5.1 Introduction

The direct and reversible electrolytic splitting of saline seawater in “seawater electrolyzers” is an early-stage technology for a wide range of energy-related application fields and markets. Fig. 5.1 shows the proposed scheme of a reversible seawater electrolyzer in which renewable electricity splits seawater selectively and directly into hydrogen and oxygen. A fuel cell back converts the oxygen and hydrogen into electricity and freshwater.

This technology enables the direct generation of hydrogen fuel in remote offshore locations near wind turbines servicing and powering maritime vehicles. It is also considered the leading emerging technology for stationary onshore power and fuel generation in arid desert zones with access to ocean water yet scares freshwater resources [1]. Back converting the produced hydrogen into electricity and freshwater could even support and not compete with the freshwater industry in hyperarid regions. Furthermore, alternative options for direct seawater electrolyzers such as combinations of typical alkaline or proton exchange membrane (PEM) electrolyzers with upstream pre-purification steps, on the one hand, consume about 1% more energy and, on the other hand, would require much more space [1].

In electrochemical cells, such as water electrolyzers and fuel cells, the catalyst layer is one of the most important components, as the catalyst determines the charge transfer resistance, and typically controls the overall reaction efficiency, the overpotential of the reaction, and all kinetic limits, and, with it, the overall device performance over large potential ranges. This is why a large number of new material candidates were developed over the past years in search of better performing catalysts [2–6]. These catalysts are compared with benchmark electro-catalysts which are commercially available for both pure fuel cells and pure electrolyzers.

However, in seawater electrolyzers, not only the energy efficiency but also the chemical selectivity (faradaic efficiency) is of pivotal importance since minor contaminating ions and impurities complicate the electrochemistry and the total electrolyzer setup. Especially the Cl\(^-\) ions, which represent the largest ionic proportion of \(\sim 55\%\) in seawater, induce competing chloride oxidation reaction, which leads to problematic side products such as toxic Cl\(_2\) gas or HClO\(_4\). Especially for offshore...
Metal Oxide-Based Nanostructured Electrocatalysts for Fuel Cells, Electrolyzers, and Metal-Air Batteries

Fig. 5.1 Renewable electric energy splits seawater into hydrogen and oxygen. The stored hydrogen can be back transformed into freshwater and electricity.

platforms or off-grid applications it is crucial to avoid these side reaction products by choosing the most suitable catalyst system.

In this context, the following chapters will outline the fundamental electrochemistry of the oxygen electrode on metal oxides and will then move to the requirements of a bifunctional OER/ORR metal oxide catalyst, followed by the discussion of the competing chloride oxidation and oxygen evolution reaction using seawater as an electrolyte. Finally, suitable materials for reversible seawater oxidation and oxygen reduction will be discussed.

5.2 Oxygen electrode chemistry

Water electrolyzers split water molecules to generate molecular hydrogen and oxygen by just using electricity as a chemical force. As shown in Fig. 5.2A, an electrolyzer consists of a cathode and an anode, where the hydrogen evolution reaction (HER) and the oxygen evolution reaction (OER) proceed, respectively. In contrast to electrolyzers, hydrogen fuel cells that catalyze the conversion of molecular hydrogen and oxygen into water and electricity, the corresponding reactions are the hydrogen oxidation reaction (HOR) and oxygen reduction reaction (ORR), now proceeding at the anode and cathode, respectively (see Fig. 5.2B).
Fig. 5.2 Sketch of electrochemical cells with the corresponding electrode reactions in alkaline media (A) electrolyzer and (B) fuel cell.
In general, the electrochemical redox reactions in electrolyzers and fuel cells split into two electrode reactions, while the overall cell potential is simply obtained by

$$E^0_{\text{cell}} = E^0_{\text{cathode}} - E^0_{\text{anode}} \tag{5.2-5.8}$$

The principal goal of catalysis research is to accelerate chemical reactions such that they operate close to their thermodynamic limits. To reach this goal, information about the reaction mechanism and intermediates is critical. In water electrolyzers and fuel cells, the oxygen electrode plays the key role in the overall cell performance due to their sluggish 4 e$^-$ transfer reaction compared to the 2 e$^-$ transfer reaction at the hydrogen electrode (see Fig. 5.2). In other words, the oxygen evolution reaction (OER) in electrolyzers and the oxygen reduction reaction (ORR) in fuel cells cause the largest electrochemical potential and thus efficiency losses. The proposed reaction mechanism for the OER is shown in Eq. (5.1)–(5.4) on metal oxides in acidic media [7]:

Anode (acidic):

\begin{align*}
2\text{H}_2\text{O} & \rightarrow \text{HO}^* + \text{H}_2\text{O} + \text{H}^+ + \text{e}^- \\
& \rightarrow \text{O}^* + \text{H}_2\text{O} + 2\text{H}^+ + 2\text{e}^- \\
& \rightarrow \text{HOO}^* + 3\text{H}^+ + 3\text{e}^- \\
& \rightarrow \text{O}_2 + 4\text{H}^+ + 4\text{e}^- \tag{5.1-5.4}
\end{align*}

It is important to mention that the reaction mechanism in fuel cells is assumed to follow the same mechanism but in the opposite direction with identical intermediates binding to the catalyst surface. In contrast to the acidic environment which requires noble metal materials, especially the alkaline media opens up possibilities for more flexible catalyst designs based on abundant cheap and non-precious metals. In this context, Eq. (5.5)–(5.8) shows the reaction mechanism of the oxygen electrode in alkaline media [7]:

Anode (alkaline):

\begin{align*}
4\text{OH}^- & \rightarrow \text{HO}^* + 3\text{OH}^- + \text{e}^- \\
& \rightarrow \text{O}^* + \text{H}_2\text{O} + 2\text{OH}^- + 2\text{e}^- \tag{5.5-5.6}
\end{align*}
\[
\rightarrow \text{HOO}^* + \text{H}_2\text{O} + \text{OH}^- + 3\text{e}^-
\]  
(5.7)

\[
\rightarrow \text{O}_2 + 2\text{H}_2\text{O} + 4\text{e}^-
\]  
(5.8)

Especially the free binding energy of the intermediate can be adjusted by changing the surface structure, various element doping or alloying resulting in faster kinetics or smaller overpotentials. To exemplify this for the oxygen electrode, the free binding energies of an ideal catalyst for the three intermediates HO*\text{, }O^*\text{, and HOO}^* at 1.23 V and at 0 V is shown in Fig. 5.3A.

The situation in Fig. 5.3A represents a perfect catalyst at an electrode potential of 0 V vs the reversible hydrogen electrode, showing identical spacings of the binding energies of all intermediates along the reaction path. At the equilibrium potential of 1.23 V, all binding energies fall on the identical straight horizontal line, implying no free energy barriers. Due to the scaling relations between the different intermediates, it is not possible to adjust each binding energy independently [7–9]. Accordingly, the two OER intermediates *—OH and *—OOH interact in a similar way with any catalyst surface, which limits the activity of even the best performing catalyst [10].

Using binding energy of one of the intermediates as a microscopic descriptor for the catalytic activity typically results in a so-called “thermodynamic” volcano curve. The volcano reflects the Sabatier principle [11]. For the OER activity, the energy of the second step from *—OH to *—O is a suitable descriptor due to the linear scaling relation between *—OH and *—OOH. Thus, this single descriptor can describe the potential-determining step for both strong and weak binding catalysts toward the OER. This is presented in the volcano curves of Fig. 5.4A in which the various catalyst surfaces at the left side of the volcano tip bind too strongly and at the right side bind too weakly.

As a consequence, for catalyst surfaces that bind too strongly, the overpotential originates from breaking a bond between the intermediates and the surface. For surfaces that bind too weakly the overpotential is related to bonds forming to the surface. Thus, the most suitable catalyst is located at the top of this volcano curves [10]. A suitable descriptor for the ORR is the Oxygen, *—O, chemisorption since each intermediate scales with the oxygen binding energy [12]. This is shown in Fig. 5.4B. Even though the scaling relations and the volcano plots are highly restricting causing overpotentials far from the thermodynamic limits, the Rossmeisl group postulated approaches to go beyond the volcano limits, by bypassing the scaling relations by introducing so-called “special active sites” [13,14]. This modified active sites consist of 3D sites which would make different intermediate binding energies possible. Different approaches to circumvent scaling relations are postulated by the group of Norskov and shown in Fig. 5.5.

The different approaches include material tuning as well as modifications of the environment, like electrolyte engineering that realizes different binding energies at
Fig. 5.3 Free energy profile of the water splitting reaction from left to right and the oxygen reduction reaction from (right to left) (A) for an ideal catalyst at 0 V and at 1.23 V and (B) for exemplary metal oxide (MeOₓ) catalyst at 0, 0.78, 1.23, and 1.60 V. Figure was inspired by J. Rossmeisl, A. Logadottir, J.K. Nørskov, Chem. Phys. 319 (1–3) (2005) 178–184.
sites close to each other. Consequently, it should be possible to modify the active site by using 3D modifications to go beyond the volcano plot. Every approach could theoretically circumvent scaling relations, even though, it is not sure if it is experimentally possible. Multisite surfaces, interfacial sites, and ensemble sites seem to be the most realistic approaches since confinement by realizing those 3D active site layers seems most challenging. In this context, it should also be possible to develop a bifunctional catalyst material that is active for the OER and the ORR having multisites with adjusted binding energies for both reactions. Bifunctional catalysts could enable new possibilities in future device design in a hydrogen-based economy. For example, cars loaded with solar panels could be filled with water and produce hydrogen during parking. Additionally, it would further enable new space savings in aerospace.

5.3 OER/ORR catalyst materials

The previous section demonstrated the challenge of identifying a single-phase catalyst material that shows a balanced bifunctional OER and ORR activity. Also, the scaling relations of the different intermediate species require artifices.

However, previously explored bifunctional oxygen catalysts for use in reversible fuel cells are still lacking long-term stability and performance. Also, even though their catalytic activity obtained in a three-electrode rotating disk electrode (RDE) setup is promising, the translation and realization of those same activities in gas-diffusion electrodes or catalyst coated membranes of single electrolyzer remain chal-

---

**Fig. 5.4** (A) Activity trends toward oxygen evolution, for rutile, anatase, Co$_3$O$_4$, Mn$_x$O$_y$ oxides. The negative values of theoretical overpotential were taken from Ref. [9]. (B) Trends in oxygen reduction activity. Reprinted with permission from J.K. Nørskov, J. Rossmeisl, A. Logadottir, L. Lindqvist, J.R. Kitchin, T. Bligaard, H. Jónsson, J. Phys. Chem. B 108 (46) (2004) 17886–17892. Copyright 2004 American Chemical Society.
Fig. 5.5 Different approaches to circumvent the scaling relations.


Thus, complementing RDE tests, catalytic performance tests using realistic membrane electrode assemblies (MEA) is mandatory.

Over time, a number of bifunctional catalyst materials appeared that started in 2010 by a work of Gorlin et al. in which a manganese-based material was shown [16]. Based on this finding, MnOx was started to be investigated even further. In fact, the different phases of Mn-oxides were investigated by X-ray techniques and DFT calculations [17,18]. These investigations revealed superior OER/ORR activity and durability of the α-MnO2 and α-Mn2O3. However, calculations indicate that the catalyst likely undergoes phase changes at the surface as a function of applied potential [17]. In contrast, also Co3O4 nanocrystals on N-doped graphene showed high activity toward the OER and ORR with an overpotential of just \( \eta_{\text{OER}} = 310 \text{ mV} \) and the latter of \( \eta_{\text{ORR}} = 400 \text{ mV} \) in 1 M KOH [19]. Since they used carbon support, this material might lack in OER long-term stability. Another study by Xu et al. showed spinel cobaltite with the stoichiometry of \( \text{Cu}_x\text{Mn}_{0.9-x}\text{Co}_{2.1}\text{O}_4 \) \( (x=0, 0.3, 0.6, 0.9) \) which were even tested in a membrane-based regenerative fuel cell [20]. While the catalyst material exhibited promising activity the large electrolytic resistance due to their used membrane affected the current density of the MEA. Also, perovskites were successfully investigated for its OER and ORR activity [21–24]. Similar to the dif-
different approaches in Fig. 5.5, a two-component approach was finally used to successfully present a competing bifunctional catalyst material and might also help for a future catalyst design.

In this context, a prominent catalyst in alkaline media is NiFe-layered double hydroxide (LDH), which shows superior OER activity [25–28]. In contrast, NiFe-LDH shows almost no sufficient ORR activity for use in a reversible electrolyzer. As shown in Fig. 5.6, also other oxide materials appear unsuitable for the ORR reaction so that oxide materials catalytically favor oxidation reactions rather than reduction reactions.

The distinct reaction conditions of OER and ORR may therefore require quite different catalyst properties. The most active and stable cathodic ORR catalysts consist of metal nitrogen-doped carbons (Me-N-C) and Pt-based metals and metal alloys [2, 29], while anodic OER catalysts consist of metal oxides [30–32]. Alternative precious metal-free catalyst candidates such as metal oxides, metal nitrides, metal oxynitrides, metal carbonitrides, and metal chalcogenides with ORR activities rivaling those of Me-N-C or platinum are unknown to date [2]. There is only one exception and that is the discovered α-MnO_2 catalyst, reaching activities very close to Pt, which could be a promising non-carbon-based ORR catalyst candidate without being OER active (Fig. 5.7) [33].

**Fig. 5.6** Diagram of different catalyst materials with the corresponding onset potential at 1 mA cm⁻² for ORR and 1 mA cm⁻² for OER.

This supports the challenge in finding a bifunctional OER/ORR active material consisting of only one single active site to equally catalyze all elementary reaction steps of two opposite chemical reactions.

Based on the suggestion of Nørskov and Rossmeisl et al., Dresp et al. [34] brought NiFe-LDH as most active OER catalyst material in atomic proximity to nanostructured Fe-N-C catalyst, a well-known ORR active catalyst material [35–40]. This two-component catalyst system now involved a number of different sites with distinct functionalities such as multisite surfaces and appeared to circumvent the limitations of a single active site (see Fig. 5.5) [41–43]. These multisites or catalytically active ensembles of surface atoms feature specialized surface sites for either the OER or the ORR. The physical mixtures of NiFe-LDH:Fe-N-C in a ratio 1:3 showed to this date unachieved bifunctional OER/ORR activity in 0.1 M KOH [34]. They explained the observed combined performance of a physical mixture by a simple two-phase system which provides two distinct and spatially separated ORR and OER catalytic sites that are sufficiently homogeneous to act as a contiguous catalyst film, yet are spatially separated enough not to interfere with each other. Further tests using an anion exchange membrane (AEM, Tokuyama A201) and a commercial reversible electrolyzer confirmed the bifunctional activity and proofed the validity for a two-component mixture even in real reversible electrolyzer devices. Also, the publication of Risch et al. showed a heterostructured Ba$_{0.5}$Sr$_{0.5}$Co$_{0.8}$Fe$_{0.2}$O$_{3-δ}$ (BSCF) on La$_{0.8}$Sr$_{0.2}$MnO$_{3-δ}$ (LSMO), which showed a clearly defined two-component surface.

**Fig. 5.7** Geometric current density (normalized to disk area) of δ-MnO$_2$,(15) β-MnO$_2$,(15), and α-MnO$_2$.(15). Reprinted with permission from Copyright 2016 Both panels contain Pt supported on carbon (Pt/C; 46 wt% TKK, Japan) (14) and glassy carbon as references. All measurements were obtained by cyclic voltammetry at 1600 rpm. Theoretical limiting currents for the four-electron and two-electron pathways are indicated by solid lines together with a ± 10% margin (dashed lines). Reprinted with permission from K.A. Stoerzinger, M. Risch, B. Han, Y. Shao-Horn, ACS Catal. 5 (10) (2018) 6021–6031. Copyright 2015 American Chemical Society.
with a combined overpotential that rivals the state-of-the-art bifunctional catalysts in literature [23].

Besides separated multisite catalyst surfaces, the interaction between the two components of the catalyst could also influence the mutual electronic and spatial structure at the boundary to form interfacial or ensemble sites, which was successfully demonstrated by theoretical DFT calculations from the group of Rossmeisl. They described Co- and Ni-modified RuO₂ surfaces which result in enhanced modified active sites that show activities beyond the volcano curve (Fig. 5.8) [13].

Consequently, the two-component concept opens a new catalyst design strategy for future bifunctional electrode applications. Important to consider is, however, the stability of the used materials. In literature many carbon-based materials are presented as highly active OER/ORR materials. But especially for the OER carbon-based materials lead to corrosion due to the high potential. Thus, they might be unsuitable for reversible oxygen electrodes even though they show high initial activity because they presumably lack long-term durability.

### 5.4 Seawater splitting fundamental (OER vs CIER)

Common water electrolyzers use highly purified freshwater. This purified water is then either alkalainized for alkaline electrolysis or directly used in PEM electrolyzers.

![Fig. 5.8](image_url) (A) Free energy diagram based on DFT calculations for conventional, Ni- and Co-modified ruthenia and the perfect catalyst for the four steps in the oxygen evolution reaction mechanism. The modified ruthenia catalysts have significantly stronger binding in S3 which is the potential limiting step for ruthenia. (B) Volcano curve of the theoretical overpotential for oxygen evolution processes based on the DFT calculations described in the literature for using the second charge transfer reaction as a descriptor. The star marks the position of an ideal catalyst, the *magenta circle* corresponds to Ni-modified ruthenia and the blue circle to Co-modified ruthenia. Reprinted with permission from N.B. Halck, V. Petrykin, P. Krtíl, J. Rossmeisl, PCCP 16 (27) (2014) 13682–13688. Copyright 2014 Wiley-VCH.
In contrast, ocean seawater represents 96.5% of the total water resources on earth and is therefore an almost unlimited resource for water electrolyzer applications. Consequently, it is desirable to utilize this reserve. Apart from solid contaminations and biological content, the major chemical problem of seawater when used as electrolyzer electrolyte are the various chemically active contaminating ions dissolved in seawater. Although the composition of seawater varies dependent on the region, the overall average salt concentration is estimated to be 3.5 wt% with a pH ~ 8 [44–47]. An overall mean ion composition of seawater with the corresponding reaction and the thermodynamic standard potential is shown in Table 5.1 [1].

Noticeable are the great shares of Na\(^+\) and Cl\(^-\) so that 0.5 M NaCl solution appears as a good adoption for natural seawater. However, also the oxidation of bromide would compete with the water oxidation, but due to the low concentration of Br\(^-\) in contrast to the Cl\(^-\) concentration, the competing oxidation reaction of Br\(^-\) is typically neglected.

Other technical challenges comprise durable electrolyzer components withstanding typical or specific seawater or wastewater contaminations such as positively charged main group or transition group metal ions, biological and bioorganic contaminants, and negatively charges electroactive complex anions. Such wastewater or seawater constituents cause serious parasitic electrocatalytic charge transfer processes at the electrolyzer electrodes. What is more, ion exchange membrane components are seriously affected by ion exchange and Coulombic interactions between functional membrane groups and contaminants. Direct seawater electrolyzer cells without polymeric ion exchange components are expected to meet the required future performance demands in terms of hydrogen yield and lifetime.

Bioorganic constituents of seawater, such as bacteria and small living organisms causing fouling processes are at the current stage not considered for the full seawater electrolyzer device so that just the chloride chemistry plays the current major role as a bottleneck for seawater electrolyzer. Thus, only the competing Cl\(^-\) chemistry is described in this section.

In 2016, Dionigi et al. presented a Pourbaix diagram based on the anodic seawater electrochemistry considering an 0.5 M NaCl concentration (Fig. 5.9) [50].

As shown in the Pourbaix diagram, the thermodynamics of the OER is favored over the anodic Cl\(^-\) oxidation for the total pH range. While at low pH the pH-independent chlorine evolution reaction (ClER) takes place, at high pH the pH-dependent hypochlorite formation occurs. Both equations are shown in Eqs. (5.9), (5.10):

\[
\text{ClER : } 2\text{Cl}^- \rightarrow \text{Cl}_2 + 2e^-;
\]

\[
E^0 = 1.36 \text{ V vs SHE, pH 0} \tag{5.9}
\]
Table 5.1

Table 5.1 Standard mean chemical composition of seawater species with the corresponding redox reaction and electrochemical standard potential $E^0$ at different pH [48,49].

<table>
<thead>
<tr>
<th>Species</th>
<th>Conc. in $[\text{mol kg}_{\text{H}_2\text{O}}^{-1}]$</th>
<th>Conc. in $[\text{g kg}_{\text{H}_2\text{O}}^{-1}]$</th>
<th>Reaction [49]</th>
<th>$E^0$</th>
<th>Reaction [49]</th>
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<td>–</td>
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<tbody>
<tr>
<td>CO\textsubscript{3}\textsuperscript{2−}</td>
<td>0.00027</td>
<td>0.0162</td>
<td>–</td>
<td>–</td>
<td>–</td>
<td>–</td>
</tr>
<tr>
<td>OH\textsuperscript{−}</td>
<td>0.00001</td>
<td>0.0002</td>
<td>–</td>
<td>–</td>
<td>–</td>
<td>–</td>
</tr>
<tr>
<td>H\textsuperscript{+}</td>
<td>–</td>
<td>–</td>
<td>H\textsubscript{2} ⇌ 2H\textsuperscript{+} + 2e\textsuperscript{−}</td>
<td>0.0</td>
<td>4OH\textsuperscript{−} ⇌ O\textsubscript{2} + 2H\textsubscript{2}O + 4e\textsuperscript{−}</td>
<td>0.401</td>
</tr>
</tbody>
</table>
Fig. 5.9 Pourbaix diagram for artificial seawater model. A chlorine system, in the case of dissolved 0.5 m NaCl aqueous solution and no other chlorine sources, with a total chlorine species (cT, Cl) of 0.5 m. The electrode potential for OER is also included (assuming oxygen partial pressure of 0.21 atm = 0.021 MPa). Two red square points show the operating potentials (vs SHE) after 1-h constant current electrolysis (10 mA cm$^{-2}$) with NiFe LDH catalyst in 0.1 m KOH + 0.5 m NaCl (pH 13) and 0.3 m borate buffer + 0.5 m NaCl (pH 9.2) electrolyte. The light blue box highlights our proposed design criterion.


Hypochlorite : $\text{Cl}^- + 2\text{OH}^- \rightarrow \text{ClO}^- + \text{H}_2\text{O} + 2\text{e}^-$;

$$E^0 = 0.89 \text{ V vs SHE, pH 14}$$

(5.10)

Both reactions are 2 e$^-$ transfer reaction with typical fast kinetics and small overpotentials. The OER is known for its sluggish 4 e$^-$ transfer reaction and the high overpotential (see Eqs. 5.1–5.8). Consequently, the difference of the thermodynamic potential of the OER and the chloride chemistry should be maximized. At low pH the difference of CIER ($E^0 = 1.36$ V$_{\text{SHE at pH = 0}}$) and OER ($E^0 = 1.23$ V$_{\text{SHE at pH = 0}}$) is smallest with only $\Delta E_{\text{CIER-OER}} = 130$ mV. At higher pH values the difference becomes larger since the CIER is pH-independent. But at pH 3 the formation of hypochlorous acid starts followed by the hypochlorite formation at roughly pH 7.5. Unfortunately, these reactions are pH-dependent so that the potential difference will not increase with even higher pH value. The maximum potential difference of $\Delta E = 480$ mV is shown at the alkaline hypochlorite formation at pH $> 7.5$. Based on this,
high pH values facilitate the selective splitting of seawater into H₂ and O₂. In fact, Dionigi et al. elaborated a thermodynamic design criterion for the selective oxidation of seawater [50]. This design criterion calls for a limitation of the final working cell potential at or below 1.72 V_{RHE}, which is the thermodynamic standard potential of the hypochlorite formation at pH values above 7.5. Electrode potentials anodic of the design criterion likely leads to competing for undesired chloride-involved reactions. This chloride chemistry involves the formation of chlorine, hypochlorous acid (HClO), or hypochlorite (ClO⁻) depending on pH. All these product species are referred to as “free chlorine.”

While the design criterion is based on thermodynamics, it does not take into account the kinetic barriers associated with the various chemical reactions. It turns out that not a lot of materials show sufficient kinetic catalytic OER activity at electrode potentials below 1.72 V_{RHE}. These catalyst materials are described in the next section.

5.5 Seawater OER materials

The first work focusing on selective seawater appeared in 1980 in which Bennett showed a porous deposit of manganese on a typical DSA by using a manganese ion-doped electrolyte [51]. Instead of acting as a selective active site, they suspected the in situ-formed MnO₂ overlayer as a diffusional barrier to chloride, blocking the chloride from the catalytical active sites of the DSA leading to high OER selectivities. Almost 40 years later in 2018, this finding was supported by a work from Vos et al. in which an in situ RRDE selectivity measurement technique combined with online electrochemical mass spectrometry (OLEMS) measurements in combination with isotopic labeling indicated the same barrier effect (Fig. 5.10) [52,53].

Vos et al. proved this blocking effect of a protecting MnOx layer that is permeable for OH⁻ and water, but impermeable for other anions [52,53]. While the IrOx sublayer is highly active for the OER the MnOx overlayer protected the IrOx from contaminating ions such as Cl⁻. Consequently, the CIER was suppressed and the OER showed higher selectivities. On the one hand, this approach might even circumvent the thermodynamics presented in Fig. 5.9. However, at more anodic potentials higher 1.6 V the MnO₃ layer might become active for the OER and CIER itself alleviating the protecting effect.

Following the track of Bennett, Hashimoto, and coworkers started to investigate selective OER electrodes using modified manganese-based electrode materials with comparably low current densities of 1 mA cm⁻² at mainly low pH electrolyte doped with 0.5 M NaCl [54–63]. They directly coated the Mn-based layer on the IrO₂/Ti electrode to increase its duration. In contrast to the findings of Bennett, they also believed in the selective catalytical OER activity of MnOx. In the same way, El-Monheim et al. tested an electrode made of electrochemical deposited Mn-Mo-W on a Ti/IrO₂ net [64].
Fig. 5.10 The MnOx forms a porous, amorphous network on top of the IrOx layer, blocking CER by preventing Cl$^-$ from reaching the IrOx underneath. Reprinted with permission from J.G. Vos, T.A. Wezendonk, A.W. Jeremiasse, M.T.M. Koper, J. Am. Chem. Soc. 140 (32) (2018) 10270–10281. Copyright 2018 American Chemical Society.

In order to find a real selectively single active material, in 1984, Trasatti pioneered the reactivity of various metal oxides toward the OER and the CIER activity and identified a scaling between the OER and CIER activity as shown in Fig. 5.11 [65].

Fig. 5.11 Plot of the potential for Cl$_2$ against the potential for O$_2$ evolution at the same current density for a number of oxides. (○) alkaline and (●) acidic solutions are indicated. Reprinted from S. Trasatti, Electrochim. Acta 29 (11) (1984) 1503–1512.
In fact, RuO₂ as most active OER catalyst material appeared as the most active material for the CIER. Consequently, a catalytically inert active site that shows high activity regarding the OER seems even more challenging.

However, in 2009, a new generation of cobalt-based catalyst materials were discovered by Surendranath et al. that show impressing high OER activity in seawater related neutral pH [66]. In 2011, Esswein et al. presented an analogical cobalt phosphate and borate-based catalyst material even tested in natural seawater [67]. In 2017, Cheng showed synergistic effect between the ions of natural seawater and the CoFe LDH catalyst material [68]. While these materials target the electrolysis in neutral pH close to the natural pH of seawater. But even though carbonate and borate ions are present in seawater, their average concentration is too low to sustain proton handling at high currents [69]. Hence, seawater might not be used without buffer or additives at current seawater electrolyzer progress but other solutions like membranes or different cell design might be possible to overcome this local pH change.

Also, NiFe-LDH appears as an ideal OER electrolyzer catalyst as it unfolded its potential before free chlorine is observed (see Fig. 5.9). Hence this material was investigated as single anode material using a full single-cell membrane-based seawater electrolyzer [70]. For benchmarking reason typical Pt/C 46.7 wt% (TKK) was used as cathode material and explored the behavior of a full single-cell seawater electrolyzer using Tokuyama A201 as AEM, NiFe-LDH as an anode, Pt/C as a cathode material. Since seawater splitting is favored at high pH, and large local pH changes toward more acidic conditions typically occur in unbuffered electrolytes near the reactive electrolyzer OER electrode surfaces [69], the artificial seawater was alkalinized with 0.1, 0.5, and 1 M KOH.

When the effect of seawater was investigated, 0.5 M NaCl-containing electrolytes showed a strong electrolyzer performance drop compared to pure KOH solutions and additional stability tests have shown that the overall cell performance decreased to 50%–70% after 100 h at 1.6 V. This was in contrast to isolated, prior catalyst tests in which NiFe-LDH proved its suitability as seawater oxidizing catalyst because no influence of NaCl on the NiFe-LDH catalyst performance was observed. Also, restarting the measurement revealed a recovery effect of the electrolyzer cell performance. From these results and complementary control tests, they conclude that the experimental instability of the seawater cell was more related to the membrane performance than the catalyst performance.

However, commercial seawater electrolyzers require faradaic efficiencies at least on par with today’s liquid alkaline electrolyzer, ideally on par with PEM electrolysis and durability of 100,000 h. In this context, Kuang et al. proofed the suitability of NiFe as a seawater anode and investigated a NiFe-/NiSₓ-coated Ni foam electrolyzer anode [71]. In strongly alkalinized seawater these electrodes showed stable current densities for about 1000 h. Whether Ni or Fe is the active site remains under debate. Using XAS analysis with DFT + U calculations Friebel et al. indicate the incorporated Fe³⁺ as an active center in the Ni₁₋ₓFeₓOOH material since the Fe incorporation into γ-NiOOH changes the chemical bonding between this cation and the intermediates involved in the OER [72]. Görlin et al. supported this finding [73] and Burke et
agreed on Fe as an active site, but emphasize an additional influence of local geometric structure on activity such as Fe in edge/defect sites vs bulk sites [74]. While Friebel et al. and Görlin et al. see a nonappearance of Fe$^{3+}$ ↔ Fe$^{4+}$ oxidation using XAS methods, especially Bard and Chen et al. have shown evidence for Fe$^{4+}$ using Mössbauer spectroscopy [75, 76].

In contrast, Dresp et al. [70] showed already a high oxidation state of Ni in the NiFe-LDH at the activated state and measured at 1.0 $V_{\text{RHE}}$. Especially in seawater, no further oxidation was observed when the potential was increased to 1.6 $V_{\text{RHE}}$. As an explanation, the group of Boettcher showed an insulating character of the reduced NiFe-LDH phase below a potential of $\sim 1.4$ $V_{\text{RHE}}$ [26], which might prevent the reduction of the overlying NiFe-LDH film which was oxidized during the activation step. Consequently, a large amount of the metal centers, which were oxidized, remain oxidized and the bulk sensitive XAS, which observes the average valence state of the bulk, cannot directly discriminate among the various centers. To optimize the investigations the catalyst film thickness should be minimized as much as possible.

EXAFS evaluation focused more on the coordination number of the metal centers. Consistent with the oxidation state, the Ni- and Fe-centers showed especially for the seawater high coordination numbers (CN) after activation at 1.0 V. The lower CN for the 0.1 M KOH at activated 1.0 $V_{\text{RHE}}$ suggests a catalyzing oxidation effect by the higher ionic strength of NaCl. The stronger the ionic strength of the electrolyte the easier the oxidation during the activation step and the higher the coordination number of the activated metal centers. This is in agreement with the electrochemical measurement since the initial Ni$^{\text{ox/red}}$ redox features appear larger in higher concentrated electrolytes. Additional degradation effects by the appearance of Cl$^-$ were not determined. The local structure in both KOH and seawater rather attained identical after prolonged operation. This also supports the idea that membrane degradation processes are largely responsible for the experimental losses in catalytic performance.

Other technical challenges comprise durable electrolyzer components withstanding typical or specific seawater or wastewater contaminations such as positively charged main group or transition group metal ions, biological and bioorganic contaminants, and negatively charged electroactive complex anions. Such wastewater or seawater constituents cause serious parasitic electrocatalytic charge transfer processes at the electrolyzer electrodes. What is more, ion exchange membrane components are seriously affected by ion exchange and Coulombic interactions between functional membrane groups and contaminants [77]. Direct seawater electrolyzer cells without polymeric ion exchange components are expected to meet the required future performance demands in terms of hydrogen yield and lifetime.

5.6 Conclusion

The high cost of electricity, limited load flexibility, often combined with the high capital cost of polymer electrolyte membrane-based hydrogen electrolysis technolo-
gies, are some of the key barriers that limit a more widespread use of electrolytic hydrogen in energy or industrial applications. In selected locations of the world with abundant renewable electricity, however, direct seawater electrolysis using cheap, abundant, yet efficient catalyst materials could soon become a promising technology for hydrogen generation and electricity storage. In combination with fuel cells, stored electricity in form of hydrogen can be back converted, while freshwater is generated.

Single active sites seem to be not suitable as a bifunctional catalyst so that a two-component catalyst concept using a mixture of a highly OER and ORR active catalyst materials might circumvent the limitations by the occurrence of so-called multi-sites. While single active sites are active for only one reaction, these two-component catalysts gained a mutual activity increase. The mixture of NiFe-LDH and MnOx is suggested to employ a carbon-free OER/ORR bifunctional catalyst in future reversible electrolyzer devices.

The two-component catalyst system can also be suggested for future preparation of bifunctional oxygen electrode catalysts that simultaneously split directly seawater into hydrogen and oxygen. In a hydrogen-based economy, this bifunctional catalyst concept could enable new possibilities in future device design such as reversible seawater electrolyzers. Used as a fuel cell to back transform the hydrogen into electricity and freshwater would additionally enable a novel source for freshwater which could help these nations in future freshwater provision. However, for water production alone the reversible seawater appears not sufficiently effective [1]. The energy loss compared to the state-of-the-art reverse osmosis is too large. Therefore, a novel probable solution for freshwater production based on seawater electrolysis could additionally be presented. Nevertheless, the simplified setup and the direct usage of seawater make the seawater electrolysis extremely flexible and attractive for the production of hydrogen in the future.

As a forecast, the seawater electrolysis could be an attractive technology for prospective hydrogen production. The electrolyzer-fuel cell combination constitutes a universal working device for renewable energy transformations. Following the concept of a two-component catalyst, but with improved overall stabilities, MnOx could be a suitable and carbon-free ORR catalyst component. While the catalyst problems are mostly addressed and solved, the most important bottleneck to tackle in future would be the membrane. Necessary collaborations with membrane experts could address the corresponding parameter which is required for suitable future reversible seawater membrane technology. Also, a new electrolyzer design with an alternative separator concept could help to circumvent the membrane-induced problems such as in alkaline media commonly used Zirfon separator.

References