Carbonaceous Oxygen Evolution Reaction Catalysts: From Defect and Doping-Induced Activity over Hybrid Compounds to Ordered Framework Structures

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Oxygen evolution reaction (OER) is expected to be of great importance for the future energy conversion and storage in form of hydrogen by water electrolysis. Besides the traditional noble-metal or transition metal oxide-based catalysts, carbonaceous electrocatalysts are of great interest due to their huge structural and compositional variety and unrestricted abundance. This review provides a summary of recent advances in the field of carbon-based OER catalysts ranging from “pure” or unintentionally doped carbon allotropes over heteroatom-doped carbonaceous materials and carbon/transition metal compounds to metal oxide composites where the role of carbon is mainly assigned to be a conductive support. Furthermore, the review discusses the recent developments in the field of ordered carbon framework structures (metal organic framework and covalent organic framework structures) that potentially allow a rational design of heteroatom-doped 3D porous structures with defined composition and spatial arrangement of doping atoms to deepen the understanding on the OER mechanism on carbonaceous structures in the future. Besides introducing the structural and compositional origin of electrochemical activity, the review discusses the mechanism of the catalytic activity of carbonaceous materials, their stability under OER conditions, and potential synergistic effects in combination with metal (or metal oxide) co-catalysts.

1. Introduction: Catalytic Activity of Pure Carbon Allotropes and Necessity of Heteroatom Doping or Surface Modification

Driven by the awareness of the global warming potential of a large-scale green-house gas emission from the combustion of fossil fuels as well as economic considerations, enormous investments in renewable energy sources were made in the last decades.[6] Generation of “green” hydrogen by water electrolysis is thereby regarded to gain importance in the upcoming years to convert and store intermittent renewable electrical energy in form of chemical energy.[2] Hydrogen as a versatile energy carrier can thereby directly be used as fuel or employed in industrial processes replacing petro-chemically generated hydrogen or even hydrocarbons (if combined with CO2 electrolysis) allowing for a decarbonization in chemical industry (also known as “Power-to-X” concept).[2,3] Prerequisite for an efficient conversion of electrical energy by water splitting is the catalysis of both half-reactions, namely, the hydrogen evolution reaction (HER: \(2 \text{H}^+ + 2e^- \rightarrow \text{H}_2\)) and the oxygen evolution reaction (OER: \(2 \text{H}_2\text{O} \rightarrow \text{O}_2 + 4\text{H}^+ + 4e^-\)) (acidic), \(4 \text{OH}^- \rightarrow \text{O}_2 + 2 \text{H}_2\text{O} + 4e^-\) (alkaline)). There is a considerable research interest in the development of novel, highly active catalysts for the OER at the anode to increase the overall efficiency of electrolysis. This is explained by the fact that the OER requires a relatively high overpotential due to a rather complex four electron and proton-coupled pH-dependent reaction mechanism.[8] The relatively recent but already advanced acidic proton exchange membrane (PEM) electrolysis technology, which enjoys an upswing in the industrial and research interest, relies on scarce noble metal OER catalyst iridium and its oxide and is therefore limited regarding a

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large-scale application.\textsuperscript{[5]} Well-established electrolysis under alkaline conditions offers the advantage of a possible use of earth-abundant, nonnoble transition metal oxides (TMOs) with a special focus on the highly OER active Fe-doped Ni(OH)\textsubscript{2}, as well as cobalt-based electrocatalysts.\textsuperscript{[6]} One drawback of alkaline OER employing conventional TMO electrodes is however the partially low intrinsic conductivity of OER active “nonnoble metal” TMOs (e.g., NiO, Co\textsubscript{3}O\textsubscript{4}) that are mainly semiconductors or insulators, and therefore allowing only a limited possible current density due to high voltage losses in the electrolysis cell.\textsuperscript{[7]}

Carbon-based OER catalysts offer distinct advantages over pure metal and metal oxide-based OER catalysts: they offer an unprecedented structural variety and, in combination with heteroatoms, also an unrestricted compositional diversity and a good to excellent electrical conductivity.\textsuperscript{[8]} From the perspective of electrode design, carbon offers a light weight combined with a high mechanical flexibility. This combination increases the electrode stability under oxygen gas evolution (bubble formation), which can otherwise deteriorate rigid, nonflexible oxide structures under high current densities.\textsuperscript{[9]} From an ecological and economical perspective, virtually unrestricted availability of carbon and inexpensive synthesis are beneficial for a potential large-scale application of electrolysis technology.

In the following work, we want to introduce the structural and compositional origin of the electrocatalytic activity of various types of pure, heteroatom-doped, and hybrid carbon-based OER catalysts to give an overview of the recent developments in this field of research.

At this point, we want to refer to series of excellent review articles published in the recent years introducing various aspects of carbon-based electrocatalysis as well as OER catalysis in particular.

The first highly recommended overview articles to be mentioned were presented by Wu et al. in 2016 on carbon nanocomposite catalyst for oxygen reduction reaction (ORR) and OER followed by a work from Zhang et al. in 2017 on carbon-based electrocatalysts for the hydrogen and OER.\textsuperscript{[10]} More recent general review articles covering the topic of carbon-based electrocatalysts and to some extent OER catalysts include papers by Lai et al. and Deng et al. on 3D porous carbon electrodes for electrocatalytic applications and electrochemical energy storage, as well as a work from Younis et al. discussing noble metal-free 2D carbon-based electrocatalysts for water splitting.\textsuperscript{[11]}

A more specific but also highly recommended review article from Zhu et al. from 2017 discusses perovskite/carbon composite catalysts concerning their application in oxygen electrocatalysis and thereby presents an overview over the different types of interactions of carbon and metal oxides affecting the OER/ ORR activity.\textsuperscript{[12]} Finally, a review by Chen et al. from 2018 should be mentioned covering the topic of nanocarbon/oxide composites as bifunctional catalysts in alkaline fuel cell applications.\textsuperscript{[13]}

Our review sets its focus first on a critical discussion of the origin of OER activity in pure and heteroatom-doped carbon structures as well as highly active transition metal (metal oxide)/carbon composite electrodes with a relation to the applied synthesis route and resulting nanomorphologies (Scheme 1). In this context, most recent and promising examples of the individual classes of carbon-based OER catalysts are discussed in more detail. Additionally, the influence of heteroatoms and dopants on the structure and OER activity is critically assessed. Besides updating the literature on the most prominent carbon-based electrocatalysts, our work adds an overview of the recently introduced class of ordered carbon framework structures for electrocatalysis that have not been discussed in the earlier reviews mentioned above. Special focus is drawn to the relatively recent developments in the field of ordered 3D carbon (covalent organic framework (COF)) and carbon/metal (metal organic framework (MOF)) framework structures for OER catalysis. By offering various advantages over classical nonordered carbons, 2D and 3D heteroatom-doped carbon structures with a precisely controllable porosity, composition and local geometry of heteroatoms, and/or metal active sites...
are envisioned to allow the synthesis of carbon-based OER catalysts with even further increased electrocatalytic activity. Finally, an often neglected discussion about the corrosion stability of carbonaceous OER catalysts completes this literature overview.

1.1. OER Activity of Undoped Carbon Structures and Necessity of Heteroatom Doping

The overall efficiency of an OER catalyst is determined by three independent material properties, namely, the number of catalytically active sites, the intrinsic activity of the sites, and the electrical conductivity of the electrode (Figure 1).[14]

The electrical conductivity of carbonaceous structures is generally moderate to high and thus is typically not regarded as the limiting factor. The conductivity of graphene-based compounds greatly depends on their composition including the type of doping and the doping level as well as the type and the amount of defects, which are very much affected by the synthesis method.

Doping with nitrogen or other foreign atoms can follow via a substitution of carbon in the graphitic structure (with the formation of so-called “graphitic” N in case of nitrogen, Figure 2), or cause topological defects which act as scattering centers in the graphene lattice (so-called “pyridinic” N and “pyrrolic” N in case of nitrogen, Figure 2). As a consequence of the distorted lattice structure, a reduction of density of states (DOS) near the Fermi energy is expected. This opens a gap in the band structure of the zero-gap semiconductor of pristine graphene, which theoretically lowers the conductivity in the doped homolog.[16] A work on chemical vapor deposition (CVD) synthesized graphene by Wei et al. showed a reduction of the mobility from 300–1200 to 200–450 cm² V⁻¹ s⁻¹ for the N-doped graphene over the undoped homolog.[16] Other carbon allotropes investigated as OER catalysts include carbon nanotubes (CNTs) which theoretically exhibit intrinsic mobilities exceeding 10⁶ cm² V⁻¹ s⁻¹ and measured mobilities of 2–8 × 10⁵ cm² V⁻¹ s⁻¹ for undoped nanotubes but also strongly depend on the amount of defects caused by the synthesis method and dopants.[17] Fragments (exfoliated graphene nanoribbons) or graphene oxide thereby show lower mobilities of only up to ~200 cm² V⁻¹ s⁻¹.[56]

There is however a conflict between the conductivity and the electrocatalytic activity of carbon structures. It is widely accepted that pristine, undoped sp² hybridized carbon exhibits only poor intrinsic OER activity, which is ascribed to the symmetric distribution of valence and conduction band.[14,18] These are rather the defects introduced by synthetic methods or heteroatom doping that create the OER active sites. This explains the intensive research activity on heteroatom (N, S, P, B, etc.) doped carbon structures for OER catalysis in the recent years, which is further discussed with selected examples in Section 3. The origin of catalytic activity is thereby assigned to lattice defects introduced by heteroatoms as schematically depicted in Figure 9. The lattice defects can i) act as active sites on their own, ii) tune the electronic structure of the surrounding carbon phase, and/or iii) modulate the hydrogen binding energy.[16,14,16] For N-doped graphene, a modulation of the electronic structure of graphene in the vicinity of dopants resulting in catalytically active carbon sites is explained by a conjugation between the nitrogen lone-pair electrons and the graphene π-system.[19] More specifically, the more electropositive nitrogen withdraws electron density from the neighboring carbon atoms to transform them into OER active sites, but does not show a favorable OER activity as active site itself.[19]

The simplest case of nitrogen doping is given by a carbon-to-nitrogen substitution resulting in an isostructural graphitic nitrogen-doped single-walled carbon nanotube (SWCNT) or graphene structure. Further possibilities include pyridinic N with a present vacancy, and a pyrrolic N. The latter is either accompanied by a vacancy or obtained by a Stone–Wales rotational defect, and can be combined with protonation or oxidation.[20]

The multistep OER mechanism on doped carbon species is not fully described on an atomistic level in detail yet. However, significant progress has been made in elucidating potential active sites, the potential-determining step (PDS), and the spatial relation to doping atoms and defects in N-doped graphene or CNTs by theoretical methods based on the assumption of a four-step single-site water nucleophilic attack mechanism.[19,20]

In a recent work by Murdachaew and Laasonen, the active sites in undoped and N-doped SWCNTs and graphene with doping concentrations of around 1 at% were theoretically examined by density functional theory (DFT) methods. The authors compared the active sites originating from different lattice defects (atomic substitutions, vacancies, and Stone–Wales rotations) and different nitrogen functionalities (graphitic, oxidized, pyridinic, and Stone–Wales pyrrolic nitrogen systems) regarding their difference in binding energy of adsorption intermediates (ΔGₓₒ−ΔGₒₓₒ) of...
the PDS of the OER mechanism to calculate respective overpotentials as depicted in Figure 3 with their corresponding structures.[20]

Initial step in the assumed OER mechanism, which is also widely accepted for transition metal (metal oxide) active sites, is the binding of an \*OH adsorption intermediate at the partially negative charged carbon atom. In a second step, an \*O intermediate is formed by a proton-coupled electron transfer reaction, followed by the formation of a peroxide (\*OOH) intermediate as third step. The second and the third steps are both regarded as possible PDS or rate-determining step of the overall reaction (indicated in Figure 3b, d with corresponding overpotential). Finally, the reaction cycle is completed by the fourth step corresponding to the release of one oxygen molecule and the regeneration of the carbon active site.

It could be further shown by DFT methods that the carbon active sites also follow the so-called scaling relation. This relation, which was introduced initially for isolated or noncooperative active sites on transition metals and metal oxides, describes a linear dependency between the absorption energies of intermediates (\*OH, \*O, and \*OOH) that does not allow for an independent optimization of the individual reaction steps by modification of the active site.[20, 21]

Besides nitrogen-doped carbon, a variety of single and multiheteroatom doping experiments were conducted to enhance the overall OER activity. The overview of heteroatom doping with some selected examples is discussed in Section 3.

Beyond nitrogen, also other nonmetal heteroatoms such as O, B, P, or S can be introduced in sp2 hybridized carbon structures to alter the electronic structure of surrounding carbon and thereby tune the electrocatalytic properties. Selected examples that show an improved OER performance include S-doped CNT-graphene nanolobes or N and O co-doped carbon hydrogel films.[22] Co-doping carbon with a second or third heteroatom can thereby further enhance the OER activity due to synergistic effects between the dopants and due to doping-induced defects.[23]

The synergistic effect of N and P co-doping was investigated by Zhu et al. on a porous 3D carbon nanofiber hybrid material. By DFT calculations on pristine, N-doped as well as N and P co-doped carbon, the authors could verify the formation of electroactive sites with optimized charge distribution, which coactivated the neighboring carbon atoms (Figure 4a) via charge transfer between the carbon and the heteroatoms.[24] Results on the calculated overpotentials versus differences in the adsorption energies of OER intermediates, which typically form a “volcano” plot (Figure 4b), further confirm a slightly lower required overpotential for the dual doped carbon as compared to the single nitrogen-doped carbon structure. The former is significantly lower than the pristine carbon or even an IrO2 reference structure. Indication of a synergistic effect of the N, P dual doped carbon could be further attributed to an increased DOS at the Fermi level as compared to single N-doped or the pristine carbon structure (Figure 4c).[24]
However, clear reaction mechanisms describing the effects of multiheteroatom-doped carbon OER catalysts are still yet to develop. It is expected that it is not the intrinsic activity alone that is the cause of an enhancement by the co-doping, but mere a combination of several factors including defect density, nano-morphology, and conductivity that leads to an even higher electrocatalytic activity as compared to single doped counterparts.

Vapor-based or wet-chemical synthesis methods that are typically employed for fabrication of doped carbon structures provide limited possibilities for rational design and arrangement of heteroatoms around active site carbon atoms. Furthermore, analysis of the sites is often limited to spectroscopic measurements of ensembles, which further complicates the investigation of the OER active sites on the atomic level required for a detailed understanding of the mechanism. A chance to overcome this issue by the use of carbon-based framework structures with precisely defined atomic arrangements inherited by molecular building blocks is introduced in Section 5.

1.2. OER Activity in Carbon/Transition Metal (Metal Oxide) Composites: Conductive Carbon Matrices and Synergistic Effects

Besides the metal-free carbon-based OER catalysts, metal and metal oxide electrodes as well as single atom catalyst bound carbon structures were intensively investigated in the recent years with results presented in Section 4 in detail. At this point, the motivation and benefits of these composite catalysts should be highlighted.

Main advantages of a carbon-based composite electrodes are the high conductivity, structural variety, and robustness as well as flexibility with a possible high surface area and porous morphology enabled by complex continuous 3D structures. As discussed in the previous section, heteroatom (N, O, B, S, P, etc.) doping can further modulate the electronic structure leading to a further increased conductivity and formation of carbon active sites, but also modify the interface for an efficient binding of an inorganic phase. The combination of nonmetal (focus on nitrogen) and transition metal doping led to the development of Me-N-carbon composites with outstanding OER activity. For an introduced Co, N co-doped porous graphene like carbon nanosheet composite, the nonmetal doping with nitrogen is expected to present potential nucleation and anchor sites for Co and Co3O4 nanocrystals. According to Zhang et al., it is however not always clear whether the transition metal actually participates in the OER, as a similarly low overpotential has been observed also for only heteroatom-doped carbons.

Another broad class of composite compounds is TMOs, nitrides, phosphides, etc., supported on various types of (heteroatom-doped) carbon substrates. The catalytic activity of these composites is mainly determined by the intrinsic activity of the typically nanosized inorganic phase. Thus, the catalytic activity of N-doped carbon composites reported by Zhang et al. follows the trend FeNi > CoNi > FeCo < Ni < Fe, which is the same as the activity trend of unsupported first-row transition metal (oxy)hydroxides in alkaline media determined in the group of Boettcher group earlier. The trend thereby follows the Sabatier principle with an optimum in the adsorption strength of OER reaction intermediates on transition metal and oxide crystal facets, which can be used for the construction of a “volcano” curve of electrocatalytic activity of composite compounds.

A synergistic effect of carbon/transition metal (metal oxide) composite catalyst is also reported for the composite class of core–shell structures. The OER transition metal (or metal
oxide) active core is covered by a thin carbon shell, which increases the stability against dissolution under operation conditions and prevents agglomeration of small metal or oxide particles, which is a well-known cause for catalyst inactivation. The core structure of transition metal particles as well as their oxides, carbides, nitrides, phosphides, sulfides, or selenides is thereby regarded to affect the electronic structure of the thin carbon shell to increase its OER activity.[20,27]

To extend our knowledge about synergistic effects on the OER mechanism of metal-heteroatom-carbon composites, a rational material design and synthesis is required, which gives a precise control over the composition, porosity, and surface functionalization acting as anchor sites for the metal active sites.[28] All these requirements can be potentially met by carbon-based framework structures known as COFs and MOF that consist of molecular building blocks and eventually metal ions as coordination sites and linking nodes, respectively. These material classes will be introduced in more detail in Section 5.

1.3. Stability of Carbon-Based Electro catalysts under OER Conditions

The stability of carbon-based OER catalyst is often referred to as insufficient for long-term industrial application in PEM electrolyzer anodes when compared to TMOs catalysts such as IrO2.[29] It has to be however kept in mind that also IrO2, the “gold standard” of OER catalysts for PEM electrolysis, undergoes corrosion, albeit at a low rate.[30] There are recent studies on carbon corrosion related to the OER catalysis concerning carbon electrodes,[31] support material,[12] and hybrid OER catalyst.[33] Furthermore, the stability of carbonaceous materials was thoroughly investigated regarding the application as ORR catalysts supports in fuel cells.[34] The major concern using carbonaceous OER catalysts and support materials is thereby an oxidation-driven corrosion process that can lead either to a degradation or inactivation of the catalyst, or a loss of contact to attached metal (or metal oxide) nanoparticles.[35]

It is the low thermodynamic stability represented by low standard electrochemical potentials of 0.207 V versus standard hydrogen electrode (SHE) for CO2 and 0.518 V versus SHE for CO formation by oxidation, respectively, that presents the challenge for the application of carbonaceous materials under OER conditions at potentials exceeding 1.23 V versus SHE.[35] However, it is the reaction kinetics (corrosion rate) that decides on the durability of the carbonaceous material under certain operation conditions.

Thus, for the use of carbonaceous materials as supports in fuel cell electrodes, it should be kept in mind that a typical operation cathode potential of ≈0.9 V versus SHE significantly exceeds the onset potential of the carbon oxidation reaction. However, even in these thermodynamically unfavorable conditions, the corrosion reaction kinetic is still slow and negligible even for long-term operation. It is mainly the prolonged extended open-circuit potential step, or startup and shutdown cycles with possible reverse current conditions and resulting high potentials, that are reported to lead to a significant carbon corrosion.[36]

At even higher potentials required for OER, the carbon oxidation is further accelerated but can still be suppressed. The total anode current is given by the sum of the OER current and the carbon oxidation reaction current. Under constant current conditions with independent and competitive reactions, the overpotential, or more precisely, the decrease in overpotential is mainly determined by the most facile reaction, so that this reaction is responsible for a dominant portion of the overall current. A highly active OER catalyst on a carbon support or a metal-free carbonaceous OER catalyst with low overpotential thereby dominate the overall reaction kinetics, resulting in a low corrosion rate and high faradaic efficiency toward oxygen evolution.[35,36]

Experimentally, carbon corrosion was investigated by means of in situ surface-enhanced infrared spectroscopy, which proposes an initial CO2 formation followed by an ongoing CO release under OER conditions.[35] Furthermore, differential electrochemical mass spectroscopy was successfully applied to investigate the reasons for the decreased faradaic efficiency of the OER (93% at a potential of 1.45 V vs reversible hydrogen electrode (RHE)) for a carbon-supported IrOx catalyst, which was attributed to an ongoing carbon oxidation.[29] At the same time, there are different examples demonstrating that carbonaceous electrocatalysts can be operated with sufficient stability even at high current densities. Thus, Lee et al. reported a stable operation of a highly OER active IrCoOx/C electrolyt over 216 h at a current density of 5 mA cm2 at a potential between 1.5 and 1.6 V versus RHE.[32] After all, this indicates the possibility of a stable intermediate term operation of carbon-based OER catalysts, but also emphasizes the requirement for the development of electrocatalyst with high intrinsic activity.

2. Undoped and Unintentionally Doped Carbon Structures: From Synthesis to Surface Modifications

2.1. Synthesis and Catalytic Activity of Low Doping Level Carbon Materials

“Pure,” defect-free carbon materials have almost no appreciable activity toward OER catalysis as shown by various literature reports.[37] However, their performance can be drastically improved by introducing (non-) metal dopants like boron,[37d] nitrogen,[37e,37f,37i,38] oxygen, and phosphorous,[37f] by inducing defects[37g] or by the formation of hybrid materials.[37a–37g,37h,39] The concepts of doping and formation of heterostructures, which are intensively discussed in literature, will be reviewed in Sections 3 and 5.

The publications on nondoped defect-rich carbon materials for OER catalysis are scarce. Thus, Jia et al. reported the OER activity of defective graphene (DG),[37h] which was prepared from nitrogen-doped graphene by a high temperature pyrolysis strategy. The heat treatment decreased the N content from around 3.7 to 0.7 at% as evidenced by X-ray photoelectron spectroscopy (XPS). The resulting DG possessed a lot of structural defects, like pentagons, heptagons, and octagons that were assembled in different manner inside the graphene network. Linear sweep voltammetry (LSV) clearly demonstrated the beneficial effect of introducing defects or dopants into carbon materials on their electrocatalytic activity, as “pure” graphene has no obvious catalytic activity toward OER. The comparison of doped and defect-rich graphene reveals that the latter has a superior performance with a current density of 10 mA cm−2 reached at
a potential of 1.57 V versus RHE, and a decreased Tafel slope (97 mV dec⁻¹) indicating a favorable kinetics. The OER activity is even in the same range as a commercial Ir/C catalyst. Moreover, the DG features also a promising long-term OER stability shown by a 60 h chronopotentiometry measurement at a current density of 5 mA cm⁻² with no obvious change in the catalytic activity. The high OER activity of DG was ascribed by Jia et al. to the large amount of highly catalytic defect atomic sites supported by mechanistic OER pathway calculations.\[37e\]

The OER catalytic activity and stability of graphene is also dependent on its structural integrity. The latter is linked to the number of stacked layers as reported by Garcia-Miranda Ferrari et al. who prepared mono-, multi-, and few-layer graphene by CVD.\[40\] The authors have shown that the OER current density of the monolayer and the few-layer graphene suffers drastically decreases upon repeated LSV scans. The reduction in the electrocatalytic activity is accompanied by the destruction of the graphene sheets, which was clearly visible in corresponding Raman maps. The authors have explained the observed degradation by an insufficient structural integrity of graphene on the macroscale, which is not high enough to accommodate the changes in oxidation state during the OER. As another reason, they have suggested the mechanical destruction of the surface of the graphene sheets by frictional forces induced by the collapse of the formed oxygen bubbles (Figure 5).

Multilayer graphene shows higher cycling stability. The destruction of the top layer in this material occurs as well, but the many underlying layers still maintain its overall stability. Interestingly, the repeated LSV measurements show an increase in the OER activity assigned to the formation of defects. Consequently, the authors concluded that only multilayer graphene grown by CVD is applicable as OER catalyst in contrast to few- or mono-layer graphene.\[40\]

The importance of defects for the catalytic OER activity of carbon materials was also reported by Zhao et al. who investigated a carbon quantum dot/graphene (CQD/graphene) hybrid material.\[39\] The hybrid material was prepared by electrochemical exfoliation of graphite in propylene carbonate followed by a solvothermal step and a final annealing step. XPS analysis of the samples revealed a small oxygen content; further impurities have not been detected or are below the detection limit of XPS. The CQD/graphene composite reached a current density of 10 mA cm⁻² at a potential of 1.58 V versus RHE in 1 M KOH being only slightly higher as compared to a commercial RuO₂ catalyst (1.56 V vs RHE). Besides the favorable kinetics, the hybrid material showed an excellent stability with almost no changes in LSV after 2000 cycles. The authors attributed the good catalytic OER performance to the intimate contact between CQDs and graphene sheets enabling a rapid charge transfer, and to the numerous edge sites/defects on CQDs and graphene sheets providing a high content of catalytic active sites.\[39\]

CNTs attracted also lots of interest as quasi “pure-carbon” based catalysts for OER. CNTs are typically produced by CVD, which entails, however, the use of metal catalysts like nickel, cobalt, or iron that cannot be removed completely. Consequently, commercially available pure and high-quality CNTs are contaminated by 0.5–2.0 wt% of metallic impurities.\[41\] These impurities drastically influence the electrochemical performance as demonstrated, e.g., by Suryanto et al.\[41\] The authors introduced a new two-step method (Figure 6) enabling the reduction of metallic impurities at the surface and the interior of multi-walled carbon nanotubes (MWCNTs) down below 0.01 wt%.\[41\] In the first step, the as-received MWCNTs are treated with acid to remove surface bond metallic impurities resulting in raw MWCNTs (r-MWCNT). The r-MWCNT is subsequently mixed with melamine and heated to 1000 °C under an inert gas atmosphere yielding MelMWCNT, followed by an additional acid treatment. These steps are repeated for multiple times. After the fourth purification cycle, the metal content is decreased to 100 ppm, equaling to a reduction of 98.8% (Figure 6b).

The authors demonstrated that the OER performance of unpurified r-MWCNT (solid black line) and acid-washed r-MWCNT (black dashed line) is very similar. The unpurified melamine-treated MelMWCNTs (solid red line) reveal an improved performance as compared to the r-MWCNT samples, together with the appearance of the characteristic Ni²⁺/³⁺ redox feature. The authors reported that Ni, Fe, and Co ions entrapped

Figure 5. Schematic pathway of oxygen bubble-induced damage of mono-layer graphene during OER. Reproduced with permission.\[40\] Copyright 2019, Wiley-VCH.
in the interior of the MWCNTs are moved to the outside, which causes an opening of the nanotubes and thus an increase in the surface area after the melamine treatment. These structural issues were accounted for the enhanced OER performance. However, the acid-treated, purified MelMWCNTs (equaling to a removal also of those metal ions that have been moved from the interior by the melamine treatment) revealed a higher overpotential and a lower current density (Figure 6), which leads to a conclusion that the OER performance of MWCNTs is highly influenced by the amount of metallic impurities.\[41\]

Cheng et al. also analyzed CNTs that had metallic impurities like cobalt, iron, molybdenum, or nickel of around 3.45 wt\%, and hydrochloric acid-treated CNTs whose trace metal content was decreased to 1.38 wt\%.\[42\] However, the authors observed only little differences in the electrocatalytic activity of both types of CNTs. Moreover, Cheng et al. could show that the number of walls drastically influence the OER performance of CNTs. The highest activity was observed for three-walled CNTs (CNTs-3) with an onset potential of 1.64 V versus RHE and a current density of 56 mA cm\(^{-2}\) at 1.8 V versus RHE. The catalytic activity of CNTs with an increased or decreased number of walls is declined following a volcano-type dependency. The authors ascribe this behavior to the dual functionality of CNTs. The outer walls offer absorption and dissociation sites for different oxygen-containing species, and the inner walls enable fast electron transfer. With increasing number of walls, there is a reduced driving force for electrons to tunnel from outer to inner walls, thus reducing the OER activity. Moreover, the authors also compared the performance of the CNTs-3 to other carbon materials like graphite or activated carbon. Among three materials, the CNTs-3 has demonstrated the highest OER activity per surface area. Additionally, its performance was even superior to conventional 20 wt\% Ru-C and 50 wt\% Pt-C electrocatalysts.\[44\] Ali et al. also observed a correlation between the number of walls of MWCNTs and their resistance and electrocatalytic performance. The authors found that the resistance of CNTs gradually decreases with increasing number of walls (from three to five), but the electrocatalytic performance does not follow this trend. For the MWCNT-3, the onset potential of 1.63 V versus RHE and a current density of 0.45 mA cm\(^{-2}\) were measured, which change to 1.60 V versus RHE and 0.89 mA cm\(^{-2}\) in case of the MWCNT-4. The performance of the MWCNT-5 is however very similar to that of MWCNT-4, thus an additional increase in the number of walls does not result in a further enhancement of the OER performance.\[44\]

To assess the true electrocatalytic activity of CNTs only not by metal impurities, Gao et al. prepared SWCNTs in a metal-catalyst-free procedure using a SiO\(_2\)-coated Si wafer as substrate.\[52\] The resulting SWCNTs have an onset potential of 1.54 V and a current density of 10 mA cm\(^{-2}\) at an overpotential of 670 mV under basic conditions (0.1 M KOH). The authors demonstrated that the electrocatalytic activity can be drastically increased by loading the SWCNTs with buckminsterfullerene (C\(_{60}\)). The best performing C\(_{60}/\)SWCNT composite revealed an onset potential of 1.46 V and a current density of 10 mA cm\(^{-2}\) at an overpotential of 460 mV, which equals to a 5.3 and 50 times higher current density as compared to pure SWCNTs and C\(_{60}\) under the same conditions, respectively. The C\(_{60}/\)SWCNT composite has even a 1.2 times higher activity in comparison to a conventional RuO\(_2\) catalyst.

Due to their good electrical conductivity, CNTs are also often combined with noncarbonaceous materials, like metal oxides, phosphides, and sulfides, improving their catalytic activity as discussed later.

A compact overview of promising undoped or unintentionally doped carbon materials is given in Table 1.

### 2.2. Surface Functionalization

Surface oxidation of CNTs is another interesting strategy to improve the performance of this material class. Surface-oxidized CNTs can be prepared by acid, O\(_2\) plasma, hydrothermal, and electrochemical treatment or a combination of two or more of these techniques.\[37c,45\] The resulting surface-oxidized CNTs have commonly a superior OER activity as compared to the raw CNTs. The improved performance is generally attributed to the typically high surface hydrophilicity and the large amount of ketonic C=O groups.
influencing the electronic structure of the neighboring carbon atoms, which increases the adsorption of water molecules and oxygenated intermediates. A subsequent hydrothermal treatment can further modulate the oxygen functional groups toward a higher amount of C=O (Figure 7). Defects are also often discussed in context of surface-oxidized CNTs and their influence on the OER activity. However, in contrast to many other carbonaceous OER catalysts, a low amount of defects is reported to be more favorable as an increased electrical conductivity can be achieved, which is also important for a high OER activity.

Lu et al. prepared surface-oxidized MWCNT by combing the three mentioned techniques of acid, hydrothermal, and electrochemical treatment. The best activity was demonstrated by mildly oxidized MWCNTs whose performance was drastically increased as compared to strongly or weakly oxidized MWCNTs. The authors showed that the activity toward OER can be further enhanced by a hydrothermal treatment followed by electrochemical activation. The resulting surface-oxidized MWCNTs reached a current density of 10 mA cm$^{-2}$ at a potential of around 1.6 V versus RHE measured in 1 m KOH, equaling to an overpotential of 360 mV. Although nickel impurities were still detected inside the nanotubes after the acid treatment, the authors demonstrated that they did not contribute significantly to the overall performance.

Surface oxidation as a means to enhance the OER activity is applicable not only to CNTs. There are also reports on surface-oxidized carbon black, graphene, and carbon cloth (CC).

### Table 1. Comparison of different undoped and unintentionally doped carbons regarding their OER activity.

| Material                           | Impurity/doping elements | Impurity/doping level | Electrolytes | Potential versus RHE at 10 mA cm$^{-2}$ [mV] | Tafel slope [mV dec$^{-1}$] | Ref. |
|-----------------------------------|--------------------------|-----------------------|--------------|---------------------------------------------|-------------------------------|------|
| Graphene                          | N/A                      | N/A                   | 1 m KOH      | No activity                                 | N/A                           | [37e]|
| Defective graphene                | N                        | 0.7 at%               | 1 m KOH      | 1570                                        | 97                            | [40] |
| Few-layer graphene                | N/A                      | N/A                   | 0.1 m KOH    | 1610@0.85 µA cm$^{-2}$                      | N/A                           | [40] |
| Multilayer graphene               | N/A                      | N/A                   | 1400@3.23 mA cm$^{-2}$ | N/A                         | [40] |
| Carbon QD/graphene                | O                        | N/A                   | 1 m KOH      | 1579                                        | 44                            | [39] |
| Raw CVD-MWCNT                     | Fe, Co, Ni, O            | Ni: 9907 ppm          | Fe: 102 ppm  | 1 m KOH                                     | N/A                           | [41] |
|                                  |                          | Co: 71 ppm            |              |                                             |                               |      |
|                                  |                          | Ni: 44 ppm            |              |                                             |                               |      |
|                                  |                          | Co: < 1 ppm           |              |                                             |                               |      |
| HCl-treated MWCNTs               | Ni: 5204 ppm             | Fe: 19 ppm            | Co: 44 ppm   | 1690                                        | 153                           |      |
| HCl/melamine-treated MWCNTs      | Ni: 107 ppm              | Fe: 13 ppm            | Co: < 1 ppm  | 1630                                        | 64                            |      |
|                                  |                          | Ni: 1 ppm             |              |                                             |                               |      |
| HCl-treated three-walled CNTs    | Fe, Co, Ni, Mo           | 1.38 wt% trace metal content | 1 m KOH      | 1680                                        | 60/120                        | [42] |
| C$_{60}$                          | N/A                      | N/A                   | 0.1 m KOH    | 2250                                        | 50.5                          | [37c]|
| SWCNT                             | O, Si                    | N/A                   |              |                                             |                               |      |
| C$_{60}$/SWCNT                    | O, Si                    | N/A                   |              |                                             |                               |      |
| Surface-oxidized MWCNT           | Fe, Co, Ni, O            | Ni: =25 ppm           | Co: < 1 ppm  | 1700@3.4 mA cm$^{-2}$                       | 73                            | [44a]|
|                                  |                          | Fe: =30 ppm           |              |                                             |                               |      |
|                                  |                          | Ni: 1.0 at%           |              |                                             |                               |      |
| Surface-oxidized MWCNT           | Fe, Co, Ni, O            | Ni: 3300 ppm          | Co: 32 ppm   | 1590                                        | 41                            | [37j]|
|                                  |                          | Fe: 3 ppm             |              |                                             |                               |      |
|                                  |                          | Ni: 2.2 at%           |              |                                             |                               |      |
| Surface-oxidized carbon black    | O                        | Ni, Fe, Co, N.D.      |              | 1850                                        | 69.1                          | [45] |
|                                  |                          | O: 8.87 at%           |              |                                             |                               |      |
| Oxidized laser-induced graphene  | O                        | Ni, Fe, Co, N.D.      |              | 1594                                        | 49                            | [46a]|
|                                  |                          | O: 11.6 at%           |              |                                             |                               |      |
| Plasma-etched carbon cloth       | O                        | 13.09 at%             | 1 m KOH      | 1680                                        | N/A                           | [46b]|
| Activated carbon cloth           | O                        | 11.3 at%              | 0.1 m KOH    | 1380                                        | 124                           | [47a]|
| Acidically oxidized carbon cloth | O                        | =4.7 at%              | 0.1 m KOH    | 1707                                        | 82                            | [47b]|
| Plasma-functionalized carbon cloth | O                      | 5.9 at%               | 1 m KOH      | 1593                                        | 66.7                          | [47c]|
| Tyramine-functionalized GO       | N, O                     | N: 34.3 at%           |              | 0.5 m KOH                                   | 1760@2 mA cm$^{-2}$           | 69   | [48a]|
|                                 |                          | O: 9.8 at%            |              |                                             |                               |      |
| Lysine-functionalized rGO        | N, O                     | N: 6.1 at%            |              | 1560                                        | 80                            | [48b]|
|                                 |                          | O: 14 at%             |              |                                             |                               |      |
| NH$_2$-functionalized carbon dots | N                      | 11.8 at%              | 0.1 m KOH    | 1600@16.5 mA cm$^{-2}$                      | N/A                           | [37g]|

**Note:** The table includes a variety of carbons such as graphene, defective graphene, few-layer graphene, multilayer graphene, carbon QD/graphene, and Raw CVD-MWCNTs, each with specific impurity/doping levels and performance metrics in terms of potential versus RHE at 10 mA cm$^{-2}$ and Tafel slope.
The increased OER activity of those materials, as compared to the untreated equivalents, is mainly associated with the increasing amount of ketonic groups.\cite{45,46,47a} Cheng et al. reported, e.g., surface-oxidized CC prepared via a piranha acid treatment.\cite{47b} Untreated CC has only a poor catalytic performance toward OER, with an onset overpotential of 474 mV and an overpotential of 649 mV to reach 5 mA cm\(^{-2}\). After acidic oxidation of the CC, a drastically improved performance can be observed. Excessive oxidation should however be avoided due to a decreased electrical conductivity of the resulting material. The best performing oxidized CC has an onset potential of 328 mV versus RHE and reaches a current density of 10 mA cm\(^{-2}\) at an overpotential of 477 mV. The oxidized CC delivers also excellent long-term durability with a loss in current density of only 9.7% over 1000 cycles.\cite{47b}

Another surface functionalization strategy of carbonaceous materials is presented by Sapner et al. who prepared tyramine-functionalized GO (T-GO) and lysine-functionalized rGO (Ly-rGO) materials as catalysts for OER.\cite{48} GO as a reference material demonstrates rather moderate catalytic activity (current density of 10 mA cm\(^{-2}\) achieved at a potential of 1.88 V vs RHE) in 0.5 m KOH.\cite{48b} After functionalization with tyramine, the potential to reach 10 mA cm\(^{-2}\) is reduced to around 1.7 V versus RHE. Chronoamperometric measurements demonstrate a high stability of T-GO during OER (Figure 8c). The improved performance is ascribed to the functional groups of tyramine, which enhance the electron transfer at the interface via a postulate four step process depicted in Figure 8.\cite{48a}

Functionalization of GO with lysine, which is accompanied by the reduction of GO to rGO, results in a further enhancement of the OER activity represented by a potential of 1.56 V versus RHE to reach 10 mA cm\(^{-2}\) and a Tafel slope of 80 mV dec\(^{-1}\) (Figure 8g,h). The authors suggest that the increased performance can be attributed to the various functional groups of lysine enabling an advanced multistep OER.\cite{48b}

Surface functionalization was applied also for carbon nanodots (CDs) to increase their OER activity.\cite{57e} Liu et al. have synthesized CDs with a particle size distribution of 4–8 nm in an electrochemical method and functionalized them with amidogen and phosphorous surface groups. Such functionalization is mandatory as the “pure” CDs have no obvious catalytic activity toward OER. The best performing NH\(_2\)-CDs reached a current density of 16.5 mA cm\(^{-2}\) at a potential of 1.6 V versus RHE, even outperforming an IrO\(_2/C\) reference catalyst (13.2 mA cm\(^{-2}\), 1.6 V vs RHE).\cite{48b}

### 3. Metal-Free, Heteroatom-Doped Carbon Composites

Beside the introduction of defects and the functionalization of the surface, the OER activity of carbon materials can be further enhanced by heteroatom doping. Various heteroatoms including B, N, O, F, P, and S have been used to tailor the structural, electrical, and chemical properties of carbon nanomaterials. The break of electroneutrality results in a doping-induced charge transfer which leads to the formation of catalytically active carbon centers while keeping the beneficial electrical conductivity.\cite{19,20} Depending on the doped element, several different configurations are possible for the implementation in the carbon network (Figure 9). In general, there exist two main synthetic approaches for the heteroatom-doping of nanocarbons resulting in single-doped, co-doped, and multi-doped OER catalysts. The first approach includes an in situ doping during carbon synthesis, and the second a postsynthetic treatment of preformed carbon materials. Several different materials with tunable molecular structure and morphology have been developed so far and will be reviewed in this chapter regarding the doping level and the doping element.

#### 3.1. Single-Atom Doping

Modulating the electronic structure of carbon-based materials often leads to a change in catalytic activity while keeping the beneficial properties like a high conductivity and a good stability, which are crucial for a potential long-term application. A compact overview of promising single-heteroatom-doped carbon materials is shown in Table 2. Nitrogen doping of different carbon materials has a long history especially for the ORR.\cite{49} However the application of this process to graphene (nitrogen-doped graphene, NG) to enhance its OER activity was
demonstrated only in 2013 by Lin et al.\[50\] NG with a doping ratio of 2.4 at% N was prepared via a simple pyrolysis of graphene oxide and polyaniline (PANI). The OER catalytic activity of this material with an overpotential of 416 mV at a current density of 1 mA cm$^{-2}$ in 0.1 M KOH outperformed the undoped graphene and a commercial Pt/C catalyst. Due to the fact that the atomic size of nitrogen is similar to that of carbon, it can be easily incorporated in the graphene framework substituting carbon in several different forms, including pyridinic N, pyrrolic N, and quaternary N. Therefore, in the same year, Zhao et al. synthesized a nitrogen-doped carbon material by pyrolyzing the hybrid of a melamine/formaldehyde polymer and nickel nitrate at 700 °C and consecutive etching of the metal oxide showing a current density of 10 mA cm$^{-2}$ at an overpotential of 380 mV measured in 0.1 M KOH.\[51\] Based on the XPS measurements of N-doped carbons with different N/C ratios, the authors proposed that the high oxygen evolution activity originates from pyridinic-N or/and quaternary-N-related active sites.

Three years later, Yang et al. also confirmed that pyridinic-N with p-type doping character is responsible for the OER.

Figure 8. a) Schematic structure of tyramine surface-functionalized GO (T-GO), b) Fourier-transform infrared spectra of GO and T-GO, c) chronamperometric current stability at 1.39 V versus RHE of T-GO and the corresponding LSV curves before and after this measurement in the inset. d) Probable OER reaction mechanism of T-GO. e) SEM and f) TEM image of lysine surface-functionalized rGO (Ly-rGO) and the resulting LSV curve, g) overpotential at 10 mA cm$^{-2}$, and h) Tafel slope. a–d) Reproduced (adapted) with permission.\[48\] Copyright 2019, The Authors. Published by The Royal Chemical Society. e–h) Reproduced (adapted) with permission.\[48\] Copyright 2020, American Chemical Society.

Figure 9. Schematic summary of the heteroatom doping configurations. Gray, green, navy, red, blue, orchid, and yellow represent C, B, N, O, F, P, and S atoms, respectively.
activity of N-doped carbons proven by X-ray absorption near-edge structure (XANES) spectroscopic measurements on N-doped graphene.[52] In a novel strategy developed by the authors, N-doped graphene nanoribbons with an interconnected 3D network architecture were synthesized via the pyrolysis of a mixture of melamine and L-cysteine under Ar atmosphere. The material showed a low overpotential of 360 mV at 10 mA cm\(^{-2}\) measured in 1.0 m KOH with a small Tafel slope of 47 mV dec\(^{-1}\), which is even lower than for Ir/C (54 mV dec\(^{-1}\)). In the XANES spectra, the broadening of the pyridinic-N peak at \(\approx 398.0\) eV from 0.8 to 1.15 eV was observed, while the other peaks, including graphitic and pyrrolic N, remained unchanged. The authors ascribed the energy increase to adsorbed OOH* and O* intermediates on carbon atoms next to the pyridinic-N during OER. Hence, a high amount of pyridinic-N seems important for a good OER performance.

Several different single N-doped graphene-based materials are known until now\(^{[50,52,53]}\). These compounds are typically synthesized by either pyrolysis of nitrogen-containing carbon precursors like PANI or melamine, or by treatment of pre-formed graphene with ammonia-based chemicals. However, the synthesis of graphene often involves TMOs like iron oxide. In this case, it is very important to remove the metal catalysts completely, as even the smallest impurities may alter the catalytic activity in a strong way.\(^{[54]}\)

Another method to the synthesis of the defect-rich and ultrathin N-doped carbon nanosheets (NCNs) was developed by Jiang et al. who prepared the OER catalyst by simply pyrolyzing a mixture of citric acid and NH\(_4\)Cl at a temperature of 1000 °C under Ar atmosphere (Figure 10).\(^{[53c]}\) NH\(_4\)Cl acts in this case not only as nitrogen source for the NCNs but also as a foaming agent to construct a cross-linked 3D porous network structure with a high surface area of more than 1700 m\(^2\) g\(^{-1}\).

Table 2. Comparison of different single-heteroatom-doped metal-free nanocarbons regarding the OER activity.

| Doping elements | Material Precursors | Doping level | Electrolytes | Potential [mV] versus RHE at 10 mA cm\(^{-2}\) | Tafel slope [mV dec\(^{-1}\)] | Ref. |
|-----------------|---------------------|--------------|--------------|---------------------------------------------|-----------------------------|-----|
| B               | Multi-walled CNTs   | Boric acid   | B 1.51–2.37 at% | 0.1 m KOH | 1881 | N/A | [57] |
| N               | Few-layer graphene  | PANI         | N 2.4 at% | 0.1 m KOH | 1646 @ 1 m KOH | N/A | [50] |
| N               | CNTs on rGO         | Ethylene diamine | N 3.9 at% | 0.1 m KOH | 1768 | N/A | [55a] |
| N               | Graphite nanomaterial | Melamine formaldehyde | N 3.54 at% | 0.1 m KOH | 1610 | N/A | [31] |
| N               | Surface N-doped CNTs | Pyridine     | N 2.38 at% | 0.1 m KOH | 17 580 | N/A | [55c] |
| N               | Graphene nanotube hybrids | Ethylene ammonia | N 0.53 at% | 0.1 m KOH | 1630 | 83 | [53a] |
| N               | Graphitic C\(_2\)N\(_4\) nanosheets/ graphene composite | Melamine | N – 57 at% | 0.1 m KOH | 1759 | 68.5 | [53d] |
| N               | Graphene            | Ammonia      | N 3.97 at% | 0.1 m KOH | 1786 @ 1 mA cm\(^{-2}\) | N/A | [53b] |
| N               | CNTs                | Acetonitrile | N 2.4 at% | 0.1 m KOH | 1680 | N/A | [55b] |
| N               | Graphite nanomaterial | Carbon cloth | N 1.92 at% | 1.0 m KOH | 1850 | 98 | [56a] |
| N               | Graphene nanoribbons | Melamine L-cysteine | N 3.9 at% | 1.0 m KOH | 1590 | 47 | [52] |
| N               | Graphitic carbon microtubes | Facial cotton | N 2.0 at% | 0.1 m KOH | 1520 | N/A | [56b] |
| N               | CNTs-supported C\(_2\)N\(_4\) | Melamine CNT-CF | – | 1.0 m KOH | 1600 | N/A | [53e] |
| N               | Multi-walled CNTs   | PANI emeraldine salt | N 0.5 at% | 1.0 m NaOH | 1550 | 68 | [37i] |
| N               | Defect-rich porous graphitic carbon | Nitrogen-enriched polydopamine analog | N 9.36 at% | 1.0 m KOH | 1590 | 57 | [56c] |
| N               | Carbon nanocages    | Ammonia      | N 3.05 at% | 0.1 m NaOH | 1690 | N/A | [56d] |
| N               | N-doped graphite on carbon black | 1-ethyl-3-methylimidazolium bromide | N 1.23 at% | 0.5 m H\(_2\)SO\(_4\) | 1700 | 226 | [56e] |
| N               | N-doped carbon nanosheets | Citric acid Ammonium chloride | N 2.46 at% | 0.1 m KOH | 1640 | 142 | [53c] |
| N               | Graphene-supported N-doped carbon | Glucaminium-based ionic liquids | N 26 at% | 1.0 m KOH | 1560 | 52 | [53f] |
| N               | Graphitic mesoporous \(\text{C}_{2}\text{N}_{4}\) | Guanidine hydrochloride | N 48 at% | 1.0 m KOH | 1606 | 52.4 | [56f] |
| F               | Fluorinated graphdiyne | Carbon Cloth, 1,3,4-triethynyl-2,4,6-triflorobenzene | – | 1.0 m KOH | 1690 | 128 | [58] |
| P               | P-doped graphene | Red phosphorus graphite | P 0.83 at% | 1.0 m KOH | 1560 | 62 | [37f] |
| P               | P-doped graphitic carbon | Sugar, sulfuric acid, red phosphorus | P 6.7 at% | 1.0 m KOH | 1690 | 179 | [59] |
| S               | CNT-graphene nanolobes | Thiourea Benzyldisulfide | S 1.19 at% | 1.0 m KOH | 1580 | 95 | [22b] |
The material has an overpotential of 410 mV at 10 mA cm\(^{-2}\) measured in 0.1 M KOH with a comparably high Tafel slope of 142 mV dec\(^{-1}\), and a stable performance over 12000 s at 1.5 V versus RHE at a current density of 2 mA cm\(^{-2}\). DFT calculations suggest that carbon atoms located at the armchair edge and adjacent to the graphitic N dopants act as the intrinsic active sites for OER.

Nitrogen-doped CNTs can also be used as single-heteroatom-doped carbon catalyst.\(^{[37i,55]}\) This material can be produced by CVD of nitrogen-containing precursor like ethylene diamine or acetonitrile on different substrates always with the need of iron as a catalyst. Another possibility is a posttreatment of preformed CNTs with nitrogen-containing species and a consequent pyrolysis step. Davodi et al. have obtained nitrogen-doped MWCNTs (NMWCNTs) by mixing preformed MWCNTs with PANI emeraldine salt followed by sonication and subsequent pyrolysis at a temperature of 800 °C for 1 h under argon atmosphere (Figure 11).\(^{[37i]}\) The obtained NMWCNTs show a superior OER catalytic activity with a small overpotential of 320 mV at 10 MA cm\(^{-2}\) measured in 1.0 M NaOH and a Tafel slope of 68 mV dec\(^{-1}\), and excellent stability in chronoamperometric measurements at a constant voltage of 1.56 V versus RHE for more than 25 h. XPS measurements reveal the important role of pyridinic N as the main active sites for OER. In addition, the metal-free catalyst shows also excellent stability in chronoamperometric measurements at a constant voltage of 1.56 V versus RHE for more than 25 h.

Graphitic nitrogen-doped carbons also demonstrate a good activity toward the OER.\(^{[56]}\) Wahab et al., e.g., used a mesoporous SBA-15 silica nanotemplate to structure polymerized guanidine hydrochloride as a single-carbon-nitrogen source (gMesoCN).\(^{[56]}\) After pyrolysis, they obtained a metal-free graphitic mesoporous carbon nitride with a nitrogen content of 48 at% and a surface area of 406 m² g\(^{-1}\). Structural characterization showed the successful formation of a graphitic carbon nitride framework with uniformly sized pore channels of 4.56 nm. The mesoporous material showed an overpotential of 376 mV at 10 mA cm\(^{-2}\) measured in 1.0 M KOH with a Tafel slope of 52.4 mV dec\(^{-1}\). In long-term stability test, they observed a 98.4% retention of current density after 24 h at a voltage of 1.6 V versus RHE.

Additionally to nitrogen doping, several other single heteroatoms such as B,\(^{[57]}\) F,\(^{[58]}\) P,\(^{[37f,59]}\) and S\(^{[22b]}\) have been used to tune the electrochemical properties for effective OER. For example, Xiao et al. realized edge-selective P doping of graphene by simply ball-milling of graphite and red phosphorus followed by several washing steps with water and annealing in argon atmosphere at 650 °C.\(^{[37f]}\) In this way, the authors were able to introduce up to 0.83 at% P in the carbon network. The P-doped few-layer graphene showed a small overpotential of 330 mV at 10 mA cm\(^{-2}\) measured in 1.0 M KOH with a Tafel slope of 62 mV dec\(^{-1}\). Besides the phosphorous doping, the authors have observed a large fraction of oxygen in the structure leading to defects with comparable effects as described in Section 2. Although traces of iron were present in their material, the authors have demonstrated that the high electrocatalytic activity mainly originates from the P dopant.

### 3.2. Multiheteroatom Doping

Numerous examples described in the previous section demonstrate that electrocatalysts with a high OER activity can be obtained via doping of different carbon materials with nitrogen atoms as elaborated in Section 3.1. A further improvement in conductivity, stability, and activity is assumed for the doping with two or more heteroatoms due to positive synergistic effects between the dopants. Difficulties lie in the control of the doping amount and the characterization of active sites and catalytic effects. Several different combinations of heteroatoms have been developed such as N,B,\(^{[60]}\) N,O,\(^{[22a,64]}\) N,F,\(^{[62]}\) N,P,\(^{[37a,63]}\) N,S,\(^{[64]}\) and even trivalent doped materials like N,O,F,\(^{[65]}\) N,F,P,\(^{[66]}\) N,P,S\(^{[67]}\) were synthesized.
An overview of these materials and their OER performance is given in Table 3. Gao et al. have developed an elegant approach to obtain a trifunctional N,P co-doped hollow carbon nanofiber membrane using the coaxial electrospinning of a triphenylphosphine containing polyvinylpyrrolidone (PVP) core solution together with a dicyandiamide containing polyacrylonitrile (PAN) shell solution.\cite{63b} Pyrolysis of the nanofibers at 1000 °C under argon resulted in N,P-co-doped hollow nanofibers with a tunable doping content depending on the concentration of used PAN. Due to the plentiful active sites, continuous pathways, and benign mass transfer channels in this material, a current density of 10 mA cm\(^{-2}\) was reached at a very low overpotential of 330 mV in 0.1 m KOH. Additionally, the N,P-doped hollow fibers showed a better stability than IrO\(_2\) under continuous operation for 20 000 s. However, the material exhibited a high Tafel slope of 248 mV dec\(^{-1}\) as compared to 97 mV dec\(^{-1}\) for IrO\(_2\), which indicates unfavorable OER kinetics.\cite{63b}

An example of controlled doping for effective synergistic effects between different heteroatoms was shown by Zhao et al.\cite{64d} Based on their previous work on site-defined doping of acetylinic groups of graphdiyne, the authors were able to synthesize a stereodefined heteroelement co-doped catalyst by introducing both S and sp-N atoms. This was achieved by heating melamine and dibenzyl sulfide together with few-layer graphdiyne at different calcination temperatures for 150 min. The highest electrocatalytic activity was measured for the material pyrolyzed at 900 °C with a nitrogen and sulfur content of 11.55 and 3.66 at%, respectively. This catalyst has shown an outstanding OER performance with an overpotential of 299 mV at 10 mA cm\(^{-2}\) measured in O\(_2\)-saturated 1.0 m KOH, and even a smaller Tafel slope (62 mV dec\(^{-1}\)) than the RuO\(_2\) (69 mV dec\(^{-1}\)), pointing to even faster OER kinetics of the carbonaceous material than the noble metal catalyst. By tuning the doping concentration, the authors found that the introduction of sp-N in addition to a higher concentration of S decreases the overpotential significantly.\cite{64d}

Shinde and co-workers extended the number of dopants even further.\cite{67} P,S-doped carbon nitride sponges (P,S-CNS) were obtained by polymerization of aminoguanidine in the presence of phosphoric and sulfonic acid followed by a pyrolysis step and a consecutive crystallization of aminoguanidine CNPs with ethylene (Figure 12). The resulting P,S-CNS with a high surface area of 1474 m\(^2\) g\(^{-1}\) exhibited a low overpotential of 330 mV at 10 mA cm\(^{-2}\) measured in O\(_2\)-saturated 0.1 m KOH. This value was even lower than that of RuO\(_2\) with 340 mV. The Tafel slope of 64 mV dec\(^{-1}\) also outperformed that of RuO\(_2\) with 88 mV dec\(^{-1}\). XPS measurements indicated significant changes in N-bonding configurations with P and S dopants as compared to that of pure C\(_3\)N\(_4\) leading to the superior performance of the system.

4. Metal (Metal Oxide)/Carbon Hybrids

TMOs are highly popular and efficient catalysts for the OER with a variety of respective reports in the literature.\cite{68} As of now, catalysts based on precious metals such as Ir or Ru are considered state of the art.\cite{68a} However, the price and scarcity of these metals make them unsustainable for large-scale applications, which motivates the search for possible earth-abundant and cheaper alternatives.\cite{69} The nonnoble TMOs are intensively investigated as OER catalysts, however they generally suffer from a low electronic conductivity limiting
the currents that can be achieved in electrode assemblies.\cite{70}

One of the most popular approaches to increase the conductivity of TMO-based electrodes is their hybridization with highly conductive carbonaceous supports to form composite OER electrocatalysts. In this section, we provide an overview of the recent nonnoble metal oxide/carbon composite, mixed metal oxides/carbon composites, and core–shell metal oxide/carbon composite materials showing promising OER performance.

### 4.1. TMO/Carbon Composites for OER

#### 4.1.1. Cobalt Oxide-Containing Composites

Cobalt oxides generally show sufficiently high OER activity, with Co$_3$O$_4$ being one of the most popular compounds especially in combination with carbon-based materials.\cite{71} Thus, Zhang et al. synthesized an electrocatalyst composed of Co$_3$O$_4$ nanoparticles anchored on a nitrogen-doped reduced graphene oxide using

| Doping elements | Material Type | Precursor | Doping level | Electrolytes | Potential [mV] versus RHE at 10 mA cm$^{-2}$ | Tafel slope [mV dec$^{-1}$] | Ref. |
|-----------------|---------------|-----------|--------------|--------------|---------------------------------|--------------------------|------|
| B, N            | Unzipped MWCNTs | Boron oxide | B 11.3 at% N 11.1 at% | 0.1 M NaOH | 1872 | N/A | [60a] |
| B, N            | Graphitic carbon spheres | Boric acid | B 1.51 at% N 7.94 at% | 0.1 M KOH | 1992 | N/A | [60b] |
| N, O            | CNT- graphene composite | Graphite oxide | N 7.59 at% O 15.72 at% | 0.1 M KOH | 1690 | 141 | [22a] |
| N, O            | Graphene nanosheets/ carbon cloth composite | Methane Carbon cloth | N 2.05 at% O 8.86 at% | 1.0 M KOH | 1580 | 38 | [61] |
| N, F            | Graphene nanosheets | Resin KF | N 0.89 at% F 0.49 at% | 1.0 M KOH | 1570 | 78 | [62a] |
| N, F            | N,F-co-doped carbon black | Melamine Polytetrafluoroethylene | N 4.78 at% F 0.7 at% | 0.1 M KOH | 1609 | 69 | [62b] |
| N, P            | P-C$_3$N$_4$-Nanosheets | Melamine-ethylene diphosphonic acid | N 13.2 wt% P 0.9 wt% | 0.1 M KOH | 1630 | 61.6 | [37a] |
| N, P            | Graphitic carbon | Aniline Phytic acid Ammonium persulfate | N 3.2 at% P 1.1 at% | 0.1 M KOH | 1950 | 330 | [63a] |
| N, P            | Hollow carbon nanofiber | Triphenylphosphine Polycrylnitrile Cyanamide Electrospinning | – | 0.1 M KOH | 1550 | 248 | [63b] |
| N, S            | Graphene/CNT composite | Urea thiourea | N 0.71 at% S 1.26 at% | 0.1 M KOH | 1908 | 103 | [64a] |
| N, S            | N,S-doped graphic sheets | Melamine, Nickel sulfate | N 2.1 at% S 0.8 at% O 3.8 at% | 0.1 M KOH | 1600 | 71 | [64b] |
| N, S            | N,S-doped CNTs | Polydopamine 2-mercaptoethanol | N 3.8 at% S 5.6 at% | 1.0 M KOH | 1560 | 56 | [64c] |
| N, S            | N,S-doped graphene nanosheets | Melamine Dibenzyl sulfide | N 11.55 at% S 3.66 at% | 1.0 M KOH | 1529 | 62 | [64d] |
| N, S            | N,S-doped graphene | Dopamine 2-mercaptoethanol | N 4.29 at% S 1.35 at% | 1.0 M KOH | 1511 | 109 | [64e] |
| N, O, F         | Porous graphite | Aniline phytic acid OOC | N 0.46 at% O 16.4 at% P 0.32 at% | 1.0 M KOH | 1660 | 84 | [65] |
| N, F, P         | N,F,P-doped graphene | PANI Hexafluorophosphate | N 7.11 at% F 0.33 at% P 0.37 at% | 0.1 M KOH | 1810 | 136 | [66] |
| N, P, S         | Sponge like C$_3$N$_4$ | Aminoguanidine hydrochloride Phosphoric acid Methanesulfonic acid | N 41.36 at% P 1.68 at% S 1.59 at% | 0.1 M KOH | 1560 | 64 | [67] |

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The table above provides a comparison of different multiheteroatom-doped metal-free nanocarbons regarding their OER activity.
hydrothermal reaction.[72] The beneficial combination of the nanosized character of the anchored particles with the high conductivity of graphene resulted in a very active catalyst with performance values similar to that of commercially available RuO$_2$.

The impact of the carbonaceous substrate on the catalytic activity of the Co$_3$O$_4$-based composite was investigated by Asiri et al. who deposited Co$_3$O$_4$ nanoparticles on graphene oxide (GO), graphene (G) and CNTs.[73] Among tested compounds, the graphene-based hybrid material exhibited the highest activity with an overpotential of 535 mV at 10 mA cm$^{-2}$ and a Tafel slope of 127 mV dec$^{-1}$ in 1.0 M KOH.

Besides the origin and the morphology of the carbonaceous substrate, the activity of composites also depends on the morphology of the cobalt oxide catalyst as shown for a hybrid material based on Co$_3$O$_4$ nanorods combined with CNTs.[74] By utilization of a dithylenetriamine-assisted synthesis, the authors obtained well-defined Co$_3$O$_4$ nanorods anchored onto MWCNTs (Figure 13a–f) resulting in a well-connected network with high

Figure 12. a) Schematics showing the synthesis of P,S-CNS catalysts, and the reaction mechanism for the formation of the C–N polymeric complex. b) Photographs of as-synthesized cylindrical sponge-like P,S-CNS structure. c,d) SEM, e) TEM, and f) HRTEM images of P,SCNS catalyst (inset show enlarged view). Corresponding g) fast Fourier transform (FFT) pattern of the crystallite in the inset of (f). h) TEM and the elemental maps of C, N, P, and S of P,S-CNS (scale, 300 nm). Reproduced (adapted) with permission.[67] Copyright 2017, American Chemical Society.
surface area. Main features of this catalyst are a low overpotential of 309 mV at 10 mA cm\(^{-2}\) in 1.0 m KOH, a very low Tafel slope of 51 mV dec\(^{-1}\), and a high stability (Figure 13g–j).

There are several additional reports on similar hybrid materials to be found in the literature with a varying morphology of metal oxide but quite a performance similar to those of some of the commercially available catalysts.\(^{[75]}\) However, one of the challenges in understanding the mechanistic aspects of composite compounds is the identification of synergistic effects between the active particles and the substrate. To address this issue, Leng et al. performed the first-principle simulations and found that the Co\(\text{O}^{\cdot}\text{C}\) bonds play a crucial role toward the OER activity by introducing an extra step in deprotonation of HO\(^*\).\(^{[76]}\) Using the first-principle simulation results, the authors proposed a method for the synthesis of Co\(_3\)O\(_4\)/graphene composites, resulting in a material with OER overpotential of 316 mV at 10 mA cm\(^{-2}\) and a Tafel slope of 46 mV dec\(^{-1}\).

4.1.2. Iron Oxide-Containing Composites

Besides cobalt oxides, iron oxides attract a lot of attention as potential OER catalysts. Being very cheap, abundant, and benign, iron oxide is however poorly conducting. Therefore, for this class of materials, the hybridization with conductive carbon-based supports generally improves the electrocatalytic performance. Thus, Bandal et al. synthesized a hybrid catalyst composed of Fe\(_2\)O\(_3\) nanorods on CNTs using simple co-precipitation method.\(^{[77]}\) The hybridization has dramatically increased the electrical conductivity of the material and improved its OER performance for OER, characterized by an overpotential of 383 mV and a Tafel slope of 61 mV dec\(^{-1}\). The authors have demonstrated that the ratio between the iron oxide and the CNTs affects the electrochemical performance, with the highest activity obtained for the composite with the equal rations of iron oxide and the CNTs.

Even better electrocatalytic performance has been achieved for the composite compound containing Fe\(_2\)O\(_3\), NiS\(_x\), and reduced graphene oxide,\(^{[78]}\) which reaches a current density of 10 mA cm\(^{-2}\) at an overpotential of 330 mV in 1 m KOH solution. The authors concluded that a beneficial charge transfer from Ni sites to Fe sites takes place, whereas the reduced graphene oxide provides a good electrical conductivity. Importantly, this catalyst exhibited a significantly higher stability than the commercially available RuO\(_2\).

Wang et al. constructed an FeP, Fe\(_3\)O\(_4\), and N-doped graphene composite by electrospinning of iron acetylacetonate and PAN followed by several chemical and heat treatment steps. The obtained material showed activity toward multiple electrocatalytic reactions including OER.\(^{[79]}\) In this composite, FeP was the active material for the hydrogen evolution, while Fe\(_3\)O\(_4\) and N-doped carbon contributed to the catalytic activity of the catalyst toward OER.

In a very recent paper, Hof et al. have shown that the average size of iron oxide nanoparticles can be tuned depending on the choice of carbon starting material (Figure 14).\(^{[80]}\) Flake graphite, micrographite, and graphitic nanocarbon solutions with a differing carbon lattice size were treated with iron(II)-tetrafluoroborate salts in tetrahydrofuran leading in a decoration of the graphite sheets with iron oxide nanoparticles. For the smaller carbon lattice size, the authors also observed a smaller nanoparticle size. The higher dispersion, surface area, and electrical contact resulted in a better OER performance with an overpotential of 430 mV at 1 mA cm\(^{-2}\) in 0.1 m KOH.

Figure 13. a) SEM image of Co\(_3\)O\(_4\). b) TEM image of Co\(_3\)O\(_4\). c) SEM image of Co\(_3\)O\(_4\)/MWCNT. d) TEM image of Co\(_3\)O\(_4\)/MWCNT. e) SEM image of Co\(_3\)O\(_4\)/MWCNT. f) TEM image of Co\(_3\)O\(_4\)/MWCNT. g) LSV curves, h) Tafel slope curves, i) galvanostatic profile at 20 mA cm\(^{-2}\), and j) stability tests of Co\(_3\)O\(_4\)/MWCNT composite materials. Reproduced with permission.\(^{[74]}\) Copyright 2014, The Royal Society of Chemistry.
4.1.3. Nickel Oxide-Containing Composites

Doped nickel oxides have the highest intrinsic OER activity among transition nonnoble metal oxide catalysts, but again a low electric conductivity limits the performance of these compounds especially in thick electrode layers. Hybridization with carbonaceous substrates is therefore actively pursued also for this class of compounds, with synthesis approaches similar to those described in the sections above. One of the best recently published catalysts based on NiO/C delivered a low overpotential of 220 mV with a Tafel slope of 55 mV dec$^{-1}$ in 1.0 M KOH solution. Dehydrated sucrose sugar was used as carbon template for NiO nanostructures deposited in a facile wet chemical method.

Xu et al. used an elegant way to obtain nickel nanoparticles encapsulated in few-layer nitrogen-doped graphene, which was realized via the pyrolysis of a Ni-based MOF obtained from 1,4-benzenedicarboxylic acid, triethylenediamine, and nickel nitrate. The thickness of the graphene layer and the level of nitrogen doping are dependent on the annealing temperature and could be tuned to achieve the maximum performance of the resulting catalyst. The highest OER activity was observed for the sample heated at 800 °C, which showed an overpotential of 280 mV at a current density of 10 mA cm$^{-2}$ in 1.0 M KOH and a relatively low Tafel slope of 45 mV dec$^{-1}$, outperforming commercial IrO$_2$. The authors concluded that the content and structure of the N-doped graphene layers as well as the electrochemically active surface area of the catalyst are crucial for the high OER activity.

In a probably unintended way, Silva et al. prepared a NiO hollow fiber/carbon composite showing a good electrochemical activity toward the OER with an overpotential of 340 mV at a current density of 10 mA cm$^{-2}$ with a Tafel slope of 84 mV dec$^{-1}$. The hollow fibers were prepared via solution blow spinning of nickel nitrate solution together with PVP followed by heating steps. Carbon from polyenic branch of PVP resisted the firing treatment and acted as an agglomerating agent, enabling a good conductivity between the formed NiO nanoparticles. Other reports include, e.g., NiO/CNT or NiO composite with N-doped graphene.

An overview on recent metal (metal oxide)/carbon hybrid materials is provided in Table 4.

4.2. Transition Metal Single-Atom Catalysts (SACs)

In recent years, SACs for OER have drawn great attention as the downsizing of nanoparticles is taken a step further in order to enhance the specific mass activity. However, reducing the metal particles size to nanoclusters or even to single atoms increases the surface free energy and makes their aggregation or Ostwald ripening easy. Anchoring and strong binding of SACs on a suitable support is therefore mandatory. Carbon-based materials have shown to facilitate the requirements for SACs as they offer a large surface area and promote a strong metal-support interaction by the implementation of heteroatoms leading to a coordinated single metallic atom center. Supported by computational calculations and advanced characterization techniques such as high-angle annular dark-field scanning-transmission electron microscopy (HAADF-STEM) and X-ray absorption spectroscopy, the structure and special catalytic activity of SACs can be revealed. More detailed reviews regarding the complete field of electrocatalytic applications of SACs have been published recently by Zhu et al. and Zhang et al., as well as by Lee et al.

Several synthetic strategies are commonly used to obtain atomically dispersed catalysts including pyrolysis of various precursors at high temperatures, impregnation of the support material with metal precursor, co-precipitation of different metal cations from solution, physical, and chemical deposition methods (e.g., atomic layer deposition or CVD), and by chemical or photochemical reduction of the active species.

A slightly different route was used by Wu et al. who grew a Co-based MOF on KCl particles and obtained nitrogen-doped carbon nanosheets with a high site fraction of single Co atoms of ~15.3 wt% after pyrolysis at a temperature of 750 °C. The presence of isolated Co atoms with a dot size of 0.10–0.40 nm on carbon sheets was confirmed by HAADF-STEM. More structural information about Co atoms was obtained from X-ray absorption fine structure (XAFS). A dominating Co–N coordination peak was attributed to a four coordination structure whereas no hint for Co–Co cluster existed. The highly dispersed Co on the nitrogen-doped carbon sheets led to a high
The herein reported materials only need overpotentials of $\approx 230$–$330$ mV in order to reach a current density of $10$ mA cm$^{-2}$. In a detailed study, Hou et al. showed that a quadruple coordination of Ni by nitrogen and/or sulfur inside a carbon nanosheet matrix resulted in a high electrochemical activity.$^{92}$ The material showed an outstanding performance with a small overpotential of 280 mV at 10 mA cm$^{-2}$ in 1.0 m KOH and a low Tafel slope of 45 mV dec$^{-1}$, and a stable performance for over 2000 cycles.

Aforementioned transition metal elements were investigated in any arrangement possible in order to get insights in coordination effects and to increase the already high catalytic activity further.$^{93}$

Beside the typically used transition metals for OER, Guan et al. used a nature-inspired mononuclear manganese embedded in nitrogen-doped graphene.$^{94}$ The authors observed a remarkable catalytic activity comprising an overpotential of 337 mV at 10 mA cm$^{-2}$ in 1.0 m KOH and a low Tafel slope of 55 mV dec$^{-1}$. The authors attributed the electrochemical activity to the mononuclear manganese ion coordinated with four nitrogen atoms in the graphene matrix, which was confirmed by structural characterization and DFT calculations.

An overview on recent SAC/carbon compounds is provided in Table 5. However, it should be noted that the research on SACs is still in the infant stage concerning synthesis, characterization, and mechanism studies at the same time. Therefore, promising future developments can be expected.

If you are looking to convert this text into a plain text representation, a sample of the Markdown code could be:

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- Electrochemical activity toward OER with an overpotential of 310 mV at 10 mA cm$^{-2}$ in 0.1 m KOH and a low Tafel slope of 74 mV dec$^{-1}$ outperforming conventional IrO$_2$ and Pt/C catalysts. Several other groups also investigated Co-based SACs on carbon-based materials and assigned the high catalytic activity to C-N$_4$ centers supported by DFT calculations and XAFS measurements.$^{89}$

The atomic fine dispersion of iron atoms was analyzed by some researching groups as well.$^{90}$ Beside nitrogen-doping, additional sulfur doping of the carbon material showed a further enhancement of the catalytic activity. Pan et al. designed a polymerization–pyrolysis–evaporation strategy to synthesize atomically dispersed Fe-N$_4$ sites anchored on N-doped porous carbon.$^{91}$ After polymerization of urea and pyromellitic dianhydride in the presence of ZnCl$_2$ and FeCl$_3$, the obtained product was heated at 920 °C for 3 h under Ar atmosphere followed by a leaching step in sulfuric acid. Structural characterization with HAADF-STEM and EXAFS measurements revealed homogeneously dispersed Fe on the carbon material with an Fe–N coordination. The resulting material delivered a potential of 1660 mV versus RHE at 10 mA cm$^{-2}$ in 1.0 m KOH and a low Tafel slope of 96 mV dec$^{-1}$.

Table 4. Comparison of different TMO/carbon hybrids regarding the OER activity.

| Transition metal elements | Carbon materials | Synthesis methods | Contents | Electrolytes | Potential versus RHE at 10 mA cm$^{-2}$ [mV] | Tafel slope [mV dec$^{-1}$] | Ref. |
|--------------------------|------------------|------------------|---------|-------------|---------------------------------|----------------------|-----|
| Co                       | N-doped carbon   | MOF derived      | Co = 33 wt% | 0.1 m KOH | 1530                           | 83                   | [71a]|
| Co                       | Co$_2$O$_2$-embedded carbon/rGO | MOF derived | N/A | 0.1 m KOH | 1612                           | 62                   | [84]|
| Co                       | N-doped rGO      | Hydrothermal synthesis | N/A | 0.1 m KOH | 1910                           | 204                  | [72]|
| Co                       | CNT, GO, graphene | Precipitation method | N/A | 1.0 m KOH | 1765                           | 157                  | [73]|
| Co                       | MWCNTs           | Diethylamine directed anchoring | Co = 49 wt% | 1.0 m KOH | 1539                           | 51                   | [74]|
| Co                       | Amorphous, graphitic carbon | Solvothermal synthesis | Co = 26.3 wt% | 0.1 m KOH | 1645                           | 53                   | [75a]|
| Co                       | B,N-decorated graphene | Precipitation method, NH$_3$ posttreatment | N/A | 0.1 m KOH | 1525                           | 57                   | [75b]|
| Co                       | Graphene         | Electrochemical synthesis | Co = 51.8 wt% | 0.1 m KOH | 1530                           | 101                  | [75c]|
| Co                       | rGO              | Electrostatic interaction and growth | Co = 7.4 wt% | 1.0 m KOH | 1576                           | 47                   | [76]|
| Fe                       | Oxidized MWCNTs  | Precipitation method | N/A | 1.0 m KOH | 1640                           | 62                   | [77]|
| Fe                       | NiS$_2$/rGO      | Solvothermal synthesis | N/A | 1.0 m KOH | 1560                           | 36                   | [78]|
| Fe                       | N,P-doped carbon nanofibers | Electrospinning | N/A | 1.0 m KOH | 1560                           | 90                   | [79]|
| Fe                       | Graphenide       | Precipitation method | Fe = 15–20 wt% | 0.1 m KOH | 1690                           | 40                   | [80]|
| Ni                       | Amorphous carbon | Facile wet chemical method | Ni = 60–80 wt% | 1.0 m KOH | 1450                           | 55                   | [81]|
| Ni                       | N-doped graphene | MOF derived      | Ni = 74.6 wt% | 1.0 m KOH | 1510                           | 45                   | [27]|
| Ni                       | Carbon hollow fibers | Solution blow spinning | Ni = 10 wt% | 1.0 m KOH | 1570                           | 84                   | [82]|
| Ni                       | N-doped carbon   | Precipitation method | Ni = 18 wt% | 0.1 m KOH | 1576                           | 70                   | [83a]|
| Ni                       | CNTs             | Precipitation method | N/A | 1.0 m KOH | 1531                           | 82                   | [83b]|
| Ni                       | Disordered and graphitic carbon | MOF derived | N/A | 1.0 m KOH | 1620                           | 100                  | [83c]|
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4.3. Mixed Metal Oxide/Carbon Composites for OER

4.3.1. Mixed TMO/Carbon Composites

Another group of popular composite materials for OER includes mixed metal oxides containing at least two different transition metals. Among investigated materials, the combination of cobalt and iron seems to be particularly promising. For example, Bian et al. synthesized a nanosized composite based on CoFe$_2$O$_4$ and graphene using simple hydrothermal method. The high catalytic activity was ascribed to the presence of PANI-modified CNTs offering more active sites for uniform CoFe$_2$O$_4$ nanoparticles attachment leading to a good electrical contact and enhanced stability.

Another way to tune the performance of CoFe$_2$O$_4$/graphene composite is to introduce doping as was shown in a recent paper by Madakannu et al.[99] The authors introduced nickel as a doping substitute for cobalt. The OER performance of the doped catalyst was dependent on the degree of doping, with Co$_{0.75}$Ni$_{0.25}$Fe$_2$O$_4$/rGO showing the highest performance. The resulting composite delivered respectable performance with a very low Tafel slope of 31 mV.

Importantly, such a catalyst delivered current density of 10 mA cm$^{-2}$ at an overpotential of 328 mV for at least 15 h with a low Tafel slope of 31 mV dec$^{-1}$.

The resulting composite delivered respectable performance for both ORR as well as OER and, importantly, a significant higher stability in OER than a reference Pt/C catalyst. The use of CNTs instead of graphene in another study resulted in an OER catalyst using Ni- and Fe-embedded PVP polymer nanofibers. The high catalytic activity was ascribed to the presence of PANI-modified CNTs offering more active sites for uniform CoFe$_2$O$_4$ nanoparticles attachment leading to a good electrical contact and enhanced stability.

Table 5. Comparison of different metal single-atom/carbon hybrids regarding the OER activity.

| Transition metal elements | Carbon materials | Synthesis methods | Electroples | Potential versus RHE at 10 mA cm$^{-2}$ [mV] | Tafel slope [mV dec$^{-1}$] | Ref. |
|--------------------------|-----------------|-------------------|------------|---------------------------------|-------------------------|-----|
| Co                       | N-doped graphene | Impregnation method | 1.0 m KOH | 1616 | 73 | [89a] |
| Co                       | N-doped carbon   | MOF Derived       | 1.0 m KOH | 1610 | 70 | [89b] |
| Co                       | CNTs            | MOF Derived       | 1.0 m KOH | 1640 | 85 | [89c] |
| Co                       | N-doped graphene | MOF Derived       | 0.1 m KOH | 1540 | 74 | [85]  |
| Fe                       | N,S-doped graphitic carbon | Impregnation method | 0.1 m KOH | 1600 | 82 | [90a] |
| Fe                       | N-doped carbon   | MOF Derived       | 0.1 m KOH | 1620 | 80 | [90b] |
| Fe                       | N,S-doped graphitic carbon | Impregnation method | 0.1 m KOH | 1640 | 59 | [90c] |
| Fe                       | N-doped porous carbon | Polymerization + pyrolysis | 1.0 m KOH | 1660 | 95 | [91]  |
| Ni                       | N-doped graphene | Hydrothermal synthesis | 1.0 m KOH | 1561 | 63 | [92a] |
| Ni                       | Porous carbon nanosheets | Hydrothermal synthesis | 1.0 m KOH | 1510 | 45 | [92b] |
| Ni                       | N-doped graphene | CVD + etching     | 1.0 m KOH | 1500 | 59 | [92c] |
| Ni                       | Defective graphene | Impregnation method | 1.0 m KOH | 1500 | 47 | [92d] |
| Ni                       | Defective carbon | Impregnation method | 1.0 m KOH | 1454 | 42 | [92e] |
| Co,Fe                    | N-doped graphitic carbon | Impregnation method | 1.0 m KOH | 1539 | 37 | [93a] |
| Ni,Fe                    | Polymeric carbon nitride | Polymerization + pyrolysis | 1.0 m KOH | 1540 | 38 | [93b] |
| Fe,Ni                    | N-doped CNTs     | Impregnation method | 0.1 m KOH | 1650 | 60 | [93c] |
| Co, Ni                   | N-doped porous, graphitic carbon | MOF derived | 0.1 m KOH | 1590 | 72 | [93d] |
| Mn                       | N-doped graphene | Impregnation method | 1.0 m KOH | 1567 | 55 | [94]  |

bases.[99] Importantly, such a catalyst delivered current density of 10 mA cm$^{-2}$ at an overpotential of 328 mV for at least 15 h with a low Tafel slope of 31 mV dec$^{-1}$.

Other metal ion combinations have been also reported, although the amount of respective publications is much lower than that of the compositions described above. For example, Xia et al. have synthesized NiCo$_2$O$_4$ composite with hierarchical porous graphene-like material.[100] To further enhance its performance, the authors have introduced an additional doping with gold in an attempt to stabilize the active Co$^{4+}$ and Ni$^{3+}$ sites. Despite the porous structure of graphene support and the gold doping, the material did not outperform the already reported compounds and have demonstrated even larger overpotentials and lower current densities than the comparable materials reported by other groups.

In terms of graphene support, nitrogen-doped graphene seems to be particularly popular due to its inherently high conductivity, which promotes the overall OER activity. Such a support was used for the CuCo$_2$O$_4$ and MnVO$_4$-based composite catalysts.[101] In both cases, the hybrid catalysts performed much better than the unsupported counterparts, which confirms the synergistic effect of graphene matrix. Importantly, both composite materials exhibited relatively low overpotentials with that of CuCo$_2$O$_4$ being superior with the value of 360 mV.

While anchoring the metal oxide nanoparticles on the surface of carbonaceous materials is probably the most popular way to obtain composite catalysts, the other hybrid morphologies such as nanowires with embedded nanoparticles can also be prepared.[102] Thus, Chen et al. have prepared a composite catalyst using Ni- and Fe-embedded PVP polymer nanofibers as precursors. In the next step, the precursor was heated in air at 250 °C to form the nickel–iron oxide/carbon composite
The catalyst prepared in this way is competitive with ruthenium and iridium oxides for OER. Its activity most likely originates from the interconnected fibrous structure that makes the active sites easily accessible. Importantly, the overpotential to reach the current density of 10 mA cm\(^{-2}\) can be as low as 310 mV for optimized catalyst composition and loading.

Apart from the inherent catalytic activity of composite materials, there is also a question of long-term stability as was shown in a paper by Wang et al.\(^{[103]}\) In their work, the authors combined nanocrystalline nickel oxide with amorphous manganese oxide suspended on graphene nanosheets. Despite the promising initial catalytic activity, the catalytic activity of this material has deteriorated within few hours of continuous use. Other mixed metal oxide composite materials include, e.g., doped MnO\(_2\) supported on carbon fibers, MoO\(_2\)-Co\(_2\)Mo\(_3\)O\(_8\)@C, or NiCo\(_2\)O\(_4\) nanoplatelets on graphene support. Although none of these catalysts has exhibited outstanding OER performance yet, the published papers open a way to the nearly endless possible combinations of transition metals and carbonaceous support, which could enable the discovery of an active and stable composite OER catalyst in the future.\(^{[104]}\)

### 4.3.2. Perovskite/Carbon Composites

A special class of inorganic materials for carbon composite formation is represented by perovskites with a general formula ABO\(_3\). The perovskite structure is thereby highly versatile, with tunable properties allowing classical applications as electro-ceramic dielectrics, metallic conductors, superconductors, or light absorbing or emitting semiconductors.\(^{[105]}\) The possibility of partial substitution of A and/or B site cations leading to a formal A\(_{1-x}\)A\(_{x}\)B\(_{1-y}\)B\(_{y}\)O\(_3\) composition allows to precisely tune the materials properties and the electronic structure, which was exploited for the fabrication of highly active perovskite OER catalyst in the recent years.\(^{[106]}\) However, a main issue concerning the application of most perovskites is their rather limited electronic conductivity, with few exceptions (e.g., LaNiO\(_{3-\delta}\)) that are not necessarily OER active and vice versa (Figure 15).\(^{[107]}\)

| Metal oxide                   | Carbon materials | Synthesis methods                  | Electrolytes | Potential versus RHE at 10 mA cm\(^{-2}\) [mV] | Tafel slope [mV dec\(^{-1}\)] | Ref.       |
|------------------------------|------------------|------------------------------------|--------------|-----------------------------------------------|-------------------------------|-----------|
| CoFe\(_2\)O\(_4\)           | rGO              | Solvothermal synthesis             | 0.1 m KOH    | 1690                                          | –                            | [95]      |
| CoFe\(_2\)O\(_4\)           | PANI-MWCNTs      | Precipitation method               | 1.0 m KOH    | 1544                                          | 31                           | [96]      |
| Co\(_2\)Ni\(_2\)Fe\(_2\)O\(_4\) | rGO         | Microwave-assisted synthesis       | 0.1 m KOH    | 1670                                          | 85                           | [97]      |
| Co, CoFe\(_2\)O\(_4\)       | rGO              | Hydrothermal synthesis             | 1.0 m KOH    | 1570                                          | 31                           | [98]      |
| CoFe\(_2\)O\(_4\)           | N-doped carbon   | Solvothermal synthesis, precipitation method | 1.0 m KOH    | 1558                                          | 31                           | [99]      |
| MnV\(_2\)O\(_4\)            | N-doped rGO      | Hydrothermal synthesis             | 0.1 m KOH    | 1650                                          | 271                          | [101]     |
| N\(_x\)Fe\(_2\)O\(_y\)     | Carbon nanofibers| Electrospinning                    | 1.0 m KOH    | 1540                                          | 42                           | [102]     |
| NiO\(_x\)@MnO\(_x\)       | Graphene nanosheets | Layer-by-layer self-assembly method | 1.0 m KOH    | 1602                                          | 40                           | [103]     |
| NiCo\(_2\)O\(_4\)          | Graphene nanosheets | Precipitation/hydrothermal method  | 0.1 m KOH    | 1680                                          | 164                          | [104a]    |
| MoO\(_2\)-Co\(_x\)Mo\(_y\)O\(_z\) | Carbon | MOF derived                        | 1.0 m KOH    | 1550                                          | 88                           | [104b]    |
| (Fe, V, Co, Ni)-doped MnO\(_2\) | Carbon fiber paper | Co-electrodeposition              | 1.0 m KOH    | 1620                                          | 104                          | [104c]    |
| SrTiO\(_3\)-Fe\(_{20}\)Ni\(_{20}\)O\(_{6-\delta}\) | CNTs                  | Sol-gel synthesis + CVD          | 0.1 m KOH    | 1710                                          | 98                           | [109]     |
| Sm\(_2\)Sr\(_2\)Co\(_2\)O\(_{1-x}\) | N-doped graphene | Electrospinning                   | 0.1 m KOH    | 1630                                          | 115                          | [106a]    |
| (PrBa\(_0.1\)Co\(_{2}\)O\(_6\)-\(\delta\)) | N-doped graphene | Electrospinning                   | 0.1 m KOH    | 1550                                          | 74                           | [110]     |
| (Nd\(_0.2\)Sr\(_{0.8}\)Fe\(_{0.85}\)Co\(_{1.5}\)Fe\(_{0.5}\)O\(_5\)) | S-doped carbon tubes | Sol-gel synthesis + CVD        | 1.0 m KOH    | 1650                                          | 89                           | [111]     |
| LaNiO\(_3\)               | N-doped CNTs     | Sol-gel synthesis + CVD           | 0.1 m KOH    | 1620                                          | 78                           | [106c]    |

Figure 15. a) Conductivity of various perovskite composition versus DFT-calculated band gaps. b) Profile of LaNiO\(_{3-\delta}\) and PBCO-SG (PrBa\(_{0.1}\)Co\(_{2}\)O\(_{6-\delta}\)) powders combining OER activity with conductivity, amount of oxygen vacancies and the flatband potential. Reproduced (adapted) with permission.\(^{[107]}\) Copyright 2018, American Chemical Society.
In addition, high calcination temperatures required for the perovskite synthesis often lead to the formation of relatively large crystalline domains, which further reduce the number of OER available active sites. This fact renders carbon composite formation a valid solution to increase the overall conductivity, which was intensively explored in the recent years. However, the carbon/perovskite composites also show various synergistic effects that further enhance the overall OER activity. A detailed summary is given in a recommended recent work by Zhu et al.\(^\text{[12]}\)

The factors influencing the OER activity of the perovskite-containing composites include the filling of the perovskite E\(_g\) band (which is influenced by the B-site cation), the number of oxygen vacancies of the perovskite, the nanomorphology of the inorganic phase, and the formed perovskite/carbon interface, as well as the amount and chemical nature (graphene, CNTs, etc., including heteroatom doping) of the carbon structure.\(^\text{[12,107,108]}\)

Synergistic effects of carbon and perovskite regarding OER catalysis depicted in Figure 16 are the ligand effect based on an electronic interaction of two neighboring metals or oxides (in this case carbon and perovskite). This charge delocalization is commonly believed to enhance the intrinsic conductivity and leads to more favorable adsorption energies of OER intermediates, increasing the overall OER activity of the composite.\(^\text{[12,106a]}\)

A second major synergistic effect discussed in the literature is the formation of interfacial heterostructures originating from the formation of covalent bonds between two neighboring phases, or the formation of a new phase with enhanced catalytic activity.\(^\text{[12,109]}\)

Finally, a spillover effect may enhance the OER performance by transferring the product species oxygen to the neighboring carbon surface to liberate active sites and therefore increase the catalytic turnover.\(^\text{[12]}\)

Recent examples of perovskite/carbon composites catalyst for water oxidation include the sol–gel synthesis of micrometer-sized Sr\(_{1.9}\)Fe\(_{0.85}\)Ni\(_{0.05}\)O\(_{3−δ}\) (STFN) perovskite particles, which are coated by CNTs via a CVD method with a reported temperature optimum of 700 °C. The resulting STFN/CNT-700 fabricated by Wu et al. shows an onset potential of 1.59 V versus RHE and a reported overpotential of 480 mV to reach 10 mA cm\(^{-2}\) with a stable operation over 30 h. In this work, the synergistic effect of the perovskite/carbon composite was validated by a reference experiment, in which perovskite and commercially available CNTs intermixed only physically without formation of chemical bonds. The reference compound exhibited a higher conductivity but showed a lower electrochemical performance as compared to the CVD grown CNTs directly on the perovskite structure.\(^\text{[109]}\)

The synergistic effects in perovskite/carbon composites were demonstrated also by Bu et al. who performed DFT calculations that were validated experimentally. In this work, the authors presented the rational synthesis of porous, perovskite-type Sm\(_{0.5}\)Sr\(_{0.5}\)Co\(_{0.5}\)O\(_{3−δ}\) hollow nanofibers (SSC-HF) that were hybridized with cross-linked, 3D, N-doped graphene (3DNG) resulting in a hybrid catalyst denoted as SSC-HF-3DNG (SSC-HG).\(^\text{[106a]}\) The materials were obtained via electrospinning of metal salt precursor, pore forming Pluronic F127 polymer, additional oil for the introduction of micro pores, and PAN polymer as further carbon source. After calcination, a hybrid structure of hollow porous fibers with a diameter of around 150 nm and high surface area of over 21 m\(^2\) g\(^{-1}\) for the perovskite alone is obtained. The 3D, N-doped graphene structure has provided a high conductivity and further enhanced the OER activity of the perovskite by synergistic effects investigated by theoretical methods. DFT calculations (Figure 17a,b) suggest an electron transfer from the N-doped carbon to cobalt atoms of the perovskite structure, which thereby increases the d-band center of these atoms and leads to a higher degree of Co-oxygen hybridization by a higher overlap of the Co 3d and O 2p band (Figure 17b). These interactions are beneficial for the OER as they promote the activation and participation of lattice oxygen.\(^\text{[106a]}\) The SSC-HG exhibits a high OER activity with a low onset potential of 1.53 V versus RHE and an overpotential of 400 mV to reach a current density of 10 mA cm\(^{-2}\), which outperforms the IrO\(_2\) reference under same conditions.\(^\text{[106a]}\)

In a second work by the same authors, a 3DNG obtained via electrospinning and calcination was employed for the formation of a composite hollow and porous fiber structure with the cation-ordered perovskite (PrBa\(_{0.5}\)Sr\(_{0.5}\)Co\(_{1.5}\)Fe\(_{0.5}\)O\(_{5+δ}\)) (PBSCF).\(^\text{[110]}\) The composite electrode showed a remarkably low onset potential of 1.52 V versus RHE compared to 1.51 V versus RHE for IrO\(_2\) tested under the same conditions and a overpotential of only 320 mV to reach a current density of 10 mA cm\(^{-2}\), which outperformed the IrO\(_2\) reference (\(η_{\text{OER}} = 440\) mV) significantly. The high OER activity of the composite was again explained by an increased covalency between transition metals and lattice oxygen in PBSCF triggered by the electron transfer of 3DNG, as has been shown above for a similar morphology but with different perovskite active material. The OER active sites are thereby supposed to be located not on the carbon but rather on the PBSCF, which is regarded to be positively affected by the interaction with the N-doped carbon framework.\(^\text{[110]}\)

Figure 16. Schematic illustration of possible origins of the synergistic effect toward OER catalysis between the perovskite and carbon structure: a) ligand effect; b) spillover effect, and c) formation of interfacial heterostructures. Reproduced (adapted) with permission.\(^\text{[12]}\) Copyright 2017, Wiley-VCH.
The composite catalyst exhibits a remarkably high OER performance in alkaline media with an onset potential of 1.48 V versus RHE, significantly outperforming the Co-Fe nanoparticle decorated perovskite (R-NSCFNb) with 1.51 V versus RHE or an IrO2 reference electrode under same measurement conditions. The low overpotential required to reach 10 mA cm\(^{-2}\) of 420 mV and an outstanding stability of 370 h under continuous operation exceeds other literature reports on the stability of perovskite OER catalysts.\[111\]

Other perovskite/carbon composite systems investigated recently include a LaNiO\(_3\) nanoparticle/N-doped CNT composite catalyst prepared by Chen et al., which exhibits a remarkable OER activity with a reported overpotential of 390 mV to reach a current density of 10 mA cm\(^{-2}\) outperforming a RuO\(_2\) reference under same measurement conditions. The high OER activity was attributed to the employed polyl synthesis method yielding small perovskite nanoparticles with more exposed active site and a strong binding of the N-doped CNTs to the LaNiO\(_3\) phase, which facilitates charge transfer and increases the OER activity by synergistic effects.\[106c\]

The introduced examples of perovskite/carbon composite OER catalysts show only a recent and small cutout of the overwhelming variety that can be achieved for this class of materials by changes in composition, nanomorphology, and synthesis procedures (e.g., carbonization or posttreatments). By combining synthetic approaches with theoretical methods, further knowledge about the electronic structure of respective composites could be gained that guides a rational synthesis toward further improved OER catalysts.

### 4.4. Metal/Metal Oxide/Carbon Composites for OER

Another interesting group of materials suitable as composite catalysts for OER are metal/metal oxides combined with conductive carbonaceous support. The advantage of these materials stems from their intrinsic high catalytic activity. Another advantage is the presence of metal oxide on the surface of deposited metal particles, which ensures that the catalysts are generally much less prone to further oxidation, making them stable for OER. Nickel and cobalt are particularly popular for this purpose as will be discussed further on. Using nickel nitrate and nitrogen-doped graphene, Faisal et al. have prepared conductive composite material with Ni/NiO nanoparticles dispersed over the graphene support.\[112\] The morphology of this composite material is shown in Figure 19a–f and its OER performance in Figure 19g–j. This catalyst exhibited good electrochemical performance in ORR, HER as well as OER where it delivered performance similar to commercial Ru/C catalyst (see Figure 19g). Similar method using a hydrothermal treatment instead of simple heat treatment resulted in a graphene aerogel decorated with Ni/NiO nanoparticles in a different paper.\[113\] It was shown that the OER overpotential is strongly dependent on the nickel content, where the overpotential values decreased gradually with nickel content reaching a low overpotential value of 320 mV at 10 mA cm\(^{-2}\). Although high electrocatalytic activity is one of the key properties for catalysts, their mechanical
properties also play a critical role as they should be as robust and/or flexible as possible. One of the feasible ways to improve mechanical properties is to deposit OER active materials on top of carbon fibers as was shown recently for Ni/NiO.\(^{[84]}\) Such a catalyst was prepared by electrodeposition of Ni followed by calcination to introduce surface oxidation of nickel coating. Due to the fibrous structure, the material can be transformed into various shapes. Even under mechanical stress such a catalyst can deliver the current density of 10 mA cm\(^{-2}\) at an overpotential of 300 mV. The authors ascribed this to the formation of Ni (III) species on the interface between carbon fibers and deposited layer. Finally, similar catalyst can be prepared using CNTs.

Another popular metal employed in metal/metal oxides composites is cobalt with several reports in the literature. The OER performance of these materials is similar to those described in the previous paragraphs with overpotentials around 350 mV at 10 mA cm\(^{-2}\). The synthetic methods were also quite similar to previous reports.\(^{[114]}\)

Recent examples of metal/metal oxide/carbon-based hybrid materials are also summarized in Table 7.

### Table 7. Comparison of different perovskite/carbon composites and metal/metal oxide composites with carbon regarding their OER activity.

| Metal oxide | Carbon materials | Synthesis methods | Electrolytes | Potential versus RHE at 10 mA cm\(^{-2}\) [mV] | Tafel slope [mV dec\(^{-1}\)] | Ref. |
|-------------|------------------|-------------------|--------------|---------------------------------------------|-------------------------------|-----|
| Ni, NiO     | N-doped graphene | Impregnation + annealing | 0.1 m KOH  | 1620                                        | 98                            | [112] |
| Ni, NiO     | Graphene aerogel | Solvothermal method + annealing | 0.1 m KOH  | 1550                                        | 61                            | [113] |
| Ni, NiO     | Carbon fibers    | Electrodeposition  | 1.0 m KOH   | 1530                                        | 60                            | [84] |
| Ni, NiO     | Carbon fibers    | Solution blow spinning  | 1.0 m KOH | 1508                                        | 88                            | [115] |
| Ni, NiO     | 3D porous carbon | Carbonization + calcination | 1.0 m KOH | 1583                                        | 97                            | [116] |
| Ni, Co\(_3\)O\(_4\) | N-doped carbon  | Impregnation + annealing | 1.0 m KOH | 1580                                        | 52                            | [117] |
| Co, Co\(_3\)O\(_4\) | N-doped carbon nanosheets | MOF derived | 0.1 m KOH  | 1580                                        | 94                            | [114a] |
| Co, Co\(_3\)O\(_4\) | N-doped graphene | Freeze drying + thermal treatment | 0.1 m NaOH | 1684                                        | 92                            | [114b] |
5. Carbon-Based Ordered Framework Structures

MOFs and COFs are classes of porous materials that consist of metal (or organic nodes) and organic linkers, offering a huge structure variability. Due to the high amount of carbon atoms, MOF and COF materials can be classified to a certain degree as carbon-based compounds. Therefore, they are discussed in this review as well. The molecular structure and resulting properties of MOFs and COFs can be precisely modulated by the selection of different building blocks with various functionalities, thus influencing structural characteristics like porosity or crystallinity and electronic properties like band gap or conductivity. Hence, MOFs and COFs can be designed for application as OER catalyst as well.[118] OER catalytic active MOFs and COFs structures are comprised of functional organic motives that contain heteroatoms like O, N, S, P, B. Moreover, in case of MOFs, catalytic active elements like Fe, Co, Ni, Mn can be chosen as metal nodes, which could additionally enhance the OER activity.[118a,119] Another important feature of MOFs and COFs is their large surface area and high porosity enabling a good accessibility of the active sites accompanied by a rapid mass transport.[118a] Moreover, the high porosity of MOF and COF structures can also be used to incorporate highly catalytic active guest species such as metal-containing particles. The periodicity of the pore structure with controllable size, morphology, and location of the pores enables the rational location of the catalytic guest species, which can induce synergistic effects between the host structure and the guest species resulting typically in an improved overall catalytic activity (Figure 20).[118a,120]

A major drawback of MOFs and COFs is however their typically low electrical conductivity, which can nevertheless be alleviated by the addition of conductive supports such as CNTs, carbon fibers, or reduced graphene oxide.[122] Another issue of many MOF and COF materials is their often limited chemical stability under acidic or basic conditions, which hamper their application as OER catalysts.[121a,122]

Besides being used directly as OER electrocatalyst, MOFs and COFs can serve as precursors or templates for the synthesis of even more active nanostructures such as heteroatom-doped carbons, transition metal-functionalized carbons, or metal oxides/sulfides/nitriles/carbides, depending on the applied postsynthetic conditions.[118a,119,123] The different strategies of designing MOF and COF-based catalysts for OER will be discussed in the following two sections. The interested reader is also referred to the recently published reviews by Liang et al.,[123b] Quin et al.,[123c] Xue et al.,[119] and Zheng et al.[120] dealing mainly with MOF and MOF-derived OER catalysts.

5.1. MOFs

There are only few publications reporting the OER catalysts of pristine MOF materials, which is mainly due to their low electrical conductivity as mentioned above. 2D MOFs seems to be however an interesting option as they have typically a sheets thickness of only a few nanometers, which enables a fast mass and charge carrier transport accompanied by a large amount of easily accessible catalytic centers.[124] Xing et al., e.g., reported a 2D hexamamotriphenylene Co-MOF (Co3(HITP)2), which demonstrates a relative high conductivity of up to 11.5 S cm⁻¹.[121a] The conductivity is induced by an in-plane π-d conjugated network formed by hybrids of transition metal node d-orbitals and frontier orbits of the conjugated ligands. Beside the good conductivity, the porous structure and the high amount of catalytic active Co-N₄ centers are additionally assigned as the main reasons for the excellent OER activity of Co3(HITP)2 resulting in a low overpotential of 254 and 300 mV to reach 10 and 50 mA cm⁻², respectively, and a low Tafel slope of 86.5 mV dec⁻¹ outperforming IrO₂ and RuO₂ reference catalysts drastically. Moreover, Co3(HITP)2 is also very stable under electrocatalytic conditions showing only 1% decay at a current density of 16 mA cm⁻² within 12 h. Additionally, the morphology and microstructure of Co3(HITP)2 remain stable during the long-term measurement. Only the Co(II) nodes are oxidized to Co(III) which is however quite common, as Co(II) is the active phase toward OER.[121a]

A further strategy for increasing the electrical conductivity and using pristine MOFs for OER was reported by Xue et al. who introduced missing linkers into a cobalt terephthalate MOF structure by partially replacing the terephthalate linkers by carboxyferrocene (Fc) (Figure 21).[125] Introducing Fc into the MOF structure induced a change of the electronic structure and generated catalytically highly active unsaturated Co²⁺ sites resulting in a drastically improved electrocatalytic performance.
The defective MOF arrays that were directly grown on a nickel foam substrate (CoBDC-Fc-NF) revealed a very low overpotentials of 178 mV to reach 10 mA cm$^{-2}$ and 267 mV to obtain 500 mA cm$^{-2}$, outperforming the nonfunctionalized CoBDC-NF material (365 mV, 500 mA cm$^{-2}$) and a RuO$_2$-NF reference catalyst (557 mV, 500 mA cm$^{-2}$). The high electrocatalytic activity was accompanied by a high stability with almost no change in the catalytic activity during 80 h chronopotentiometric measurements at 100 mA cm$^{-2}$.

The use of bimetallic or multimetallic MOFs is another strategy to increase the conductivity and the catalytic activity of MOFs through synergistic effects. Yang et al., e.g., prepared different Co, Ni and Co, Fe 2D MOFs and analyzed their catalytic performance. The CoFe-MOF demonstrated the highest activity yielding an overpotential of 355 mV to obtain 10 mA cm$^{-2}$, thus outperforming the monometallic Co-MOF (397 mV at 10 mA cm$^{-2}$). Interestingly, the bimetallic CoNi-MOF has an inferior catalytic activity featuring a higher overpotential (501 mV at 10 mA cm$^{-2}$) as compared to Co-MOF.

Another Co, Fe 2D MOF reported by Xu et al. has an even lower overpotential of 277 mV to reach 10 mA cm$^{-2}$. The superior performance can be assigned to the unique interpenetrating mesopore and micropore networks of the MOF, which is very favorable to achieve a high accessibility of the catalytic active sites and enable a rapid mass transport.

For a more detailed overview on multimetallic MOF OER catalysts, the interested reader is recommended to the minireview of Xue et al.

The formation of MOF/carbon composites can be another strategy to improve the electrical conductivity and thus the OER activity. Different MOF/carbon heterostructures have been reported using, e.g., rGO, CNTs, or carbon black as carbonaceous support materials. Zheng et al. combined the strategies of using a bimetallic MOF and a carbonaceous support. The bimetallic porphyrin-based CoNi-MOF has superior electrocatalytic properties (381 mV at 10 mA cm$^{-2}$) as compared to the monometallic Co- and Ni-MOFs (432 and 435 mV at 10 mA cm$^{-2}$, respectively). The performance of the bimetallic CoNi-MOF can be further improved by formation of a composite with rGO. The resulting CoNi-MOF/rGO composite has an overpotential of 318 mV at 10 mA cm$^{-2}$. The good performance can be ascribed to the synergistic effects between the CoNi-MOF and rGO. Thereby, rGO improves the overall conductivity and prevents the CoNi-MOF nanosheets from agglomeration, thus increasing the amount of accessible catalytic sites. Recently, Thangavel et al. reported a trimesic acid-based NiFe-MOF/graphene nanoplatelet (GNP) composite, which has a superior OER performance with a very small overpotential of 220 mV to obtain 10 mA cm$^{-2}$ outperforming the monometallic Ni-MOF (317 mV) and the bimetallic NiFe-MOF (240 mV). The performance can be further increased by replacing the carbon fiber paper substrate by 3D nickel foam resulting in an overpotential of 180 mV to obtain 20 mA cm$^{-2}$. Moreover, the NiFe-MOF/GNP composite has also a high durability with no obvious change in activity during a 96 h measurement at an applied potential of 10 mA cm$^{-2}$. The authors attributed the excellent performance to the increased electrical conductivity achieved by using GNPs as conducting support and a partial replacement of the Ni nodes by Fe. A further advantage of the NiFe-MOF/GNP composite is its fast charge transfer kinetics. The authors evaluated the performance of the NiFe-MOF/GNP composite also as an anode for the OER in alkaline anion exchange membrane water electrolysis (AAEMWE) using MoNi$_4$/MoO$_2$ as cathode and ultra-pure water as electrolyte. The AAEMWE reached a high current density of 540 mA cm$^{-2}$ at an applied cell voltage of 1.85 V accompanied by a superior stability of >1000 h in continuous electrolysis, which renders MOF-based materials suitable for practical application.

In the mentioned examples, the carbonaceous materials are used as conducting supports improving the electrical conductivity at the macroscopic scale. On the local level, however, the limited conductivity of MOFs is still an issue caused by size exclusion effects that are defined by the pore aperture, hence hindering the full exploitation of the inherent OER potential of MOFs. Using graphene oxide as an integral building unit in the construction of MOFs could be a possible strategy to utilize the full OER potential of MOF materials.

The porous structure of MOF materials renders them also an ideal host for OER active metal and metal-based nanoparticles. The MOF framework typically confines the size and the shape of the incorporated catalysts and prevents them from leaching and agglomeration during the electrocatalytic reactions, thus resulting in a highly active and stable OER performance. A nanoparticle-functionalized MOF was recently reported by Zhang et al. who prepared CoFe$_2$O$_4$ nanoparticles embedded into a monolayered benzimidazole-based Co-MOF (M-PCBN) and demonstrated a drastically improved electrocatalytic performance as compared to the bulk equivalent and the pristine MOF which resulted in overpotentials of 232, 316, and 348 mV at 10 mA cm$^{-2}$, respectively, demonstrating the benefits of introducing highly catalytic active nanoparticles. Beside a very small Tafel slope of...
32 mV dec⁻¹ (Figure 22c), M-PCBN also exhibited good electrocatalytic stability evidenced by a 60 h chronoamperometric measurement at 1.48 V versus RHE. The authors also demonstrated that the OER performance is highly dependent on the utilized substrate. Coating M-PCBN onto copper foam instead of CC resulted in an even lower overpotential of 185 mV at 10 mA cm⁻². As the main active catalytic sites, high-valent Co atoms located at the interface of the CoFeOₓ nanoparticles and the M-PCBN framework were suggested, which was also supported by spin-polarized DFT calculations. The Fe atoms were shown to be inactive toward OER due to their saturated octahedral configuration.[131]

Formation of nanoparticles inside the MOF framework can be also achieved by a controlled partial pyrolysis strategy, which preserves the skeleton structure of the MOF while generating catalytically highly active nanoparticles.[132] MOFs and their modified/functionalized analogs can be also pyrolyzed or calcined completely serving as periodically arranged precursors for preparation of doped carbons, metal incorporated (doped) carbons, and diverse metal-containing compounds with a controlled morphology.[132c] In this context, the interested reader on MOF-derived carbon-based materials and composites is also advised to the recently published reviews by Wang et al.[133] and Du et al.[132d]

As has been mentioned in Section 2, metal-free doped carbons are of great interest as OER catalysts. However, the homogenous distribution of the dopants inside the carbon structure is very challenging. In contrast, MOFs exhibit a homogenous distribution of the heteroatoms which can be even maintained after pyrolysis. MOFs containing low boiling point metal nodes can even be used for the formation of metal-free doped carbons, as these metals are carbothermally reduced and evaporated during the pyrolysis procedure.[134]

The standard approaches for catalyst synthesis usually produce materials that suffer from aggregation and low electrical conductivity. For this reason, MOFs have been shown to be promising templates for advanced catalyst design. One of reported examples uses MOFs based on MFe₂O₄ (where M = Mn, Fe, Co, Ni) and 2,5-dioxido-1,4-benzenedicarboxylic acid.[135] Via a simple pyrolysis of PANI-decorated nickel foams, one can obtain a porous composite material (Figure 23a) whose performance and stability are shown in Figure 23b–e. The resulting material has a highly porous structure, which enables facile electron transfer and results in an overall high OER catalytic performance with overpotential values as low as 240 mV. The use of nickel foam as a porous support has also been reported previously.[136] Similarly, structured composite material based on Co oxides can be prepared by a two-step thermal conversion strategy. Unlike the previously mentioned material, this composite exhibits much higher overpotential and a lower Tafel slope possibly due to lower porosity of the mentioned composite material. An interesting concept of design was reported by Sun et al.[137] The authors used core–shell structure of particles with the composition of CoₓNi₁₋ₓ@CoₓNi₁₋ₓO. Due to used MOFs precursors, a highly porous nanostructured material was obtained whose performance was highly dependent on the composition of the core as well as shell particles. Optimal performance was achieved using the molar Co:Ni ratio of 1:1. The reported synthetic route paves the way for future composites with even higher OER performance.

Apart from the composition of MOFs, their morphology also plays a crucial role in the OER activity of the catalysts. In a recent paper, the authors compared 1D, 2D, and 3D MOFs as supports for Co, Ni, and Cu oxides.[138] Their findings show that the as-prepared composites were highly oriented
and, importantly, delivered the overpotential of 208 mV at 10 mA cm$^{-2}$ for Co$_3$O$_4$/C composite. This value is one of the best for MOFs-derived composites in the literature.

5.2. COF Structures

Besides MOFs, COF-based materials attracted recently considerable attention for application as OER catalysts. COFs consist of organic building blocks that are linked reversibly by covalent bonds resulting in crystalline porous organic polymers with a controllable and predictable porous structure. COFs are very interesting as their porosity, pore size, and their electronic and catalytic properties can be controlled by the design of the building blocks and their linkage motives.[118d,119] In order to design OER active COF structures, the results on heteroatom-doped graphene are often used as a scaffold. On this basis, DFT calculations reported by Yang et al. proposed a high OER activity for a phenazine-linked 2D-COF (COF-C$_4$N) featuring a graphene like structure, an N-enriched character, hexagonal pores, and a good chemical stability, which was confirmed experimentally (Figure 24). COF-C$_4$N demonstrates an excellent OER activity and stability equaling to an overpotential of 349 mV at 10 mA cm$^{-2}$ outperforming other N-doped carbonaceous materials. Partial DOS and molecular orbital wave function calculations revealed that the C4 sides as the mainly
active catalytic centers inside the COF-C$_4$N structure, resulting in a preferential downhill trend in the corresponding reaction pathway calculation.

The thiadiazole-based COF reported by Mondal et al. exhibits an even lower overpotential of 320 mV to reach a current density of 10 mA cm$^{-2}$ outperforming the benchmark catalyst IrO$_2$/C. Moreover, the authors also demonstrated that the crystallinity of the analyzed COFs plays a substantial role for OER activity. The thiadiazole-based COF is additionally very stable as shown by time-dependent chronopotentiometry measurements current densities of up to 50 mA cm$^{-2}$. Post analytical characterization after the stability test revealed no change in the crystalline structure. The active site inside the COF structure was calculated to be the C$_2$-site confirming the practical results.

The electrocatalytic performance can be further enhanced by introducing co-catalysts like Co$_{0.5}$V$_{0.5}$, Ni$_{0.5}$N$_{0.5}$, Ni(OH)$_2$, or Co(OH)$_2$ into the COF framework. Gao et al. reported, e.g., a COF-SO$_3$H obtained by a condensation reaction of 2,5-diaminobenzenesulfonic and 2,4,6-triformylphloroglucinol, which was further functionalized by ammoniation to obtain NH$_4$@COF-SO$_3$. The NH$_4$@COF-SO$_3$ material was then used to synthesize metal-incorporated Ni$_x$Fe$_{1-x}$@COF-SO$_3$ and Co$_x$V$_{1-x}$@COF-SO$_3$ via cation exchange reactions. The metal-free NH$_4$@COF-SO$_3$ system demonstrated a rather poor OER activity equaling to an overpotential of 543 mV to reach 10 mA cm$^{-2}$. Interestingly, the bimetallic Co$_0.5$V$_0.5$ can be removed by concentrated HCl and reincorporated by ammoniation and subsequent ion-exchange without losing the crystallinity and the high OER activity. Despite the possibility to remove the Co$_0.5$V$_0.5$ particles, they remain stable in the COF structure during the electrocatalytic measurements without leaching into the electrolyte, as proven by inductively coupled plasma atomic emission spectroscopy. Gao et al. attributed the excellent OER activity and stability of Co$_0.5$V$_0.5$@COF-SO$_3$ to the unique coordination of the Co$_0.5$V$_0.5$ particles inside the COF structure and to the high catalytic activity of the Co$_0.5$V$_0.5$ sites enabled by the strong electronic interactions between Co and V.

Even higher activity for the same NH$_4$@COF-SO$_3$ system was reported by Feng et al. who exchanged the NH$_4$ group by Ni$_{0.5}$Fe$_{1-x}$ cyclen complexes. Their best performing composite, (Ni$_x$Fe$_{1-x}$ cyclen)@COF-SO$_3$, reached 10 mA cm$^{-2}$ at an overpotential of 276 mV accompanied by a large time-of-flight of 0.69 s$^{-1}$ at 300 mV and a high OER stability indicating a high atom-utilization efficiency. The materials having both micro- and macropores are beneficial for the fast mass transport and especially for enhancing the diffusion-limited OER. The microporosity yields a high surface area providing more active sites, which ameliorate the formation of O$_2$ via the OER reaction. The macropores enable a high fast transport of the formed O$_2$ bubbles away from the surface.

Synthesis of COFs with large pores is however quite challenging. Zhao et al. developed a new strategy to assemble COFs with their inherent microporous nature into a superstructure having interconnected macropores by using monodisperse polystyrene (PS) spheres as hard template. Moreover, the bipyridine units of the resulting macroporous COF (macro-TpBpy) can be used to coordinate Co(OAc)$_2$ (macro-TpBpy-Co) (Figure 25b) while still maintaining the macroporosity as evidenced by SEM image (Figure 25c). Functionalization of macro-TpBpy with Co-containing species drastically improves the OER activity resulting in overpotentials of 380 and 430 mV to reach 10 and 50 mA cm$^{-2}$, respectively, as compared to the pure macro-TpBpy COF that is practically inactive. Moreover, due to the macroporous structure of macro-TpBpy-Co, the mass transfer and the accessibility of the active sites are increased, which is especially beneficial at high applied potentials equaling to high oxygen pressures.

COFs typically contain a large number of uniformly distributed heteroatoms like B, N, O, and S, which make COFs attractive precursors for heteroatom-doped carbons.
advantage of using doped carbons have been intensively discussed in Sections 1 and 3. Additionally, carbonization of the highly porous COF materials results typically in porous carbons. A high porosity can be beneficial for the infiltration with electrolyte increasing the accessibility of the catalytic active sites and a rapid charge transfer.\cite{145b,146} In order to ensure the porosity after the pyrolysis step, the use of templates can be helpful as was demonstrated by Xu et al. In their work, a 2D triazine-based COF was functionalized with phytic acid as a template, resulting after pyrolysis in hierarchical porous N,P-co-doped 2D carbons. The COF-derived carbons exhibited an excellent OER performance reaching a current density of 10 mA cm$^{-2}$ at a potential of 1.99 V versus RHE drastically outperforming the Pt/C reference catalyst (1.01 mA cm$^{-2}$ at 1.99 V vs RHE).\cite{145a}

The combination of high porosity and a large amount of functional groups renders COFs also suitable hosts for uniformly incorporated and anchored metal-containing species as mentioned above. The resulting modified COFs can be additionally converted into porous carbons loaded with metal or metal oxide nanoparticles. The pores of the COFs thereby limit the growth of the metal (metal oxide) particles, prevent them from aggregation and migration, and assure their homogenous distribution in the resulting carbon material.\cite{145c,147} Using this strategy, Co$_3$O$_4$,\cite{148} FeS,\cite{149} RuO$_2$,\cite{147} Fe/Co,\cite{145b} and Ni/Fe\cite{145c} carbon composites have been successfully prepared and evaluated as OER catalysts. Among the mentioned examples, the RuO$_2$/carbon composite exhibited the highest OER activity. Micro-mesoporous N-rich carbons with homogenously distributed RuO$_2$ nanoparticles were derived by heating a triazine-based COF (IISERP-COF1) loaded with Ru(acac)$_3$ at 370 °C in air. The composite revealed a current density 10 mA cm$^{-2}$ at a potential of 1.44 V versus RHE.\cite{147}

A compact overview of COF and COF-based materials is given in Table 8.

6. Conclusion and Perspective

Carbonaceous OER catalysts gained considerable attention in the recent years due to their high structural and compositional variety and ultimately by their promising electrocatalytic
activity competing with or surpassing that of conventional metal oxide or metal hydroxide electrodes and even noble-metal reference electrodes, mostly under alkaline conditions. The outstanding OER activity with low overpotentials is achieved due to the combination of high intrinsic OER activity provided by defect and heteroatom-doped structures, high possible surface areas, and also due to the high electrical conductivity. Based on the analysis of the most recent developments, the intention of this review was to highlight the material parameters with applied synthesis approaches that influence the OER activity of carbon atoms as active sites in such catalysts and hybrid structures. Strategies such as defect engineering and heteroatom doping were discussed. Although these strategies are undoubtedly required to induce the OER activity of carbon atoms in carbonaceous materials, they often decrease the electrical conductivity that is however required for an overall high OER electrode activity and becomes decisive at high current densities.

3D (porous) N-doped as well as multiheteroatom-doped graphene type carbon structures are considered the best nano-morphology for “pure” or hybrid carbonaceous OER catalysts known today. Hybrid catalysts employing these structures together with nanosized transition metal or metal oxide particles reach a current density of 10 mA cm\(^{-2}\) at overpotentials as low as ≈300 mV for S, N co-doped carbon and ≈315 mV for hybrid structures such as NiO/C. This can be explained by a combination of a high surface area and conductive network heteroatom-doped carbon structure, the highly OER active inorganic nanoparticles with high available surface area, and additional synergistic effects further enhancing the OER activity of neighboring carbon atoms due to a modulation of the electronic structure. However, the wet-chemical or vapor-based synthesis
methods that are typically employed for fabrication of these structures provide limited possibilities for a rational design and arrangement of heteroatoms around active site carbon atoms.

A relatively new group of promising OER active materials is SACs. The main advantages of SACs are their high surface area and the strong metal-support interaction resulting in a promising OER activity. Research is however still in the infant stage, as synthesis of single metal atoms or at least nanoclusters without aggregation is quite challenging.

A main focus of this work was also dedicated to the relatively recent advances in the field of ordered 3D carbon (COF) and carbon/metal (MOF) framework structures for OER catalysis, which are envisioned to possess the potential for highly active carbon-based OER catalyst in the future. The 3D framework structures offer various advantages over classical 3D porous carbon. Through the choice of molecular linkers and metallic (MOF) or carbonaceous (COF) nodes, their geometry and composition can be precisely tuned, providing a defined porosity and a defined spatial location and content of the heteroatoms. By the choice of specific building blocks (e.g., electron donor or acceptor moieties), the electronic structure of the crystalline framework structures can further be manipulated, possibly enabling a faster electron/hole transfer from the catalytically active sites on the surface and throughout the structure also by an enhanced electrical conductivity.

The framework structures can also be pyrolyzed to further increase their electrical conductivity. This approach of ordered framework structures for OER catalysis already led to the formation of composite catalysts with outstanding performance surpassing that of nonordered structures. For a defective cobalt MOF on a nickel foam substrate, the overpotential as low as 178 mV at a current density of 10 mA cm$^{-2}$ was reported, combined with a high stability upon potential cycling and continuous operation. Metal-free COF structures also showed promising OER performances, with the lowest overpotential of 320 mV at 10 mA cm$^{-2}$ reported for a thiadiazole-based COF, outperforming an IrO$_2$/C benchmark catalyst.

The structural and compositional control in periodic framework materials can also be used to attach small OER active transition metal (metal oxide) nanoparticles or SACs via functional groups or coordination sites incorporated by the molecular building blocks. This strategy enables a rational design and precise control over spatial distribution of catalytically active sites not accessible in conventional 3D carbon structures, which may further be used to deepen our understanding of the OER mechanism on carbonaceous materials and synergistic effects of metal/carbon structures.

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Conflict of Interest

The authors declare no conflict of interest.

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[1] a) S. Oberthür, C. R. Kelly, Int. Spect. 2008, 43, 35; b) Dollars from Sense – The Economic Benefits of Renewable Energy, Report (DOE/GO-10097-267), National Renewable Energy Laboratory (U.S. Department of Energy – DOE), Washington, DC 1997.
[2] S. Inage, Wiley Interdiscip. Rev.: Energy Environ. 2015, 4, 115.
[3] N. Armario, V. Balzani, ChemSusChem 2010, 4, 21.
[4] M. E. Lyons, S. Floquet, Phys. Chem. Chem. Phys. 2011, 13, 5314.
[5] M. Bernt, A. Hartig-Weiβ, M. F. Tovini, H. A. El-Sayed, C. Schramm, J. Schröter, C. Gebauer, H. A. Gasteiger, Chem. Ing. Tech. 2020, 92, 31.
[6] a) M. S. Burke, S. Zou, L. J. Enman, J. E. Kellon, C. A. Gabor, E. Pledger, S. W. Boettcher, J. Phys. Chem. Lett. 2015, 6, 3737; b) M. S. Burke, L. J. Enman, A. S. Batchelor, S. Zou, S. W. Boettcher, Chem. Mater. 2015, 27, 7549.
[7] a) D. Adler, Radiat. Eff. 1970, 4, 121; b) Y. Matsumoto, E. Sato, Mater. Chem. Phys. 1986, 14, 397.
[8] B. Marinho, M. Ghislardi, E. Tkalya, C. E. Koning, G. de Witz, Powder Technol. 2012, 221, 351.
[9] R. Zhang, A. Palumbo, J. C. Kim, J. Ding, E.-H. Yang, Angew. Phys. 2019, 531, 1800507.
[10] a) G. Wu, A. Santandreu, W. Kellogg, S. Gupta, O. Ogoke, H. Zhang, H.-L. Wang, L. Dai, Nano Energy 2016, 29, 83; b) L. Zhang, J. Xiao, H. Wang, M. Shao, ACS Catal. 2017, 7, 7855.
[11] a) J. Lai, A. Nsabimana, R. Luque, G. Xu, Joule 2018, 2, 76; b) X. Deng, J. Li, L. Ma, J. Sha, N. Zhao, Mater. Chem. Front. 2019, 3, 2221; c) M. A. Younis, S. Lyu, Q. Zhao, C. Lei, P. Zhang, B. Yang, Z. Li, L. Lei, Y. Hou, X. Feng, BMC Mater. 2019, 1, 6.
[12] Y. Zhu, W. Zhou, Z. Shao, Small 2017, 13, 1603793.
[13] M. Chen, L. Wang, H. Yang, S. Zhao, H. Xu, G. Wu, J. Power Sources 2018, 375, 277.
[14] M. Wu, J. Liao, L. Yu, R. Lv, P. Li, W. Sun, R. Tan, X. Duan, L. Zhang, F. Li, J. Kim, K. H. Shin, H. Seok Park, W. Zhang, Z. Guo, H. Wang, Y. Tang, G. Gorgolis, C. Galiotis, J. Ma, Chem. – Asian J. 2020, 15, 995.
[15] H.-F. Wang, C. Tang, Q. Zhang, Adv. Funct. Mater. 2018, 28, 1803329.
[16] D. Wei, Y. Liu, Y. Wang, H. Zhang, L. Huang, G. Yu, Nano Lett. 2009, 9, 1752.
[17] a) T. Dürkop, B. M. Kim, M. S. Fuhrer, J. Phys.: Condens. Matter 2004, 16, R553-R580; b) G. Pennington, A. Aukuru, N. Goldsman, in Int. Semiconductor Device Research Symp., IEEE, Piscataway, NJ 2003, pp. 412–413.
[18] V. Mazāņek, J. Luxa, S. Matějková, J. Kucera, D. Sedmidubský, M. Pumera, Z. Sofer, ACS Nano 2019, 13, 1574.
[19] M. Li, L. Zhang, Q. Xu, J. Niu, Z. Xia, J. Catal. 2014, 314, 66.
[20] G. Murdachaew, K. Laasonen, J. Phys. Chem. C 2018, 122, 25582.
[21] A. J. Medford, A. Vojvodic, J. S. Hummelshøj, J. Voss, F. Abild-Pedersen, F. Stoldt, B. Bligaard, A. Nilsson, J. K. Norskov, J. Catal. 2015, 328, 36.
[22] a) S. Chen, J. Duan, M. Jaronic, S.-Z. Qiao, Adv. Mater. 2014, 26, 2925; b) A. M. El-Sawy, I. M. Mosa, D. Su, C. J. Guild, S. Khalid, R. Joesten, J. F. Rusling, S. L. Suib, Adv. Energy Mater. 2016, 6, 1501966.
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