition of impurities on the cathode leads to an increase in cell voltage. II) Inactive material covers electrode surface area reducing the active surface area. III) Addition of catalyst particles to the electrolyte. A self-assembling and self-healing catalyst film forms and covers the inactive layer with a catalytic layer which results in a decrease in cell voltage below the initial value.

Zinc was chosen as model impurity to demonstrate the proof of concept for the inhibition of cathode deactivation by means of self-assembling films. Zinc impurities can originate from different sources. Degradation of any plastics, e.g. tubing or gaskets, can release zinc ions since zinc is heavily used in plasticizers of almost every industrially relevant plastics [312]. Zinc can also be present in the salt (KOH) employed to prepare the electrolyte solution [11] and zinc is one of the main components of brass which may be present in some elements of the system due to its low cost. Thus, it is considered to be a highly interesting model element.

A Ni//Ni electrolyzer was assembled as described in section 4.5.1 & section 6.4.3 and a current density of 50 mA cm$^{-2}$ was applied. The cell voltage at the applied current density reached a steady value at around 2.6 V (Figure 74 green triangles). Controlled amounts of Zn were directly added to the electrolyte to accelerate the cathode deactivation. Addition of Zn (0.067 mg mL$^{-1}$) to the catholyte (3 M KOH) resulted in a sharp increase of the cell voltage until a steady cell voltage of around 3.1 V was reached and kept constant for at least 6 h (Figure 74 grey rectangles).
4 Results and discussion

4.5 Self-assembling and self-healing electrocatalyst films

Figure 74. Cell voltage vs time transients of Ni//Ni electrolyzer with and without Zn contamination and Ni,B.

Post-mortem analysis of the deactivated Ni cathode by means of SEM and XPS revealed clear evidence of the formation of a Zn layer. The initially smooth surface of the Ni cathode was covered by dendrite-shaped structures (Figure 75a&b). XPS analysis of the dendrite modified Ni cathode showed that the covering layer consisted of Zn (Figure 75d). The Ni2p peaks which were clearly visible for the bare Ni foil at binding energies of 852.3 and 896.5 eV, indicating metallic Ni species, disappeared for the cathode used in the electrolyzer in the presence of zinc indicating the formation of a relatively thick and dense layer on the Ni electrode. Zn signals at binding energies of 1021.2 and 1044.4 eV dominated the XP spectrum revealing the deposition of metallic Zn. Figure 63a shows that the HER (@ 50 mA cm⁻²) at Ni electrodes occurs at -1.55 V (vs. Ag/AgCl/3 M KCl). Considering that the standard potential for the reduction of zincates in solution to metallic Zn is -1.43 V (vs. Ag/AgCl/3 M KCl) [313], electrodeposition of Zn should take place at the necessary potential of -1.55 V (vs. Ag/AgCl/3 M KCl). After deactivation of the cathode by the electrodeposited Zn, the Ni,B catalyst for HER was added to the catholyte. The addition of Ni,B resulted in an instantaneous voltage drop of ca. 0.7 V, reaching a stable cell voltage below 2.4 V at an applied current density of 50 mA cm⁻² (Figure 74 red triangles). This value was not only lower than that of Ni//Ni in the absence of impurities, but also lower than that of the Ni//Ni,B @ Ni electrolyzer without zinc layer (Figure 74 yellow rectangles), which is attributed to the increased surface area. The deposited Zn dendrites roughen the electrode surface leading to an increase in the surface area on which the Ni,B catalyst can be immobilized. The voltage difference of 200 mV between Ni/Ni and Ni//Ni,B @ Ni originates from a lower overpotential of 200 mV for HER. As a consequence, the necessary...
potential for HER should be above that of the reduction of zincates preventing rather cathode deactivation. SEM analysis of the cathode after the subsequent additions of impurities and NiₓB revealed a change in the surface morphology. The dendrite shaped surface observed after the addition of Zn led to a particulated morphology after the subsequent addition of NiₓB. 

Figure 75c).

![SEM micrographs of electrolyzer cathodes; a) bare Ni foil cathode; b) Ni foil cathode covered with Zn; c) NiₓB film formed on Zn covered Ni foil cathode; d) XPS survey spectra of the electrodes of a), b) and c).]

XPS analysis showed that a film of NiₓB was formed on the Zn covered Ni electrode. The Zn signals at binding energies of 1021.2 and 1044.4 eV that dominated the spectrum before the addition of NiₓB were not detectable in this spectrum. Instead, the XP spectrum displayed strong signals from Ni in an oxidized form at binding energies of 855.2 and 872.4 eV and a weak B signal at 191.4 eV (Figure 75d). The oxidized state of the elements presumably arised
from surface oxidation of the very oxygen sensitive metal boride species under storage at atmospheric conditions prior to XPS analysis. Thus, XPS confirmed that the particulated film formed on the Zn covered electrode consisted of Ni$_x$B particles.

As case study of the capability of self-assembling films to prevent deactivation of the cathode by electrolyte impurities, we evaluated the performance of an electrolyzer which contained cheap Viton gaskets instead of highly stable PTFE gaskets [314] used in the previous section. Viton is a highly chemical resistant fluoropolymer elastomer that is widely used as gasket material [315]. A Ni/Ni electrolyzer using Viton gaskets was operated in 3 M KOH at a current density of 50 mA cm$^{-2}$. The cell voltage reached a steady value of 3.2 V, which was close to the cell voltage of the the intentionally poisoned Ni//Zn @ Ni electrolyzer (Figure 76a). Post-mortem XPS analysis after disassembly of the electrolyzer cell revealed the presence of a covering layer of Zn, which is indicated by the dominant Zn signals at binding energies of 1022.4 and 1046 eV (Figure 76b). Furthermore, optical inspection of the used gaskets especially of the anode compartment showed a change of the material upon exposure to the harsh conditions. The former soft and flexible gaskets became harder and brittle, suggesting a loss of plasticizers. Although the electrolyte circuits were separated, the dissolved zinc species presumably crossed the anion exchange membrane as zincates ([Zn(OH)$_4$]$^{2-}$) [316] to the cathode side, where zinc deposited on the cathode. In addition, release of Zn from the Viton gaskets of the cathodic compartment cannot be ruled out. Thus, the presence of impurities released from the gaskets caused an increase of the cell voltage of the model Ni//Ni electrolyzer of 0.6 V (compared to the PTFE sealed electrolyzer) at the applied current density (Figure 76a). The addition of Ni$_x$B to the catholyte led to the formation of a particle suspension, which was pumped through the cathode compartment. The cell voltage significantly dropped after the addition of Ni$_x$B until it reached a steady value at around 2.45 V, which was a similar value to that of a Ni//Ni$_x$B @ Ni electrolyzer in the absence of zinc impurities (Figure 76a). Optical inspection directly after disassembly of the electrolyzer confirmed the formation of a film as already shown in section 4.5.1. The morphology of the cathodes of electrolyzers that used Viton gaskets (Figure 76c-e) resembles that of the electrodes obtained by direct addition of Zn in the electrolyte (Figure 75a-c). The case study of Zn impurities exemplifies the potential of the self-assembling and self-healing film formation approach not only as a powerful tool to attain stable catalytically active films on electrode surfaces without pre-electrolysis electrode modification, but also as an effective strategy to prevent the deactivation of the cathode by electrolyte impurities during alkaline water splitting.
4.5 Self-assembling and self-healing electrocatalyst films

Figure 76. a) Evolution of the cell voltage with time for a Ni//Ni electrolyzer in the absence and in the presence of Zn impurities and Ni$_x$B. b) XPS survey spectra of the electrodes of c), d) and e); SEM micrographs of electrolyzer cathodes. c) Bare Ni foil cathode. d) Ni foil cathode covered with Zn. e) Ni$_x$B self-assembled film on the Zn-covered Ni foil cathode.
5 Conclusion

Enormous research effort is currently directed toward the development of highly active electrocatalytic materials with the aim of promoting the advancement of electrochemical water splitting. A large number of the newly developed electrocatalysts are available in the form of nanopowders. Thus, approaches for tight fixation of such powders on electrode surfaces to ensure their long term operation under industrial conditions are crucially needed. Novel methodologies for preparation of highly stable catalyst powder/electrode assemblies were developed and presented in this work.

Polybenzoxazines were for the first time employed as precursors for a carbon-matrix based catalyst fixation. Conventionally used organic polymeric binders, e.g. Nafion, embed the catalytically active particles in an insulating environment, thus necessitating the addition of conductive additives, which are commonly carbon based. The intrinsic unique properties of pBO networks, i.e. the near-zero volumetric shrinkage upon polymerization and the high residual char yield after carbonization, allowed the direct conversion of the organic and hence insulating binder matrix into a conductive carbon matrix. Prussian blue analogues (PBA) were successfully used as catalyst precursor. The actual catalyst was formed during pyrolysis of the pBO matrix with embedded PBA particles. Screening of various PBA unveiled a MnCo based PBA to be the most interesting in terms of OER activity. This specific PBA was thoroughly investigated for structural characteristics of the formed electrode coating and the influence of the PBA to BO monomer ratio during electrode preparation. BO monomers were deposited together with the PBA $K_m\text{Mn}_n[\text{Co(CN)}_6]_y \times n\text{H}_2\text{O}$ on an electrode surface followed by temperature-induced polymerisation, leading to the formation of a homogeneous polymer/PBA composite film, which upon subsequent pyrolysis formed a N-doped carbon matrix embedding catalytically active Mn$_x$Co$_y$O$_z$ nanocubes. The pBO content showed a significant impact on the catalytic activity. The as-prepared catalyst films had to be cycled in order to remove inactive carbon coverage and to expose catalytically active sites to the electrolyte. A Ni foam electrode modified with the composite material showed high stability under OER conditions.

The formation of N-doped carbon upon pBO pyrolysis was further explored for preparation of bifunctional oxygen electrocatalysts. By pyrolysis of Co/Co$_x$B and Co/Co$_x$P pBO composites directly on an electrode surface a conducting and stable N-doped carbon matrix was formed with the catalyst particles embedded in it. The prepared materials were investigated for their electrochemical activity towards the ORR, the OER, and as bifunctional OER/ORR catalysts. Co/Co$_x$B/NC and Co/Co$_x$P/NC showed good performance for both reactions preferentially
5 Conclusion

reducing $O_2$ to $OH^-$ and exhibiting low overpotentials for both the ORR and OER. The round-trip voltage between the ORR at -1 mA cm$^{-2}$ and the OER at 10 mA cm$^{-2}$ was only 0.81 V. The prepared catalyst films show high stability on the electrode surface. The cycle lifetime of the catalysts has to be however further improved by optimization of the oxidative stability of the ORR active sites.

The influence of Ni to Co ratio in mixed Co and Ni phosphides on their oxygen evolution activity was investigated to gain a better understanding of the phenomenon of enhanced activity when Co/Co$_2$P was supported on a Ni foam electrode. XRD analysis revealed significant changes occurring when 5 up to 90 n/n% Ni was introduced into the synthesis of Co/Co$_2$P. The presence of Co nanoparticles was observed only in materials with up to 10 n/n% Ni. The OER overpotential, which is necessary to achieve a current density of 10 mA cm$^{-2}$ decreased with increasing Ni content. The potential difference between the most and least active phosphides, Ni/Ni$_x$P$_y$ and Co/Co$_2$P, respectively, at 10 mA cm$^{-2}$ was 50 mV. At a higher and therefore more interesting current density envisaged for practical application, the Co nanoparticles in the low Ni content materials presumably increase the conductivity resulting in a substantial decrease in overpotential with respect to the most active Ni/Ni$_x$P$_y$ at low current densities, reaching a potential difference of 120 mV between the most and least active material. In conclusion, the results presented in section 4.2 validate a synergistic effect between Ni and Co/Co$_2$P, thus supporting Co/Co$_2$P on Ni based electrodes might alter the initial structure and form new active centers. In addition, it was demonstrated that not only the potential at the mostly compared current density of 10 mA cm$^{-2}$ and the Tafel slope in the kinetically dominated region should be taken into account in the evaluation of catalyst activity. Comparison of the performance of electrocatalysts for the OER as well as hydrogen evolution at high current densities can be very interesting especially bearing in mind the envisaged conditions for technical applications of these materials at industrial scale.

The pBO carbonization procedure was adapted in order to make it compatible with NiFe LDH, one of the most active OER catalysts in alkaline media reported to date. Furthermore, the interlayer galleries of the LDH were organophilized by anion exchange of nitrate by SDS, which enhanced the penetration of BO monomers into the LDH galleries. The highest catalytic activity was obtained using a 3:1 ratio of NiFe SDS:BA-a monomer. XRD, XPS and TEM results show that the final catalyst consisted of NiFe LDH as well as NiO embedded in a carbon matrix. The calcined nanocomposite was electrochemically activated by potential cycling in aqueous 0.1 M KOH leading to regeneration of the NiFe LDH structure due to the post-calcination memory effect of LDHs. Using this approach, NiFe LDH layers embedded in a high
electrically conducting and stable carbon matrix were directly grown on electrode surfaces leading to very stable and active OER catalyst films. NiFe/C directly prepared on nickel foam demonstrated highly stable electrochemical response when subjected to aggressive electrochemical conditions involving galvanostatic polarization at 200 mA cm\(^{-2}\) in 5 M KOH at 60 °C for 100 h. Although, the NiFe/C catalyst was transformed from NiFe LDH to a mixture of NiO and NiFe\(_2\)O\(_4\) nanoparticles during the OER, the catalyst film remained attached on the electrode showing the high feasibility of the presented approach for fixing not only LDH but also other powder catalysts on electrode surfaces, which enabled observation of structural changes of the catalyst. Several different BO monomers or oligomers were investigated for their influence on the activity and stability of LDH/pBO composites, however, only minor differences were obtained with respect to the initially used BA-a. Furthermore, it was shown that bifunctional oxygen electrocatalysis could be derived from LDH and TM-N4 hybrid materials. However, the activity was comparatively low in relation to catalysts derived from LDH/pBO composites. Nonetheless, the performance of the catalysts derived from the LDH/TM-N4 composites might be improved by systematic studies of various parameters, especially the starting LDH, the BO, LDH to BO ratio, and the conditions of the thermal treatment, particularly through optimization of the atmosphere, temperature and duration, and through variation of the transition metal of the N4 macrocycle, among others.

In addition to the fixation of catalyst powder by means of embedding into a highly stable pBO based carbon matrix, a second novel and innovative approach was developed. This approach is the self-assembling of self-healing catalyst films which is based on the electrostatic interaction between polarized electrodes and surface charged particles. This strategy allows for \textit{in-situ} modification of electrodes while an electrolyzer is operating. Catalyst powders are simply added to the electrolyte reservoirs forming a suspension that is pumped through the electrochemical cell. Particles with negatively and positively charged surfaces are immobilized on the anode and cathode, respectively, owing to electrostatic attraction leading to the formation of catalytic films with self-healing properties. The proof-of-concept was achieved in a home-made non-zero gap alkaline electrolyzer using NiFe LDH and Ni\(_x\)B catalyst powders for anode and cathode, respectively. Catalyst films formed on Ni electrodes were stable for at least 22 days of continuous electrolysis at various current densities in the range of 50-100 mA cm\(^{-2}\). The employment of a more active catalyst for the HER demonstrated that a further decrease in the operating cell voltage is possible. Furthermore, the presented approach is able to overcome the cathode deactivation caused by deposition of inactive electrolyte impurities. Highly active HER
catalyst particles covered the deactivated electrode with a self-assembled and self-healing film, hence reducing the cell voltage.

In conclusion, on the one hand, the influence of possible nickel inclusions into Co/Co$_2$P on its OER activity was revealed and, on the one hand, two novel approaches for the development of highly stable catalyst/electrode assemblies, namely the use of pBO based carbon matrices and the self-assembling formation of self-healing catalyst films, were developed.
6 Experimental part

6.1 Chemicals and equipment

6.1.1 Chemicals

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<td>Potassium Chloride</td>
<td>VWR International GmbH (D)</td>
</tr>
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</table>
6 Experimental part

Potassium hydroxide  
Pure Milli-Q water  
Sodium borohydride  
Sodium dodecyl sulfate  
Sodium hydroxide  
Triethanolamine  

6.1 Chemicals and equipment

6.1.1 Consumables

Potassium hydroxide  
Sodium borohydride  
Sodium dodecyl sulfate  
Sodium hydroxide  
Triethanolamine  

6.1.2 Instruments

Potassium hydroxide  
Sodium borohydride  
Sodium dodecyl sulfate  
Sodium hydroxide  
Triethanolamine  

DTS1070 cuvette  
Fumasep® FAA-3-PK-130  
Glassy carbon, Sigradur®  
Ni foam  
Ni Foil  
Para-film  
Pasteur pipettes  
Pipette tips  
Polishing cloth  
PVC peristaltic pump tubes  

Ag/AgCl/3 M KCl reference electrode  
Autolab potentiostat/galvanostat  
Disk exchangeable RRDE  
Minipuls3 peristaltic pump  
Pt counter electrode  
RDE rotator  
Rotating disk electrodes(RDE)  

DTS1070 cuvette  
Fumasep® FAA-3-PK-130  
Glassy carbon, Sigradur®  
Ni foam  
Ni Foil  
Para-film  
Pasteur pipettes  
Pipette tips  
Polishing cloth  
PVC peristaltic pump tubes  

Ag/AgCl/3 M KCl reference electrode  
Autolab potentiostat/galvanostat  
Disk exchangeable RRDE  
Minipuls3 peristaltic pump  
Pt counter electrode  
RDE rotator  
Rotating disk electrodes(RDE)  

Carlo Roth (D)  
SG Water (D)  
Sigma-Aldrich (D)  
AppliChem GmbH (D)  
Carl Roth (D)  
Sigma-Aldrich (D)  
Malvern Instruments (D)  
Fumatech BWT GmbH (D)  
HTW (D)  
Goodfellow (D)  
Metall Jobst (D)  
Brand GmbH (D)  
VWR (D)  
Eppendorf AG (D)  
LECO GmbH (D)  
Gilson Inc. (USA)  
Metrohm AG (D)  
Metrohm AG (D)  
Pine research (USA)  
Gilson Inc. (USA)  
Workshop of Ruhr-University Bochum  
Workshop of Ruhr-University Bochum
6 Experimental part

Rotating ring disk electrodes (RRDE)  Metrohm AG (D)
RRDE rotator  Gamry Instruments (USA)
Sonopuls HD 3100  Bandelin Ultraschall (D)
VMP3 potentiostat/galvanostat  Bio-Logic Science Instruments (F)

6.1.3 Software

Citavi 4, 5  Swiss Academic Software (CH)
EC-lab  Bio-Logic Science Instruments (F)
MS Office 2013, 2015, 365  Microsoft (D)
MS Windows XP and 7  Microsoft (D)
Nova 1.10, 1.11  Metrohm (D)
Origin 2015-2017  Origin Lab Corp. (USA)

6.2 Materials synthesis

6.2.1 Layered double hydroxide synthesis

6.2.1.1 NiFe layered double hydroxide (LDH)

NiFe NO$_3$ LDH: Ni(NO$_3$)$_2$·6 H$_2$O (4.362 g, 15 mmol) and Fe(NO$_3$)$_3$·9 H$_2$O (2.02 g, 5 mmol) were dissolved in decarbonated ultra-pure water (100 mL) in the presence of triethanolamine (1.86 g, 12.5 mmol). Ammonium hydroxide solution (c = 25 wt.%) was added to the salt mixture under nitrogen atmosphere until a pH value of 8.5 (~4 ml NH$_4$OH) was reached. Afterwards, the mixture was stirred for 2 h at room temperature and then at 60 °C for 14 h. The resulting mixture was filtered and washed with decarbonated ultra-pure water (500 mL). The precipitate was dried at 70 °C for 24 h. For XRD characterization see section 4.4.

NiFe SDS LDH: Sodium dodecyl sulfate (SDS) (6 g, 20.8 mmol) was dissolved in decarbonated ultra-pure water (100 mL) and kept under nitrogen atmosphere. NiFe NO$_3$ (0.6 g) was suspended in ethanol (100 mL) and added to the SDS solution. The mixture was stirred for 48 h at RT. The resulting product was filtered and washed with decarbonated ultra-pure water (500 mL). The precipitate was dried at 70 °C for 24 h. For XRD characterization see section 4.4.
6.2.1.2 *TM-N4 intercalating NiFe LDH*

Anion exchange reaction:

**NiFe-NiN4 LDH:** 0.5829 g (0.59 mmol) Nickel (II) phthalocyanine-tetrasulfonic acid tetrasodium salt were dissolved in 100 ml decarbonated ultra-pure water. The solution was then purged with nitrogen for 15 min. Afterwards, 0.25 mg NiFeNO₃ LDH (~2.38 mmol for an estimated M = 105 g/mol) and 100 ml ethanol were added to the solution. The mixture was stirred for 48 h at RT. The resulting products were filtered and washed with 500 ml decarbonated water. The precipitate was dried at 70 °C for 24 h. For XRD characterization see section 4.4.

**NiFe-CoN4 LDH:** 0.250 g (0.254 mmol) Cobalt (II) phthalocyanine-tetrasulfonic acid tetrasodium salt were dissolved in 100 ml decarbonated ultra-pure water. The solution was then purged with nitrogen for 15 min. Afterwards, 0.25 mg NiFeNO₃ LDH (~2.38 mmol for an estimated M = 105 g/mol) and 100 ml ethanol were added to the solution. The mixture was stirred for 48 h at RT. The resulting products were filtered and washed with 500 ml decarbonated water. The precipitate was dried at 70 °C for 24 h. For XRD characterization see section 4.4.

**Coprecipitation**

**NiFe-NiN4 LDH:** 0.87 g (3 mmol) Ni(NO₃)₂•6 H₂O and 0.404 g (1 mmol) Fe(NO₃)₃•9 H₂O were dissolved in 20 mL decarbonated water in the presence of 0.372 g (2.5 mmol) triethanolamine. The obtained solution was added in droplets to a solution of nickel (II) phthalocyanine-tetrasulfonic acid tetrasodium salt dissolved in nitrogen purged decarbonated water (0.489 g; 0.5 mmol; 20 mL). Ammonium hydroxide solution (0.7 M) was added to adjust the pH value to 8.5. The mixture was stirred for 2 h at RT and then heated at 70 °C for 48 h. The resulting compound was separated by centrifugation (4000 rpm, 15 min) and washed with 250 ml decarbonated water. For XRD characterization see section 4.4.

**NiFe-CoN4 LDH:** 0.87 g (3 mmol) Ni(NO₃)₂•6 H₂O and 0.404 g (1 mmol) Fe(NO₃)₃•9 H₂O were dissolved in 20 mL decarbonated water in the presence of 0.372 g (2.5 mmol) triethanolamine. The obtained solution was added in droplets to a solution of cobalt (II) phthalocyanine-tetrasulfonic acid tetrasodium salt dissolved in nitrogen purged decarbonated water (0.490 g; 0.5 mmol; 20 mL). Ammonium hydroxide solution (0.7 M) was added to adjust the pH value to 8.5. The mixture was stirred for 2 h at RT and then heated at 70 °C for 48 h. The resulting
mixture was centrifuged and washed twice with decarbonated water (200 ml). The precipitate was dried at 70 °C for 24 h. For XRD characterization see section 4.4.

6.2.1.3  **CoMn LDH**

CoMn LDH was synthesized according to the procedure proposed by *Song and Hu* [102]. Briefly, Co(NO$_3$)$_2$•6 H$_2$O (1.085 g, 3.75 mmol), Mn(NO$_3$)$_2$•4 H$_2$O (0.4705 g, 1.875 mmol), NaNO$_3$ (0.765 g, 9 mmol) and NH$_4$F (0.925 g, 25 mmol) were dissolved in ultra-pure nitrogen purged water (500 mL). After 30 min of vigorous stirring, H$_2$O$_2$ (30 wt%, 125 µL) was added. The pH value of the solution was adjusted to 10 by dropwise addition of NaOH (0.1 M, 250 mL). The final suspension was aged at room temperature for a period of 20 h. The product was isolated and washed with water and ethanol yielding a brownish solid. **Figure 77** shows the XRD pattern of CoMn LDH having the characteristic LDH signals.

![Figure 77. XRD pattern of CoMn LDH.](image)

6.2.2  **Transition metal phosphide synthesis**

Transition metal phosphides were prepared according to the synthesis strategy described elsewhere [49]. Cobalt and nickel phosphides were prepared by the thermal decomposition of their dichloro triphenylphosphine complexes under a reductive atmosphere, i.e. at 400 °C in an atmosphere containing 10 % hydrogen and 90 % nitrogen. Mixed metal phosphides were prepared by mixing the precursor complexes dichlorobis(triphenylphosphine)colbat(II) and dichlorobis(triphenylphosphine)nickel(II) in various n/n ratios containing 5, 10, 50 and 90 n/n% Ni. The solid mixtures were ground together prior to thermal treatment in order to achieve a homogeneous Co and Ni distribution. For XRD characterization, see section 4.2. The following
reference patterns were used for peak assignment: Co (04-002-1029), Co$_2$P (04-001-9150; 01-072-9563), CoNiP (04-001-4562; 04-001-6153), Co$_{4.6}$Ni$_{7.2}$P$_5$ (04-019-5181); Ni$_2$P (04-004-3139; 01-074-1385), Ni$_3$P (04-006-1990), Ni$_{12}$P$_5$ (04-003-6050), Ni (04-004-6330; 03-065-0380).

6.2.3 Transition metal boride synthesis

Ni/Ni$_x$B: Aqueous NiCl$_2$•6 H$_2$O (20 mL, 0.5 M) placed in a round-bottomed Schlenk flask was deaerated by means of a Schlenk vacuum line, flushed with argon and maintained at 0 °C using an ice-bath. NaBH$_4$ (1.0 M) in NaOH (0.1 M) separately deaerated and flushed with argon was slowly added to the NiCl$_2$•6 H$_2$O by means of a syringe.

Co/Co$_x$B: The Co/Co$_x$B synthesis was done according to a procedure published elsewhere [317]. Aqueous CoCl$_2$•6 H$_2$O (20 mL, 0.5 M) was deaerated by means of Schlenk vacuum technique, then flushed with argon and kept at 0 °C using an ice-bath. NaBH$_4$ (1.0 M) in NaOH (0.1 M) separately deaerated and flushed with argon was slowly added to the CoCl$_2$•6 H$_2$O solution by means of a syringe.

Figure 78. SEM and EDX characterization of Ni/Ni$_x$B.
6 Experimental part

6.3 Physical characterization

6.3.1 Scanning electron microscopy

Scanning electrochemical microscopy (SEM) images and energy dispersive X-ray spectroscopy (EDX) for the samples described in section 4.1 were performed using a Quanta 3D FEG SEM operated at 20.0 kV for SEM imaging and at 30 kV for EDX analysis and mapping. For SEM analysis of the samples described in section 4.4, a Quanta Inspect F50 with a field emission gun (FEG) with 1.2 nm resolution and an energy dispersive X-ray spectrometer (EDXS) having 133 eV resolution at MnKα was used.

The reaction equation is given in equation (36) [317].

$$2 \text{TMCl}_2 + 4 \text{NaBH}_4 + 9 \text{H}_2\text{O} \rightarrow \text{TM/ TM}_x\text{B} + 4 \text{NaCl} + 12.5 \text{H}_2 + 3 \text{B(OH)}_3$$  (36)

As a precaution, vigorous frothing occurs if NaBH₄ solution is added rapidly to the metal salt solution. Instantaneous formation of a dark precipitate was observed. The precipitate was collected by filtration and washed with large amounts of tri-distilled water, followed by washing with ethanol.

It is noteworthy, that the characterization of the as prepared transition metal borides by XRD is not possible due to their amorphous nature. However, the shown EDX spectra give hints about the presence of boron, although, boron is very difficult to detect reliably by EDX. Detailed characterization of Co/CoₓB and Ni/NiₓB was published elsewhere [46,47].

Figure 79. SEM and EDX characterization of Co/CoₓB.

Scanning electron microscopy (SEM) images and energy dispersive X-ray spectroscopy (EDX) for the samples described in section 4.1 were performed using a Quanta 3D FEG SEM operated at 20.0 kV for SEM imaging and at 30 kV for EDX analysis and mapping. For SEM analysis of the samples described in section 4.4, a Quanta Inspect F50 with a field emission gun (FEG) with 1.2 nm resolution and an energy dispersive X-ray spectrometer (EDXS) having 133 eV resolution at MnKα was used.
6.3.2 Transmission electron microscopy

Transmission electron microscopy (TEM) analysis of the samples described in section 4.1 were conducted using a field-emission gun FEI Tecnai F20 microscope operated at 200 kV, which was equipped with a HAADF detector and Quantum Gatan Image Filter (GIF) for EELS analyses. TEM images of the samples in section 4.4 were taken using a FEI Tecnai F30 G2STWIN HR-TEM microscope working at 300 kV.

6.3.3 X-ray photoelectron spectroscopy

X-ray photoelectron spectra (XPS) were recorded either on a Thermo Scientific K-Alpha instrument equipped with a monochromatic AlKα source (1486.6 eV) or using a UHV set-up equipped with a Gammadata-Scienta SES 2002 analyzer. The measurements using the former equipment were performed at a base pressures of 2×10⁻⁹ mbar with pass energies of 200 and 20 eV for survey and high-resolution spectra, respectively. The measurements using the latter equipment were performed at a base pressure of 5×10⁻¹⁰ mbar. Monochromatic AlKα (1486.6 eV; 14.5 kV; 30 mA) was used as incident radiation and a pass energy of 200 eV was chosen resulting in an effective instrument resolution higher than 0.6 eV. Charging effects were compensated using a flood gun, and binding energies were calibrated based on positioning the main C 1s at 284.5 eV. Deconvolution of the C 1s and N 1s peaks was performed after back-ground subtraction.

6.3.4 X-ray diffraction

X-ray diffraction (XRD) measurements were performed using a PANalytical theta-theta powder diffractometer equipped with a CuKα radiation source. Scans were run from 5 to 80° with a step width of 0.01° for the PBA sample. XRD data were obtained using a Panalytical X’PERT MPD X-ray diffractometer with a CuKα radiation source (λ = 1.5418 Å) in the 20 range of 10-80° for phosphide samples, or 1-80° for LDH samples.

6.3.5 Raman spectroscopy

Raman spectra of the samples described in section 4.1 were recorded using a Jobin-Yvon iHR550 spectrometer equipped with a TE cooled charge coupled device. Excitation was done with a laser MPC 6000, Model Ignis 660 at a wavelength of 661 nm (in-situ) or 532-nm (D and G band). The typical laser power was 11 mW and the spectra were acquired for 10 s. To focus the laser in solution an immersible objective (Olympus, Japan) with a 60 times magnification
Experimental part

was employed. Raman spectra for the samples described section 4.4 were registered on a DXR Raman Microscope from Thermo Scientific using a laser source of 532 nm with a power of 3 mW.

6.3.6 Thermogravimetric analysis

TGA curves were recorded on a TA Instruments Q500. A combination of non-isothermal and isothermal steps were run under nitrogen (Section 4.1) or ambient atmosphere (Section 4.4), following a similar heating program like the one used for the electrode preparation:

Section 4.1: 10 °C min⁻¹ ramp from 20 to 160 °C, isothermal for 2 h at 160 °C, 10 °C min⁻¹ ramp from 160 to 200 °C, isothermal for 2 h at 200 °C, 10 °C min⁻¹ ramp from 200 to 220 °C, isothermal for 1 h at 220 °C, 10 °C min⁻¹ ramp from 220 to 240 °C, isothermal for 1 h at 240 °C, 10 °C min⁻¹ ramp from 240 to 600 °C, isothermal for 2 h at 600 °C, cooling at 1 °C min⁻¹ from 600 to 190 °C.

Section 4.4: 10 °C min⁻¹ ramp from 20 to 180 °C, isothermal for 2 h at 180 °C, 10 °C min⁻¹ ramp from 180 to 200 °C, isothermal for 2 h at 200 °C, 10 °C min⁻¹ ramp from 200 to 220 °C, isothermal for 1 h at 220 °C, 10 °C min⁻¹ ramp from 220 to 240 °C, isothermal for 1 h at 240 °C, 10 °C min⁻¹ ramp from 240 to 450 °C, isothermal for 2 h at 450 °C.

6.3.7 Zeta potential determination

The zeta potentials of the different catalysts were measured in aqueous 3 M KOH using a Malvern Zetasizer Nano ZS equipped with a He-Ne-laser with a wavelength of 633 nm using laser Doppler micro electrophoresis.

6.4 Electrochemical characterization

6.4.1 Electrode preparation

Glassy carbon electrodes (HTW, Germany) were polished successively with polishing pastes of decreasing particles sizes (3 µm diamond paste, 1 µm and 0.3 µm Al₂O₃ paste; Leco, USA) to obtain a clean mirror-like surface. The polished electrodes were immersed into a 1:1 mixture of ethanol and ultra-pure water and sonicated for 15 min to remove residual polishing paste. Clean and polished electrodes were modified by drop-coating according to the specific catalytic system used.
Section 4.1: Carbon-Mn$_x$Co$_y$O$_z$ modified glassy carbon electrodes were prepared according to the following procedure: glassy carbon rods ($\phi = 3$ mm, $A_{\text{geom.}} = 0.072$ cm$^2$; HTW, Germany) were drop-coated with an ink (7.2 µL) containing $K_m\text{Mn}_x[\text{Co(CN)}_6]_y \times n\text{H}_2\text{O}$ (5 mg mL$^{-1}$) and Araldite 35600 CH (Huntsman, USA) (0, 0.1, 0.5, 1, 2 or 5 mg mL$^{-1}$) in acetonitrile (J. T. Baker, The Netherlands), leading to an initial loading of 0.5 mg cm$^{-2}$. The catalyst inks were sonicated for 20 min prior to drop-coating. The drop-coated electrodes were placed into a three-zone tube furnace and a multi-step heating program was applied (160 °C / 2 h; 180 °C / 2 h; 200 °C / 2 h; 220 °C / 1 h; 240 °C / 1 h; 600 °C / 2 h) under Ar atmosphere. Electrodes prepared with a pBO/PBA ratio of 1:1 and 5 mg mL$^{-1}$ PBA had an estimated final loading of 0.15 mg cm$^{-2}$ calculated from the weight loss of 70% as shown in the TGA.

Ni foam electrodes (1.6 mm thickness, $A_{\text{geom.}} = 0.64$ cm$^2$; Goodfellow, Germany) were spray-coated with a PBA/Araldite ink (ratio 1:1) and heat treated as described above. The resulting electrodes had a catalyst loading of 0.625 mg cm$^{-2}$.

Section 4.2: Polished and clean glassy carbon RDEs ($\phi = 3.8$ mm, $A_{\text{geom.}} = 0.113$ cm$^2$, Workshop of Ruhr-University Bochum) were drop-coated with an ink of the catalyst dispersed in water/ethanol/Nafion (49:49:2; ink concentration 5 mg mL$^{-1}$). The final catalyst loading on the electrode surface was 210 µg cm$^{-2}$. The catalyst inks were sonicated for 15 min in a sonication bath prior to drop-coating in order to achieve a homogeneous particle dispersion. The catalyst films were left to dry for 20 min in ambient air prior to the measurements.

Section 4.3: Catalyst modified glassy carbon electrodes (GC-RDE, $\phi = 3.15$ mm, $A_{\text{geom.}} = 0.078$ cm$^2$, HTW, Germany) were prepared according to the following procedure: Polished electrodes were drop-coated with the catalyst ink (7.8 µL) containing the catalytically active powder (5 mg mL$^{-1}$) in a solution of BA-tepa (5 mg mL$^{-1}$ in 1 %v/v acetic acid). The catalyst inks were sonicated for at least 20 min prior to drop-coating in order to get a homogeneous suspension. Catalyst film modified electrodes underwent subsequent polymerization and pyrolysis by heat treatment in an Ar atmosphere (180 °C for 2 h, 200 °C for 2 h and 600 °C for 2 h; the heating ramp was always 10 K min$^{-1}$).

Section 4.4: The glassy carbon electrodes and graphite paper were drop-coated with a specific volume of catalyst suspension (5 mg mL$^{-1}$ in ethanol) to obtain an initial catalyst loading of 0.5 mg LDH cm$^{-2}$. All LDH-to-BO monomer ratios were calculated with respect to a LDH concentration of 5 mg mL$^{-1}$. Prior to use, the catalyst suspensions and catalyst/BO mixtures were sonicated with a sonotrode for 10 min to obtain a stable and homogeneous suspension.
Polymerization and further calcination were performed in a tube furnace under ambient atmosphere. The temperature was first raised to 180 °C and kept constant for 2 h, then to 200 °C and maintained for 2 h and finally to 450 °C and kept for another 2 h. The temperature ramp was 10 K min\(^{-1}\) for each heating step. Following this heating procedure, a residual char of 44 % was obtained for NiFe SDS/pBO (3:1) according to TGA analysis.

The NiFe/C modified Ni foam electrode (\(A_{geom.} = 1 \text{ cm}^2\)) was prepared by drop coating the catalyst suspension (5 mg mL\(^{-1}\) in ethanol, NiFe SDS/pBO (3:1)) on the Ni foam until a loading of 6 mg cm\(^{-2}\), prior to calcination, was achieved. The same thermal treatment as in the case of the modified carbon electrodes was applied.

Glassy carbon rod electrodes without initial insulation were sealed either with PTFE tape or with PTFE tube in order to achieve a disk shaped electrode surface with a defined surface area exposed to the electrolyte.

### 6.4.2 Three-electrode measurements

If not explicitly stated otherwise all three-electrode measurements were conducted with a Pt mesh counter electrode, a Ag/AgCl/3 M KCl reference electrode and Ni, glassy carbon or graphite paper working electrode. Potentials were corrected for the resistance of the solution according to the equation \(E_{corr} = E_{meas} - i \cdot R_{sol}\). The solution resistance (\(R_{sol}\)) was determined by means of electrochemical impedance spectroscopy (EIS) in the frequency range from 100 kHz to 10 Hz with a perturbation voltage of 5 mV (RMS). The corrected potential was taken for the conversion of the measured potential to the reversible hydrogen electrode (RHE) scale according to \(E_{RHE} = E_{meas} + E^0_{Ag/AgCl | 3 M KCl} + 0.059 \text{ V} \cdot \text{pH}\). Overall cell voltages were not corrected for the cell resistance.

EIS for charge transfer comparison in section 4.2 were done galvanostatically at a current density of 1 mA cm\(^{-2}\) in the frequency range of 1 kHz to 0.01 Hz with a perturbation current of 500 µA (RMS) with pre-conditioned electrodes.

Generally, modified electrodes underwent a conditioning process by means of CV scans in the reaction specific range with a scan rate of 50 to 100 mV s\(^{-1}\) until reproducible scans were obtained.

OER, HER and ORR activity was determined by means of LSV or CV in the reaction specific potential window with a scan rate of 5 mV s\(^{-1}\). Fast potential cycling for catalyst
6 Experimental part

activation/regeneration in section 4.1 and 4.4 was done by CV in the OER potential window with a scan rate of 50 mV s\(^{-1}\).

6.4.2.1 Rotating disk electrode measurements

Rotating disk electrode measurements were conducted using a software/manually controlled RDE/RRDE rotation unit connected to the potentiostat/galvanostat. A glassy carbon rotating disk electrode was used as the working electrode, a Pt mesh as counter electrode and a Ag/AgCl/3 M KCl electrode as reference electrode. After electrode conditioning and EIS measurements for later iR drop compensation, OER and/or ORR measurements were done under various rotation speeds. The rotation speed for OER measurements was typically 1600 rpm in order to facilitate bubble departure. ORR was done at various rotations speeds, i.e. 0, 100, 400, 900, 1600 rpm in order to correlate the rotation speed to the number of transferred electrons according to the KL analysis.

6.4.2.2 Galvanostatic stability test (GSS test)

The GSS test was performed according to an adapted protocol of Maljusch et al. [240]. The GSS test performed at RT was carried out either in a homemade flow-cell (flow rate of 60 mL min\(^{-1}\)) with a modified graphite paper (\(\phi = 8 \text{ mm}, A = 0.5 \text{ cm}^2\)), a modified Ni foam (flow rate of 60 mL min\(^{-1}\)) or a using a glassy carbon RDE (GC-RDE, \(\phi = 3.15 \text{ mm}, A_{\text{geom}} = 0.078 \text{ cm}^2, 1600 \text{ rpm}\)) as working electrode, a platinum mesh as counter electrode and a Ag/AgCl/3 M KCl as reference electrode in O\(_2\)-saturated 0.1 M KOH as electrolyte solution. The stability test consists of repeating cycles of EIS, CV (1 cycle, 5 mV s\(^{-1}\)) and galvanostatic chronopotentiometry (900 s).

The galvanostatic stability test in high concentrated KOH (5 M) at elevated temperature (60 °C) was carried out in a three-electrode configuration with NiFe/C modified nickel foam (AC) (Goodfellow, \(A_{\text{geom}} = 1 \text{ cm}^2\), loading prior to calcination was 6 mg cm\(^{-2}\)) or Ni foam alone as working electrode, a Pt mesh as counter electrode and a Ag/AgCl/3 M KCl reference electrode. The procedure was similar to the one mentioned before except that the applied current density during galvanostatic polarization was 200 mA cm\(^{-2}\). The whole electrochemical cell was heated to 60 °C. The electrolyte was stirred to maintain a homogeneous temperature distribution and to facilitate gas bubble departure from the electrodes. The lack of reliable activity coefficients for 5 M KOH at 60 °C does not allow the conversion of the potential scale from the used
Ag/AgCl/3 M KCl to the scale of the RHE [318]. The electrolyte volume was maintained constant only during the day.

The obtained data was semi-automatically processed as described elsewhere [240].

6.4.2.3 Faraday efficiency determination with rotating ring disk electrode

The Faradaic efficiency (FE) of OER catalysts was determined by means of rotating ring disk electrode (RRDE) measurements in argon saturated electrolyte at 1600 rpm as previously described [24,49,236,289]. The glassy carbon disk (φ = 5 mm, A_{geom} = 0.1963 cm²) of a (disk exchangeable) RRDE (Pine Instruments) was prepared with the catalyst following the described procedures. Oxygen, which is evolved at the disk electrode, is reduced at the platinum ring electrode. The collection efficiency (CE) of the RRDE was determined prior to the faradaic efficiency measurements using the modified disk electrode. Fe^{3+} ions of 5 mM K_3Fe(CN)_6 in 0.1/1 M KOH electrolyte were reduced at the disk electrode and reoxidized at the ring at potentials were the current was limited by diffusion at both electrodes. The CE was calculated according to: CE = i_{ring}/i_{disk}. The FE was determined by means of chronoamperometry at a potential delivering a current density of 1 mA cm⁻² at the disk while the ring potential was fixed at -0.7 V vs. Ag/AgCl/3 M KCl. The ring background current was determined at a disk potential of 0 V for 300 s. The FE was calculated as average of the last 240 s according to FE = i_{ring}/(i_{disk}•N); with i_{ring} as current measured at the ring, i_{disk} as the current measured at the disk and N as collection efficiency. **Figure 80** shows exemplarily the measurements for the CE and FE determination of Co/Co₂P.

![Figure 80](image_url)

**Figure 80.** Linear sweep voltammograms of K₃[Fe(CN)₆] (5 mM) in 1 M KOH recorded on a RRDE for the determination of the collection efficiency (a) and chronoamperometric faradaic efficiency measurement (b).
Experimental part

6.4 Electrochemical characterization

6.4.2.4 Differential electrochemical mass spectrometry

Oxygen gas produced at the NiFe/C electrode was detected by means of differential electrochemical mass spectrometry (DEMS). The mass spectrometer is a GAM 400 (InProcess Instruments). The porous Teflon membrane (Gore Tex) with a pore width of 20 nm and a thickness of 75 µm separates the volatile products from the liquid phase and allows their transfer to the Balzers quadrupole mass spectrometer (QMG-422) with IPI-Quadstar software. The recorded mass was detected by the analog output of the mass spectrometer. The pressure inside the QMS was below 6•10⁻⁶ mbar during measurements. A NiFe/C modified GC electrode prepared as described above with an active surface area of 0.283 cm² was used as the working electrode, a Ag/AgCl/3M KCl as reference electrode, a Pt-wire at the electrolyte outlet was used as counter electrode. All experiments were conducted in argon saturated 0.1 M KOH at room temperature. The cyclic voltammograms and chronopotentiometry measurements were performed with an Autolab PGSTAT 204 (Metrohm), meanwhile, the MSCV and MSCP for m/z=32 (for oxygen) as well as the potential were simultaneously recorded during the experiment. The currents for oxygen (i₃₂) detected by DEMS were baseline corrected. To activate the catalyst and reach the AC state, 50 cycles between 0.98 V_RHE and 1.58 V_RHE at 50 mV s⁻¹ were conducted at an electrolyte flow rate of 200 µL min⁻¹. Afterwards a CV was recorded between 0.98 V_RHE and 1.58 V_RHE at 5 mV s⁻¹ with an electrolyte flow rate of 6.5 mL min⁻¹. The chronopotentiometric measurement was performed at an applied current density of 2.1 mA cm⁻² and an electrolyte flow rate of 6.5 mL min⁻¹.

6.4.2.5 Electrochemistry coupled Raman spectroscopy

In-situ Raman spectra were recorded during chronoamperometric measurements at different potentials in KOH (0.01 M). Catalyst modified graphite paper was used as working electrode, a Pt mesh as counter electrode and a Ag/AgCl/3 M KCl as reference electrode.

6.4.2.6 Three-electrode electrochemical measurements with the catalyst suspended in the electrolyte

Catalyst immobilization was carried out using a three-electrode cell configuration in which a piece of Ni foil (surface area of ca. 4 cm²), a piece of Ni foil in a separate compartment filled with particle free electrolyte and a Ag/AgCl/3 M KCl electrode acted as working electrode (WE), counter electrode (CE) and reference electrode (RE), respectively (Figure 81). A catalyst suspension (1.3 mg mL⁻¹) in 3 M KOH and catalyst-free 3 M KOH were used as electrolyte in
the WE and CE compartments, respectively (Figure 81). The suspension was continuously stirred to provide a homogeneous suspension during immobilization and to increase the collision frequency of particles with the electrode. The immobilization potential of ±200 mV vs. pzc\textsubscript{Ni}, i.e. -0.120 V and +0.280 V vs. Ag/AgCl/3 M KCl for materials with positive (Ni\textsubscript{xB} and Co\textsubscript{x}P) and negative (NiFe LDH and CoMn LDH) zeta potential, respectively, was applied for 60 min. After immobilization, the electrodes were taken out from the suspension, thoroughly rinsed with deionized water and then dried in air. The formation of self-assembling catalyst films was similarly performed at a temperature of 60 °C in 5 M KOH.

The electrocatalytic activity of the modified electrodes for the HER and the OER was investigated by means of LSV. LSVs were recorded within the specific potential window for the HER or OER at a scan rate of 5 mV s\textsuperscript{-1}. For the electrochemical measurements, the modified Ni foil was screwed into an electrochemical cell (Figure 82), with a 5 mm opening which defined the electrode surface.

**Figure 81. Schematic representation of the three-electrode electrochemical cell used for immobilization of suspended particles by applying pzc\textsubscript{Ni} ± 200 mV.**
6.4.3 Two-electrode electrolysis

The setup of the non-zero gap alkaline electrolyzer is shown in Figure 83. The electrochemical cell consisted of two compartments separated by an anion exchange membrane. Each compartment was composed of a metallic end plate, a peek plate, a Teflon gasket, the electrode (Ni foil, thickness 100 µm, or graphite paper) and a Teflon sealed flow channel. The active electrode area was defined by the electrolyte flow channel to be 4 cm². Both compartments were stacked together and fixed with six screws. The electrolyte was pumped through the cell in two separate circuits by means of a peristaltic pump, i.e. anolyte and catholyte circuit. Electrolysis was conducted galvanostatically at various applied currents. The pH value of the electrolyte was kept constant manually by the addition of controlled amounts of deionized water.

For the alkaline electrolysis discussed in section 4.4, a NiFe/C modified graphite paper was used as anode and a Ni foil as cathode. The anode was modified following similarly to the procedure described in section 6.4.1. Electrolysis was carried out using an electrolyte (3 M KOH) flow rate of 30 mL min⁻¹ at an applied current density of 30 mA cm⁻².

For “in-operando” formation of self-assembling and self-healing catalyst films Ni foil acted as anode and cathode in 3 M KOH as electrolyte solution. Catalyst powders were directly added to either the anolyte or the catholyte. The concentration of catalyst in the electrolyte was ca. 1.3 mg mL⁻¹. The catalyst suspensions were stirred to prevent settling of the particles. The resistance of the electrolytes, 3 M KOH and the catalyst suspensions (1.3 mg mL⁻¹) in 3 M KOH, were determined by means of electrochemical impedance spectroscopy using an ac perturbation of 10 mV (rms) at open circuit potential in the frequency range from 100 kHz to 10 Hz in a three-electrode configuration (Pt CE, glassy carbon WE and Ag/AgCl/3 M KCl RE, particles in 3 M KOH). Cell top positioner with detachable cell cap allows fixing the distance between electrodes minimizing the difference in distance between WE and RE for different...
measurements. Values of $3.98 \pm 0.04 \, \Omega$ (3 M KOH), $4.08 \pm 0.01 \, \Omega$ (CoMn LDH), $3.99 \pm 0.01 \, \Omega$ (Co$_x$P), $4.01 \pm 0.04 \, \Omega$ (Ni$_x$B) and $3.99 \pm 0.01 \, \Omega$ (NiFe LDH) were obtained (mean of five independent measurements and standard deviation). For measurements in section 4.5.5, the Teflon gaskets were exchanged by Viton®.

6.4.4 Scanning electrochemical microscopy

Scanning electrochemical microscopy (SECM) was done in a four electrode configuration with a catalyst modified glassy carbon electrode as sample electrode (WE1, $\sigma = 5$ mm), a Pt mesh as CE, a Ag/AgCl/3 M KCl as RE and a Pt micro electrode as tip electrode (WE2, $\sigma = 25$ µm). The working distance of the tip electrode was 12.5 µm (Figure 83). The collection efficiency (CE) of the tip towards possibly produced hydrogen peroxide at the sample was determined using a Hg drop sample electrode to ensure a 2 electron process on both WEs [319] A constant potential of -0.4 V vs. Ag/AgCl 3 M KCl was applied at the WE1 and a constant potential of 0.7 V vs. Ag/AgCl/3 M KCl at the WE2. The CE was calculated according to $CE = -\frac{i_{tip}}{i_{sample}}$ with $i_{tip}$ as tip current and $i_{sample}$ as current measured at the sample. The CE was determined to be $3.7 \times 10^{-4}$. The number of transferred electrons ($n$) was determined by applying a LSV in the potential window used before for the ORR ($5 \, \text{mV s}^{-1}$) at the sample electrode and a constant potential of 0.7 V vs. Ag/AgCl/3 M KCl at the tip electrode.

Figure 83. Schematic representation (a) and optical image (b) of the used electrolyzer cell.
Experimental part

6.4 Electrochemical characterization

The measured currents were used for calculation of the number of transferred electrons ($n$) and the percentage of hydrogen peroxide generated ($x_{H_2O_2}$) according to the literature [273]:

$$n = \frac{4i_{sample}}{i_{tip} + i_{CE}}$$

(37)

The amount of detected hydrogen peroxide was calculated according to:

$$x_{H_2O_2} = \frac{4-n}{2} \times 100 \%$$

(38)
7 References


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8 Appendix

8.1 TEM report

The TEM characterization of the samples discussed in section 4.1 was done by Aziz Genc\textsuperscript{1} and Jordi Arbiol\textsuperscript{1,2}.

Pre-treated sample

![TEM micrographs](image)

Figure 85. HAADF STEM and TEM/HRTEM micrographs showing the general features of the sample.

Figure 85 shows a selection of HAADF STEM and TEM/HRTEM micrographs obtained from the sample, revealing the presence of small nanoparticles embedded in a matrix. In general, the

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sample was contaminating a lot and it was hard to obtain high quality STEM micrographs and STEM-EELS maps. However, it was still possible to obtain some useful data. As seen in Figure 85, nanoparticles with sizes smaller than ~40 nm (usually around or smaller than 10 nm) are nicely distributed in a matrix. In the lower row, several TEM/HRTEM micrographs are presented, revealing that the nanoparticles are crystalline and the matrix is C where the typical (0002) planes of the graphitic C phase (space group = P63/mmc) with lattice parameters of $a = 0.246$ nm and $c = 0.671$ nm are clearly observed.

![Figure 86. HRTEM micrograph showing some nanoparticles embedded in the matrix, detail of the red squared region and its corresponding power spectrum.](image)

Figure 86 shows a HRTEM micrograph of several nanoparticles with various sizes within the matrix. Detail of the red squared region is shown on the right along with its corresponding power spectrum (FFT). The FFT revealed that this nanoparticle has a body centered tetragonal CoMn$_2$O$_4$ phase (space group = I41/amd) with lattice parameters $a = b = 0.5723$ nm and $c = 0.9295$ nm. The nanoparticle is visualized along its [100] zone axis. It should be stressed here that we have identified this nanoparticle being CoMn$_2$O$_4$ phase because it was a better fit but it is also possible to identify it as a body centered tetragonal Mn$_3$O$_4$ phase (space group = I41/amd) with lattice parameters $a = b = 0.5762$ nm and $c = 0.9439$ nm. The error margin of fitting was about 5-6% better for the case of the CoMn$_2$O$_4$ phase. In fact, the identified
CoMn$_2$O$_4$ phase is generated by replacing one Mn with Co in the lattice of Mn$_3$O$_4$ resulting in slight change in the lattice parameters as the ionic radius of Mn is slightly larger than that of Co. We have identified several different nanoparticles as being composed of the CoMn$_2$O$_4$ phase and some of them are presented in the following. The above presented concern is also valid for all these cases.

**Figure 87.** HRTEM micrograph some nanoparticles embedded in the matrix, detail of the red squared region and its corresponding power spectrum revealing that the nanoparticle is composed of the same tetragonal CoMn$_2$O$_4$ phase and visualized along its [010] zone axis.
Figure 88. HRTEM micrograph of an ~8 nm spherical nanoparticle embedded in a C matrix, detail of the red squared region and its corresponding power spectrum revealing that the nanoparticle is composed of the same tetragonal CoMn$_2$O$_4$ phase and visualized along its [100] zone axis.

Figure 89. A selection of HRTEM micrographs.
Figure 90. HAADF STEM micrograph showing an ensemble of nanoparticles in the C matrix and EELS composition maps of the white squared area. Individual Mn (red), Co (green), O (blue) and C (turquoise) maps along with the composites of Mn – Co – O, Mn – Co, Mn – O and Co – O. Scale bar is the same for all composition maps.

Figure 90 shows the STEM EELS results obtained from the area indicated with white rectangle in the HAADF STEM micrograph, which reveals the presence of an ensemble of nanoparticles with various sizes. Individual EELS composition maps of Mn (red), Co (green), O (blue) and C (turquoise) and the composites of Mn – Co – O, Mn – Co, Mn – O and Co – O are also shown in this figure. As stated above, the contamination during the analysis was a big obstacle and these results are obtained under severe C contamination. Therefore, the individual C map is generated by contributions of both C matrix and the contamination. Mn and Co maps substantially coincide with each other except 2 nanoparticle having only Co and several nanoparticles/parts of the nanoparticles being Co rich. When we have a look at their composite with each other and with O, we can see that Mn is always in the oxide form however, some Co nanoparticles seem to be in the metallic form. Upper left nanoparticle is likely to be a core-shell nanoparticle with a metallic Co core and Mn-Co-O shell. On the lower left, a nanoparticle richer in Mn is also noticeable. Although we could only identify the presence of mixed oxide phase via HRTEM analyses, these EELS maps clearly suggest that the sample comprises mixture of different phases.
Figure 91. HAADF STEM micrograph showing several nanoparticles in the C matrix and EELS composition maps of the white rectangle area. Individual Mn (red), Co (green), O (blue) and C (turquoise) maps along with the composites of Mn – Co – O, Mn – Co, Mn – O and Co – O. As seen in these EELS maps, the presence of Mn-rich oxides and Co-rich oxides are present in the sample, where, similar to the Figure 90, the amount of Co is higher in Mn-rich oxides than the amount of Mn in Co-rich oxides.
As-prepared sample

Figure 92. HAADF STEM and TEM micrographs showing the general features of the as-prepared sample.

Figure 92 shows a selection of HAADF STEM and TEM micrographs obtained from the as-prepared sample, revealing the presence of small nanoparticles embedded in a matrix. General features of the sample are almost the same as the above presented “Pre-treated sample”. The main difference is the presence of flake-like regions as shown in both STEM and TEM micrographs. At the first instance, the idea of the C matrix being 2D graphene-like seem plausible yet, further TEM and STEM-EELS analyses have shown that these flake-like regions are metal oxides.
Figure 93. A selection of HRTEM micrographs, revealing the presence of nanoparticles embedded in C matrix and the crystallinity of the flake-like regions. These flakes are identified as being composed of the same CoMn$_2$O$_4$ phase which are visualized along their [111] zone axes.

Figure 94. HAADF STEM micrograph showing several nanoparticles in the C matrix and EELS composition maps of the white rectangled area. Individual Mn (red), Co (green), O (blue) and C (turquoise) maps along with the composites of Mn – Co – O, Mn – Co, Mn – O and Co – O.

The as-prepared sample was not contaminating as the above presented pre-treated sample, therefore, we could obtain better quality STEM-EELS maps. Figure 10 shows the STEM EELS results obtained from the area indicated with white rectangle in the HAADF STEM micrograph. Individual EELS composition maps of Mn (red), Co (green), O (blue) and C (turquoise) and the composites of Mn – Co – O, Mn – Co, Mn – O and Co – O are also shown in this figure. The main features of these EELS maps are the presence of Mn-rich Mn-Co mixed oxide and some nanoparticles with metallic Co cores. The core-shell morphologies of several nanoparticles are visible in the HAADF STEM micrograph.
Figure 95. HAADF STEM micrograph showing several nanoparticles in the flake-like structures and the C matrix and EELS composition maps of the white squared area. Individual Mn (red), Co (green), O (blue) and C (turquoise) maps along with the composites of Mn – Co – O, Mn – Co, Mn – O and Co – O.

Figure 95 shows the STEM EELS results obtained from the area indicated with a white square in the HAADF STEM micrograph. Individual EELS composition maps of Mn (red), Co (green), O (blue) and C (turquoise) and the composites of Mn – Co – O, Mn – Co, Mn – O and Co – O are also shown in this figure. Similar to the above presented EELS results, the presence of Mn oxide, Mn-rich mixed oxide and some metallic Co nanoparticles are revealed. What is important to note here that the flake-like structure is a mixture of Mn-Co oxides, confirming the results obtained by HRTEM analyses. In addition a C layer (possibly graphene) is covering the whole structure.

Figure 96. HAADF STEM micrograph showing several nanoparticles in the flake-like structures and the C matrix and EELS composition maps of the white rectangled area. Individual Mn (red), Co (green), O (blue) and C (turquoise) maps along with the composites of Mn – Co – O, Mn – Co, Mn – O and Co – O are also shown in this figure, revealing the similar features as the above presented maps.
8.2 Publications and presentations

8.2.1 Publication list


* These authors contributed equally.


8.2 Publications and presentations


* These authors contributed equally.

8.2.2 Oral presentations


8 Appendix


8.2.3 Poster presentations


8.3 Patent application

European patent application EP17150558.9:
Self-assembling and Self-healing Nanoparticle-based Catalyst Films for Alkaline Electrolysers

8.4 Awards

1 out of 3 winners of the “Erfinderwettbewerb 2016” of the Ruhr-Universität Bochum:
Selbstheilende Elektrokatalysatorfilme
8.5 List of abbreviations

<table>
<thead>
<tr>
<th>Abbreviation</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.6dah</td>
<td>1,6-diaminohexane</td>
</tr>
<tr>
<td>AC</td>
<td>After cycling</td>
</tr>
<tr>
<td>BA</td>
<td>Bisphenol A</td>
</tr>
<tr>
<td>BC</td>
<td>Before cycling</td>
</tr>
<tr>
<td>BO</td>
<td>Benzoxazine</td>
</tr>
<tr>
<td>CE</td>
<td>Counter electrode</td>
</tr>
<tr>
<td>CNTs</td>
<td>Carbon nanotubes</td>
</tr>
<tr>
<td>Cp</td>
<td>4-Cyanophenol</td>
</tr>
<tr>
<td>CV</td>
<td>Cyclic voltammetry</td>
</tr>
<tr>
<td>DEMS</td>
<td>Differential electrochemical mass spectrometry</td>
</tr>
<tr>
<td>DFT</td>
<td>Density functional theory</td>
</tr>
<tr>
<td>ECSA</td>
<td>Electrochemically active surface area</td>
</tr>
<tr>
<td>EDX</td>
<td>Energy dispersive X-ray spectroscopy</td>
</tr>
<tr>
<td>EELS</td>
<td>Electron energy loss spectroscopy</td>
</tr>
<tr>
<td>EIS</td>
<td>Electrochemical impedance spectroscopy</td>
</tr>
<tr>
<td>GC</td>
<td>Glassy carbon</td>
</tr>
<tr>
<td>GSS</td>
<td>Galvanostatic stability</td>
</tr>
<tr>
<td>HER</td>
<td>Hydrogen evolution reaction</td>
</tr>
<tr>
<td>HOR</td>
<td>Hydrogen oxidation reaction</td>
</tr>
<tr>
<td>KL</td>
<td>Koutecky-Levich</td>
</tr>
<tr>
<td>LDH</td>
<td>Layered double hydroxide</td>
</tr>
<tr>
<td>LSV</td>
<td>Linear sweep voltammetry</td>
</tr>
<tr>
<td>mel</td>
<td>Melamine</td>
</tr>
<tr>
<td>NF</td>
<td>Nickel foam</td>
</tr>
<tr>
<td>NPMC</td>
<td>Non-precious metal catalysts</td>
</tr>
</tbody>
</table>
OER  Oxygen evolution reaction
ORR  Oxygen reduction reaction
PBA  Prussian blue analogue
pBO  Polybenzoxazine
PEEK Polyether ether ketone
PTFE Polytetrafluoroethylene
RDE  Rotating disk electrode
RE   Reference electrode
RHE  Reversible hydrogen electrode
RRDE Rotating ring disk electrode
SDS  Sodium dodecyl sulfate
SECM Scanning electrochemical microscopy
SEM  Scanning electron microscopy
TEM  Transmission electron microscopy
tepa Tetraethylenepentamine
TGA  Thermogravimetric analysis
TM   Transition metal
WE   Working electrode
XAS  X-ray absorption spectroscopy
XPS  X-ray photoelectron spectroscopy
XRD  X-ray diffraction

8.6 List of symbols

A Ampere
A Surface area
Å Ångström
List of symbols

- **B**: Levich constant
- **C_0**: Concentration of the reactant
- **D_0**: Diffusion coefficient of the reactant
- **e**: Electron
- **E**: Potential
- **E^0**: Reversible potential
- **E_{appl}**: Applied potential
- **F**: Faraday constant
- **I**: Current
- **i**: Current
- **i_0**: Exchange current density
- **I_d**: Diffusion limited current
- **i_D**: Disk current
- **I_k**: Kinetic current
- **i_R**: Ring current
- **n**: Number of exchanged electrons
- **N**: Collection efficiency
- **R**: Universal gas constant
- **T**: Temperature
- **U_{cell}**: Cell voltage
- **V**: Volt
- **α**: Transfer coefficient
- **η**: Overpotential
- **υ**: Kinematic viscosity
- **ω**: Angular velocity