Interfacial Effects on the Catalysis of the Hydrogen Evolution, Oxygen Evolution and CO₂-Reduction Reactions for (co-)Electrolyzer Development

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Abstract

Our progressive transition from a society energetically dependent on fossil fuels towards one relying on renewable sources requires novel, environmentally friendly energy conversion and storage concepts. Hydrogen is widely regarded as an energy carrier that could circumvent this need, particularly in sight of the foreseeable spread of fuel cell cars that would use this “renewable H₂”. The latter would be produced using electrolyzers, which in their better established form cannot fulfill the targeted H₂-price due to the low current densities ($< 0.5 \text{ mA} \cdot \text{cm}_{\text{geom}}^{-2}$) associated to their liquid electrolyte. Alternatively, devices based on proton- and anion-exchange membranes are currently under development, and a new kind of co-electrolysis cell in which CO₂ is reduced into hydrocarbons is also envisaged. Electrocatalysts play a crucial role in all of these systems, but the interplay between their surface and the reaction medium (in the so-called *interface*) is often overlooked in the quest towards better performance. With this motivation, this review discusses the current knowledge of the interfacial catalysis of the three (co-)electrolysis relevant reactions (i.e., the evolution of H₂ and O₂, and the reduction of CO₂). From this, we identify pH and surface oxidation state as the key electrolyte- and surface-related parameters for which further understanding could lead to improved kinetics, and propose strategies for the tentative design of better electrocatalysts.

TOC Figure

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Introduction

In recent years, the negative impact of anthropogenic CO₂-emissions on our planet's climate has motivated a progressive transition from a global energy scenario heavily reliant on fossil fuels to one based on environmentally benign, renewable energy sources. Among these, wind and solar display the greatest growth potential, but their inherent intermittency often results in a mismatch between energy production and demand that renders the development of novel energy storage and conversion systems urgent [1]. An often-envisaged solution is the transformation of this excess electricity into storable hydrogen [2] that can subsequently be used in fuel cell (FC) cars (whose market presence will steadily increase in the coming years) [3,4], in stationary H₂-O₂ fuel cells allowing highly efficient reconversion into power [5], or be fed into the natural gas network (directly as H₂ or after chemical transformation into CH₄) [6,7]. Within this problematic, alkaline water electrolyzers (AWEs) currently constitute the best-established technology for this energy-to-fuel transformation. Their operation relies on the use of two compartments filled with a highly concentrated base (e.g., $\approx 30\%$ KOH) and separated through a diaphragm that minimizes the crossover of the oxygen and hydrogen produced at the compartments' electrodes (anode and cathode, respectively). These O₂- and H₂-evolution reactions (OER, HER) appear formulated in Table 1 and are typically catalyzed using non-noble transition metals and their oxides (e.g., Ni and CoO_x). On the other hand, the high resistivity ($\approx 1\ \Omega\cdot\text{cm}_{\text{geom}}^{-2}$) [8] of this liquid electrolyte results in a large ohmic overpotential that limits AWE-operation to current densities $< 0.5\ \text{A}\cdot\text{cm}_{\text{geom}}^{-2}$. As a result, large and costly systems are required in order to reach significant H₂-production rates (typically $\leq 50\ \text{kg}_{\text{H}_2}\cdot\text{h}^{-1}$) with costs that remain $\geq \$5\ \text{kg}_{\text{H}_2}^{-1}$ [9], ≈ 3 -fold larger than the US-DOE target of $\$2\ \text{kg}_{\text{H}_2}^{-1}$ for hydrogen devoted to FC car refueling [10].

Alternatively, proton exchange membrane electrolyzers (PEMEs) can routinely operate at current densities $\geq 2\ \text{A}\cdot\text{cm}_{\text{geom}}^{-2}$ owing to the substitution of the AWE's liquid electrolyte with a highly proton conductive PEM (with a conductivity of $\approx 0.1\ \text{S}\cdot\text{cm}^{-1}$ and thicknesses in the order of 10s to 100s of micrometers). Unlike in AWEs, though, the strong acidity of the PEME's reaction medium ($\text{pH} \approx 0$) implies the need for noble metals as HER- and OER-catalysts, which typically consist of Pt and IrO₂, respectively. Despite their high price (currently $\approx \$30\ \text{g}_{\text{Pt}}^{-1}$ and $\approx \$18\ \text{g}_{\text{Ir}}^{-1}$) [11], these metals only constitute a minor fraction of the capital cost (and corresponding H₂-price) of the large ($\geq 1\ \text{MW}$) PEMEs being deployed worldwide. More precisely, considering an envisaged power density of $\approx 5\ \text{W}\cdot\text{cm}_{\text{geom}}^{-2}$ [12], along with typical Pt- and Ir-loadings of $\approx 2\ \text{mg}_{\text{Pt,Ir}}\cdot\text{cm}_{\text{geom}}^{-2}$ [13] and the metal prices quoted above, the combined noble metal cost ($\approx \$20\ \text{kW}^{-1}$) accounts for only $\approx 2\%$ of the estimated capital investment of $\approx \$1,000\ \text{kW}^{-1}$. More critical, on the other hand, is the amount of electricity consumed to make this H₂, set by the efficiency with which the electrolyte can fulfill this task. To exemplify this, the quotient between the nominal power of 1 MW and an assumed cell potential of 2 V (corresponding to an efficiency of $\approx 75\%$ on the basis of hydrogen's high-heating value) yields a H₂-production rate of $18\ \text{kg}_{\text{H}_2}\cdot\text{h}^{-1}$ (or $56\ \text{kWh}\cdot\text{kg}_{\text{H}_2}^{-1}$); assuming electricity costs of $\$0.05\ \text{kWh}^{-1}$ [14], this would translate into operation-related H₂-production costs of $\$2.8\ \text{kg}_{\text{H}_2}^{-1}$ before factoring capital expenses.

Even if the price of PEME-produced H₂ may display little dependency on the device's noble metal catalyst loading (unlike in PEMFCs, whereby this parameter is of crucial importance) [4,15], PEME development could be severely hindered by the catalytic metals' scarcity, particularly in the case of Ir. Considering a power-specific Ir-loading of $\approx 0.4\ \text{mg}_{\text{Ir}}\cdot\text{W}^{-1}$ (from $\approx 2\ \text{mg}_{\text{Ir}}\cdot\text{cm}_{\text{geom}}^{-2}$ and $\approx 5\ \text{W}\cdot\text{cm}_{\text{geom}}^{-2}$, see above), the installation of 1,000 megawatt PEMEs would require $\approx 400\ \text{kg}_{\text{Ir}}$, which corresponds to

$\geq 5\%$ of iridium's yearly (and highly inelastic) production [16]. In the short term, this will be circumvented by progressively decreasing the Ir-loading, e.g., by substituting the Ir-black currently used in PEME anodes with novel catalyst concepts like 3M[®]'s nano-structured thin films, which have already demonstrated outstanding performances using only $\approx 0.25 \text{ mg}_{\text{Ir}} \cdot \text{cm}_{\text{geom}}^{-2}$ [17]. Within a further-sighted perspective, however, OER-catalysts completely free of rare metals like Ir or Ru will need to be developed in order to allow for a long-lasting widespread of this promising technology.

In principle, such Ir-free, high-performance electrolyzers could be realized by combining AWEs' alkalinity (which would allow the implementation of non-noble metal OER-catalysts) with PEMEs' highly conductive electrolyte, substituting the PEM with an anion-exchange membrane (AEM). While still in the research and development stage [18], AEMs' OH^- conductivities are already in the 10s of $\text{mS} \cdot \text{cm}^{-1}$ (i.e., only ≈ 2 -fold short of PEM values); however, when CO_2 -containing reactants are fed into the system, the ensuing carbonization of the membrane (from $\text{OH}^- + \text{CO}_2 \rightleftharpoons \text{HCO}_3^-$) shifts its pH towards quasi-neutral values and its conductivity decreases by one order of magnitude [19]. Beyond the possibility of avoiding this effect by feeding decarbonized water into the electrolyzer, adding complexity to the system, recent results using intentionally carbonated AEMs [20] have demonstrated low current density performances similar to those of 2009 commercial PEMEs ($\approx 85\%$ efficiency at $\approx 400 \text{ mA} \cdot \text{cm}_{\text{geom}}^{-2}$) [21,22]. Hopefully, the potential of this promising technology shall be realized through significant performance and durability improvements in AE-membranes and ionomers [18], along with the development of non-noble metal OER-catalysts that can reliably operate at alkaline and/or quasi-neutral pHs.

Interestingly, anion exchange membrane electrolyzers (AEMEs) implementing a carbonated membrane could additionally be used as so-called co-electrolysis cells if the AEME's cathodic HER were to be substituted with the reduction of CO_2 . Numerous experimental studies on the latter reaction performed in aqueous media have reported a wide variety of reduction products that include CO, formate, methane or methanol (cf. half-reactions listed in Table 1), for which yield and distribution depend on the catalyst of choice. Beyond the difficulties in tuning the reaction's selectivity, the mere recognition of the products of interest constitutes a challenge of its own that is beyond the scope of this manuscript [23]. Suffice to say, however, that CO_2 -consumption in co-electrolysis cells is unlikely to significantly diminish CO_2 -atmospheric levels [24], and that the fabrication of supposedly appealing (yet abundant) products like CH_4 or C_2H_4 using this electrochemical approach will hardly ever become cost-competitive [25]. In an illustrative rough estimate, if $\approx 20\%$ of the yearly ethylene production ($\approx 150 \text{ Mt} \cdot \text{year}^{-1}$) [25] were to be produced electrolytically at the electricity cost of $\$0.05 \text{ kWh}^{-1}$ quoted above and an optimistic operative potential of 2.5 V, operating costs alone would account for $\approx \$3\text{-}5 \text{ kg}_{\text{C}_2\text{H}_4}^{-1}$ (assuming 30-50% efficiency), which is ≈ 3 -fold larger than current market prices [25]. ~~Instead~~ Thus, only the production of particular, added-value chemicals or their precursors appears ~~more~~ realistic, and the feasibility of this concept should be pondered in full cells that take advantage of the AEME configuration.

While this brief contextualization highlights the crucial role of the interplay between electrolyte and catalyst (surface) on (co-)electrolyzer performance, such interfacial effects are seldom addressed simultaneously in the existing literature. Thus, in this perspective we provide a unified picture by reviewing the existing literature dealing with electrolyte and catalyst surface effects on these three reactions (i.e., HER, OER and CO_2 -reduction). Each of the sections that follow is then devoted to one of them, and systematically structured as follow: after briefly discussing the current understanding of the corresponding reaction mechanism, we summarize the electrochemical parameters used to

quantify the catalytic activity and the descriptors that determine it; we then discuss effects related to the electrolyte (e.g., pH) on the catalytic activity; and finally, we look into catalyst surface effects (e.g., oxidation state). In all cases, we try to highlight those aspects that remain unclear in the existing literature, and additionally propose methods that may aid to clarify them. The perspective is then finalized with a summary of the aspects common to all three reactions, both from the point of view of their fundamental understanding and of the research and development directions that may lead to an improvement of the catalytic and device performance.

The Hydrogen Evolution Reaction

Often considered as a model faradaic reaction extensively discussed in classic electrochemistry textbooks [26,27] and book chapters [28], the evolution of hydrogen formulated in Table 1 is in terms composed of a combination of two out of the following three microscopic steps (hereby arbitrarily formulated in the acid form) [28]:

Additionally, the reaction kinetics on those surfaces that can catalyze both the hydrogen oxidation and evolution reactions (HOR, HER) can be described using a simple form of the Butler-Volmer equation [26]:

$$i_{\text{kin}} = i_0 \cdot \text{RF} \cdot \left(e^{\frac{\alpha_a F}{RT} \eta} - e^{-\frac{\alpha_c F}{RT} \eta} \right) \quad [4]$$

where i_{kin} is the so-called kinetic current (i.e., in the absence of mass transport limitations), η is the overpotential, i_0 is the exchange current density, RF is the roughness factor, and α_a and α_c are the anodic and cathodic transfer coefficients, respectively. As we will discuss in greater detail below, the HOR/HER-activity of a given metal is preferably quantified in terms of its i_0 -value; however, the experimental difficulties associated to the proper determination of this kinetic parameter (often resulting from the extremely high HOR/HER-rates on many metals surfaces) have led to underestimated values and false mechanistic interpretations [26,29,30]. Thus, prior to undertaking the discussion of specific catalytic effects on reaction rates, we will briefly review the experimental improvements which have allowed for an accurate evaluation of i_0 -values, focusing on those metals of practical interest for the development of electrolyzers cathodes (i.e., Pt, Ir, Ru, Pd, Rh, Ni, Au and Cu).

Rotating disk electrode (RDE) voltammetry is a widely extended technique for the quantification of electrochemical reaction parameters. However, upon using this tool to study the H_2 -oxidation reaction (HOR) in acid electrolyte, ohmically-corrected polarization curves measured on metals possessing i_0 -values greater than the diffusion-limited current set by the RDE-rotation speed (e.g., in 0.1 M HClO_4 , $i_{\text{lim}} \approx 4.2 \text{ mA} \cdot \text{cm}_{\text{geom}}^{-2}$ at 3,600 rpm) [31] directly match the Nernstian diffusion overpotential (η_{diff}), and therefore do not provide any meaningful kinetic information [32]. Even when the reaction kinetics become significantly slower (e.g., upon transitioning to alkaline media), kinetically controlled HOR curves derived from RDE-measurements can be rigorously assessed only

after subtracting η_{diff} to the iR -corrected potential [33]. Discriminating kinetic- from diffusion-controlled currents is even more complicated for the HER, since no diffusion *plateau* arises from the limited transport of reactant towards the electrode surface (except upon measurements in unbuffered electrolytes of $4 < \text{pH} < 10$) [34,35]. Nevertheless, limitations in the HER branch could originate from the slow mass transport of the reaction product (H_2) away from the electrode surface [36], which would explain the overpotential of $\approx 20 \text{ mV}$ at $\approx -10 \text{ mA}\cdot\text{cm}_{\text{geom}}^{-2}$ typically observed by RDE in acid media on PGM electrodes for which no measurable overpotential is expected at this current [37]. As a result of this limitation, the rigorous quantification of the HER/HOR kinetics on the most active catalysts requires the use of experimental setups featuring mass transport resistances significantly lower than that of an RDE (i.e., with larger i_{lim} 's). Among the plethora of possibilities, only three approaches have been proved to yield unambiguous, mass-transport free HER/HOR kinetics: a H_2 -pump implemented in a PEMFC configuration [38], the so-called floating vacuum carbon filtered electrode described in Ref. [39], and the scanning electrochemical microscopy (SECM) technique [40,41]; the i_0 -values on Pt-electrodes derived from these setups are compiled in Figure 1, where the results from RDE-measurements are underestimated by up to 2 orders of magnitude.

Upon transitioning from PGMs to less active metals like nickel (which remains the state-of-the-art catalyst in AWE cathodes), kinetic parameters can be estimated using steady-state polarization curves and electrochemical impedance spectroscopy [42-44]. i_0 values for Ni electrodes obtained with these techniques [45-49] range between $3\cdot 10^{-4}$ and $3\cdot 10^{-3} \text{ mA}\cdot\text{cm}_{\text{Ni}}^{-2}$; this large uncertainty is mostly imparted by reports dealing with highly porous Ni electrodes [50-52], and could originate from differences in the measurement conditions (i.e., nature and/or concentration of the electrolyte, absence of iR correction), the electrode history [53] and the delicate normalization of i_0 values with respect to the electrode roughness factor. In this respect, even if the methods for estimating the electrochemical surface of Ni electrodes are well established [54,55], such is not the case for the alloyed or surface-modified electrodes often applied for increasing nickel's HER-activity [30].

Beyond the use of i_0 as the HER-activity quantity, the so-called Tafel slope (i.e., the $(\alpha\cdot F)/(R\cdot T)$ -quotient in the exponential relation between i_{kin} and η formulated in Eq. 4) can be used to identify the reaction's rate-determining step (RDS) [29]. More precisely, a Tafel slope (TS) of $120 \text{ mV}\cdot\text{dec}^{-1}$ is indicative of a Volmer RDS, while $\approx 30 \text{ mV}\cdot\text{dec}^{-1}$ corresponds to a Tafel RDS, and $\approx 40 \text{ mV}\cdot\text{dec}^{-1}$ has recently been assigned to a Heyrovsky RDS [56,57]. On the other hand, great care must be taken upon evaluation of these slopes, since they can be affected by the changes in the surface coverage of adsorbed hydrogen within the potential window used in the evaluation of the kinetic results (note that this adsorbate coverage term is not considered in Eq. 4) [46,58,59]. Beyond this aspect, the recent use of setups free of mass transport limitations has yielded truly kinetic slopes of $120 \text{ mV}\cdot\text{dec}^{-1}$ for the HER on PGMs [10,41], even if in the past TS-values of only $30 \text{ mV}\cdot\text{dec}^{-1}$ were routinely observed using (diffusion-controlled) RDE-voltammetry, which led to multiple mechanistic misinterpretations [60]. From the latest experimental evidences, the HER/HOR on Pt proceeds through a dissociative adsorption (Tafel) reaction combined with a one-electron transfer (Volmer) RDS; this mechanism is irrespective of platinum's surface structure and of pH [33,61], and could be applicable to all other PGM catalysts [32]. In the case of non-PGMs, though, the HER in alkaline environment proceeds *via* a Volmer-Heyrovsky mechanism. On Ni, low TS-values of $\approx 45 \text{ mV}\cdot\text{dec}^{-1}$ are reported at low overpotentials [62,63], while the double slope often observed using porous electrodes [62-64] is probably related to morphological differences, mass transport limitations

and/or the presence of surface oxides [50,65,66], rather than to intrinsic discrepancies in electrode kinetics.

As for plausible descriptors unifying HER-activity trends along a wide variety of materials, by the late 1950's Parsons had already predicted a qualitative, Volcano-like relation linking $i_0(\text{HER})$ and the free energy of hydrogen adsorption (ΔG_{H^*} , whereby the maximum HER-activity corresponds to $\Delta G_{\text{H}^*} = 0$ eV) [67]. However, the lack of means to estimate actual ΔG_{H^*} -values on different metals in that time prevented Parsons from including experimental data on his plot; this limitation was only amended by the gas-phase measurements of metal-hydrogen bond strength by Krishtalik [68], which allowed Trasatti to draw a single Volcano trend for more than 30 different metals [69]. Much later, the emergence of more sophisticated calculation tools lead to the computation and use of ΔG_{H^*} as an activity descriptor [70], along with the subsequent demonstration of the proportionality between the measured metal–hydrogen adsorption strength and the computed hydrogen binding energy (HBE), except for some surfaces like Ni or Co [71]. Since then, HBEs have been estimated in multiple occasions and used as the activity descriptor in Volcano plots drawn on the basis of experimental i_0 -values evaluated in acid [70,72-75] or alkaline electrolytes [76]. Nevertheless, since the PGM i_0 -values at low pH conditions reported in those studies [70,72-75] were mass-transport limited, the resulting Volcano plots displayed slopes of $\approx 0.35 \cdot (k \cdot T)^{-1}$ (at 25 °C, $\equiv 0.022$ eV·dec⁻¹, where k refers to the Boltzmann constant), instead of the $1 \cdot (k \cdot T)^{-1}$ ($\equiv 0.056$ eV·dec⁻¹) expected from the kinetic model by Nørskov and coworkers [70], as critically discussed by Schmickler and Trasatti [71].

In an effort to verify this discrepancy between theoretically expected and experimentally determined HER-activities, in Figure 2 we have revisited the relation between Nørskov's HBEs [70] and up-to-date i_0 -values in acid (Figure 2a) and alkaline media (Figure 2b) for seven metals. In doing so, only PGM HER-activities in acid electrolyte evaluated with the mass-transport free setups discussed above were considered; additionally, in sight of the structure insensitivity of the HER on PGMs (further discussed below) [31], i_0 -values estimated for nanoparticles and polycrystalline surfaces were averaged to obtain the standard deviations listed in Table 2 [77,78,79]. In the case of the binding energies, their scatter arises from hydrogen coverage differences (θ_{H} spanning between a quarter and a full monolayer) [70], while possible pH effects on the HBE-value that have only been scarcely addressed in computational studies [77] are not considered. Interestingly, upon inclusion of these revised i_0 -values, the Volcano plot in acid medium (Figure a) agrees excellently with the kinetic model, even if the latter assumed a Tafel-RDS that would contradict more recent experimental results that point at a Volmer-RDS (keeping in mind the expected effect of the RDS on the Volcano's slope, first pointed out by Parsons) [67]. In the alkaline case, **Figure** Figure 2b, the comparatively lower HER-activity of the most active PGMs points at non-trivial origin of the pH effect on the HER-kinetics that should be the object of further theoretical consideration in sight of its implications to the development of alkaline fuel cells and electrolyzers [31].

Electrolyte-related effects

pH effects.— The dependency of the HER-rate on the electrolyte pH had been greatly overlooked until the recent advent of experimental setups allowing for a proper evaluation of the fast HER-kinetics in acid media. The marked pH effect that has been evidenced ever since affects in a greater extent the most active metals (e.g., the HER-activities of Pt, Ir or Pd decrease by factors of 210, 120 and 90,

respectively, by transitioning from pH = 0 to pH = 13) [61], while the effect is less drastic on non-PGM electrodes (cf. the 10-fold loss of HER-activity on Au [79,80], Ni [69,76] or Cu [69,76]). Additional measurements in neutral media have shown that this activity decrease is linearly related to the pH scale [81].

While the reason for this pH-effect remains the subject of ongoing debate, the two hypotheses that currently gather most of the attention propose (i) that H₂-oxidation in alkaline medium requires the added presence of OH⁻ adsorbed on the metal surface [82], or (ii) that the pH has a great (and so far non-computed) effect on the hydrogen binding energy in alkaline medium [61]. The former explanation has led to the development of tailored surfaces with oxophilic properties and improved HER-activities [83-85], but the latter has served to rationalize many experimental results while still holding some contradictions [81,86,87]. As an example of this, the increase of the HBE would justify the positive potential shift of the hydrogen underpotential deposition (H_{upd}) on PGM-electrodes observed upon transitioning from acid to alkaline electrolyte; however, the Pt(111) surface barely suffers from this H_{upd}-shift, while displaying a much lower HER-activity in alkaline than in acid electrolyte [88-90]. Moreover, in agreement with Figure 2 [70,73,76], a generalized increase of the HBE would imply an improvement of the catalytic activity of the metals that bind hydrogen weakly (i.e., those on the right side of the Volcano plot, like Au), which is the opposite of what is observed experimentally [80]. Thus, in order to clarify this effect, improved understanding of the structure of adsorbed hydrogen intermediates and water adlayers on the catalyst surface and their subsequent role in the HER is required. The development of computational methods that can reach beyond HER activation energies [31,72,91] and additionally account for pH effects is particularly urgent; recent efforts in this direction by Rossmeisl and coworkers [77,92] have linked the loss of activity at high pH to a change in configurational entropy of the proton upon crossing the outer Helmholtz plane, as illustrated in Figure 3 [92]. Further insights into this complex interplay between HER/HOR and electrolyte should also benefit from the recent development of highly sensitive X-ray emission techniques [93] allowing the direct monitoring of metal-hydrogen bond properties, better suited to this purposes than conventional X-ray absorption [94-96], electrochemical impedance [88,97-99] or laser pulse techniques [89,100].

Cation/anion effects.— A number of studies have dealt with the effect of strong anion adsorption on the kinetics of pseudo-capacitive and Faradic processes on PGM-surfaces [101-104]. Anions—adsorb adsorption on the electrode surface can also take place to a certain extent at potentials below the potential of zero charge and typically within the H_{upd} region, therefore affecting Pt-H_{ad} energetics and theoretically leading to changes in the HER-kinetics. From a practical viewpoint, anionic contamination by SO₃⁻ moieties possibly released upon degradation of the polymer electrolyte membrane concomitant to electrolyzer/fuel cell operation could detrimentally affect the device's performance and durability, particularly when operating with ultra-low PGM-loadings. This issue has been scarcely investigated for the ORR [105,105-108] and is almost undocumented for the HER/HOR, for which studies conducted under conditions of enhanced H₂/H⁺ (and contaminants) transport [109] have reached contradicting results. While Br⁻ and I⁻ were found to severely decrease the overall HER/HOR rates [40,110], similar activities were measured in H₂SO₄- and HClO₄-based electrolytes, possibly because (unlike halides) their counteranions do not adsorb on the catalyst surface at HOR/HER-relevant potentials in the vicinity of ≈ 0 V_{RHE} [111]. Moreover, since these results in acid media may still be affected by mass transport limitations inherent to the measurement setups, the impact of adsorbed anionic impurities should be unambiguously clarified by taking advantage of the slower HER/HOR kinetics at high pH conditions. On the other hand, studies in such alkaline media

have already showed that the HER/HOR-rate is not affected by the nature of the counter cation (i.e., Li^+ , Cs^+ , Na^+ or K^+) as long as the latter is not electroactive in the potential range used to study this effect [112]. As an example of this, KOH-based electrolytes are preferable to NaOH-ones for the HER on Ni, since the former minimize the formation of metallic hydrides and the corrosion of the electrode [113,114].

Effect of electrolyte impurities.— ~~The~~ Trace amounts of metal cations in the electrolyte can particularly affect the HER-activity of surfaces with low i_0 -values, on which the HER triggers at potentials sufficiently low to allow the plating of these impurities onto their surface. These contaminants can originate from the electrolyte itself or from the Pt- and Au-counter electrodes often used in these measurements (which balance the HER at the working electrode by evolving oxygen, thus reaching corrosion-inducing potentials). Their effect on the HER-activity of the substrate metal can be both positive [115] or negative [116], and their presence can be minimized by shielding the counter-electrode and/or by submitting the electrolyte to the pre-treatment further discussed in the CO_2 -reduction section.

Catalyst-surface effects

Structure sensitivity and particle size effect.— the number of literature reports dealing with the structure sensitivity of the HOR/HER on (single crystal) metals is relatively scarce. In the case of Pt (see Figure 4), the activity decreases in the order $(110) > (100) > (111)$ in alkaline electrolyte, whereby Pt(110) is 10-fold more active than Pt(111) [117]. ~~The same activity difference is observed f~~ For Au single crystals in acid electrolyte, ~~yet in this case~~ the activity decreases in the order $(111) > (100) > (110)$ [118], and a one-order of magnitude difference is again observed between the most- and the least-active planes. The HER on Cu in acid electrolyte decreases from (111) to (100), but this order is inversed at high overpotentials [119]. Finally, Ni does not display a clear HER-activity trend with respect to its crystallographic surface orientation [120]. Thus, it is extremely difficult to extract a general reactivity trend on the basis of this limited number of studies, especially when considering the added possibility that the HOR/HER on these metals may display different RDSs. As a result, there is high interest in extending these measurements to other metals and corresponding surface orientations; however, in acid media this would require the use of the SECM technique [40,41] that, as discussed above, is the only method based on the use of a liquid electrolyte (required for single crystal studies) that yields meaningful kinetic information free of mass transport limitations.

As for the metal nanoparticles (NPs) envisaged for device implementation, the dependency of the HER/HOR-kinetics on the particle size of PGMs in acid electrolyte has exclusively been studied for Pt-based catalysts (≈ 2 , ≈ 4 , ≈ 6 and ≈ 10 nm NPs supported on Vulcan-carbon) using the H_2 -pump PEMFC approach; ultimately, the HOR/HER i_0 -values (normalized to platinum's active surface area) of all these catalysts was the same [121] and equal to that reported for polycrystalline Pt using the SECM configuration [40]. Interestingly, this matching of the i_0 -values estimated for NPs and polycrystalline surfaces extends to Ir and Rh electrodes (although no data are available for different particle sizes) [32,41] and also applies to alkaline media, whereby ≈ 4 nm Pt-NPs display the same HOR/HER-activity as polycrystalline Pt [31]. Thus, the HER/HOR appears to be the sole fuel cell- and (co-)electrolyzer-relevant process unaffected by surface orientation and particle size effects [122], pointing at a RDS involving a single surface site, as in the case of the Volmer or Heyrovsky steps. This possibility is,

however, contradicted by the behavior displayed by gold, on which the HER rate is determined by the Tafel step (involving two surface atoms) and is enhanced on small NPs [123,124]. Besides this mechanistically-related exception, the lack of size sensitivity for most of the metals discussed here implies that catalysts with NPs as small as possible should be targeted in the design of these devices' electrodes in order to maximize their mass-normalized activity.

In the case of non-PGM electrodes, different studies have tried to unveil the HER kinetics on Ni surfaces in the form of polycrystalline/smooth thin films [125], porous structures [50,51,62,64,126-128] and micro- and nanoparticles [49,52,129]. High surface area, porous or nanostructured electrodes display an apparent increase of their HER-activity, even if a fraction of their surface may become blocked by H₂ bubbles [62]. Indeed, a comparison between surface-normalized i_0 -values proves that the HER-activity of Ni increases with the defects on its surface, pointing at a particle size effect that scales with the strain in the material (and leads to differences in electronic structure) [49]. As in the case of Au discussed above, this discrepancy with the general behavior observed for PGMs is probably related to a difference in the RDS (i.e., a Tafel-step) upon HER on Ni-surfaces.

Surface modification.— The increase of the HOR/HER-activity of PGM-single crystals brought along by their decoration with oxophilic transition metals (e.g., Ni) has been extensively studied by Markovic and coworkers [82-85], who justified this effect on the basis of a mechanism [82] in which the reaction rate would be limited by the adsorption of OH⁻, promoted by the oxophilic component (as discussed above). However, this explanation remains highly debated, since OH⁻ could also be provided by the fast dissociation of water molecules present (in great excess) in the vicinity of the surface [61,92]. Moreover, unlike single crystals, Ni-decorated polycrystalline electrodes (of Pt, Ir, Ru, Au, Cu, Ag and Ti) only displayed an improved HER-activity when the performance of the substrate metals was worse than that of Ni (i.e., in the case of Ag, Cu, Au and Ti), whose activity was matched as a result of the Ni-deposition [85]. Beyond these studies, no further proof has been provided concerning the improvement in HOR/HER kinetics in alkaline electrolyte upon surface decoration with an oxophilic component.

Following a complementing approach, the decoration of Ni electrodes with Ru or Pd resulted in an activity improvement related both to the superior HER- activity of Ru and Pd and to an increase of the electrochemical surface area [45,130]. Moreover, the addition of reduced graphene oxide layers to Ni foam promoted the HER activity [131] by enabling H-spillover from the Ni foam. Improved HER-kinetics can also be achieved by modifying the material's electronic structure, as in the case of Ni-P [132-138], MoS₂ [139-141] or Ni-Mo [142] alloys which are additionally stable in acid. Unfortunately, these materials remain a few orders of magnitude less active than Pt and thus their implementation in acid-operating devices does not appear viable.

The Oxygen Evolution Reaction

As it will be discussed in further detail below, the applicability of a given OER-catalyst is ultimately determined by the operative pH of the envisaged electrochemical device, which is in terms set by its liquid- or polymer-based electrolyte. In acidic media, the poor corrosion resistance of most transition metals translates in the need for OER-catalysts based on noble-metal oxides; among these, IrO₂ displays an optimum balance between activity and stability, and is therefore currently implemented in the great majority of *state-of-the-art* PEMFCs. On the other hand, the shift towards high pH

environments intrinsic to AWE/AEME-operation allows for the use of a greater variety of materials based on non-noble (and less expensive) transition metals, with Ni-, Co- and perovskite-oxides featuring both adequate OER activity and stability.

Leaving aside these pH-related constraints, several OER-mechanistic schemes have been suggested both for acidic and alkaline medium, in all cases involving different elementary reaction steps and surface-adsorbed intermediates [143]. Back in the 1950's, Bockris proposed a number of well-known OER mechanisms that are often referred to as the “(electrochemical) oxide path” [144], while in more recent years Rossmeisl and co-workers formulated a four step mechanism that was used in the computation of OER-overpotentials [145]. Table 3 displays a comparison of both pathways (arbitrarily formulated in the acid form), which share the first two reaction steps; the “oxide-path” then foresees a final chemical reaction, while the four step mechanism continues with two additional electrochemical steps implying the formation of $^*\text{OOH}$ as a reaction intermediate prior to the final evolution of O_2 .

On top of these discrepancies regarding reaction schemes, the definition of plausible activity descriptors for the OER on metallic oxide surfaces remains an added source of ongoing debate. Most descriptors based on experimental observations are related to bulk properties like the number of d -electrons [146], the e_g -filling [147], or the electronic conductivity [148]. Man *et al.* [149] linked the OER-activity of several compounds to the difference between the energy states of surface-adsorbed $^*\text{O}$ and $^*\text{OH}$ intermediates, ($\Delta G_{\text{O}^*} - \Delta G_{\text{HO}^*}$), and obtained a volcano-like relation between this descriptor and the computed OER-overpotential. In Figure 5a, we have revised this relation for several LaBO_3 perovskites (with $\text{B}=\text{Ti, Cr, Mn, Fe, Co, Ni, or Cu}$); among these, the catalyst displaying the lowest overpotential (i.e., LaNiO_3) is that on which the intermediates adsorb with an optimum, moderate strength, in agreement with Sabatier's principle. Complementarily, bulk thermochemistry (quantifiable as the bulk oxide's energy of formation, $\Delta G_{\text{form,bulk}}$) has been showed to correlate with surface adsorption energetics through the number of outer electrons of the corresponding transition metal oxide; as a result, another volcano-like relation (also included in Figure 5a) arises between the OER-activity of transition metal oxides and their corresponding $\Delta G_{\text{form,bulk}}$ [150]. Additional Volcano relations based on experimental results are featured in Figure 5b, whereby the OER-activity of a larger number of perovskite oxides is again related to the (surface) binding strength of the $^*\text{OH}$ intermediate or the (bulk) e_g -orbital filling [146,147].

The definition of correlations between theoretical predictions and experimental evidences can be further complicated by the potential-induced transformation of the catalyst surface into an (oxy)hydroxide [151-155] with substantially different local structure, composition and oxidation state from the underlying bulk oxide. As an example, Figure 6 features a schematic representation of the formation of such a disordered (oxy)hydroxide layer on the surface of a doped- NiO catalyst. This surface (oxy)hydroxide phase consists of disordered stacks of single atomic sheets of metal cations that have been proposed to be more accessible to the electrolyte than in the case of a dense, crystalline surface [151]. Nevertheless, the precise structure, composition and chemical state of these surface oxides has been only scarcely studied under operando conditions, and thus poses one of the major challenges for understanding the interplay between OER mechanism, active sites and the experimentally observed relation between oxide activity and stability. This task is further complicated by the generalized use in the literature of different OER-activity parameters, which renders the comparison between studies and materials extremely difficult. A very detailed comparison of different OER-activity parameters (such as exchange current density or overpotential

at a given current – normalized, e.g., by geometrical or N₂-sorption surface area, catalyst mass or electrochemical capacitance) is provided in Refs. [143,156], whereby the advantages and disadvantages of each activity quantifier are taken into consideration.

Electrolyte-related effects

pH effect.– Most recent studies regarding the OER activity of metal-based oxides are carried out in acid or alkaline solutions representative of the operative conditions of ~~PEWEs~~ PEMEs and AEMEs ~~AWES~~ (whereby pH $\approx$ 0 and $\approx$ 14, respectively) [153,157-161]. As we discussed above, though, the latter (alkaline) devices are likely to undergo carbonation upon operation, and the resulting quasi-neutral operative pH is also expected to apply to co-electrolysis cells. The ensuing interest in developing catalysts that can operate at intermediate pH conditions renders the investigation of the pH effect on the OER activity and stability of metal-based oxides crucial, but systematic studies on this topic are still missing in the literature. Lee *et al.* compared the OER mass activity of rutile IrO₂ and RuO₂ nanoparticles at pH 1 and 13 [159], and reported that both oxides display greater activity in acid medium than in alkaline (at η = 0.25 V and pH = 1, $i_{\text{OER}}(\text{IrO}_2) = 4 \mu\text{A}\cdot\text{cm}_{\text{ox}}^{-2}$ and $i_{\text{OER}}(\text{RuO}_2) = 10 \mu\text{A}\cdot\text{cm}_{\text{ox}}^{-2}$, as compared to $i_{\text{OER}}(\text{IrO}_2) = 2 \mu\text{A}\cdot\text{cm}_{\text{ox}}^{-2}$ and $i_{\text{OER}}(\text{RuO}_2) = 3 \mu\text{A}\cdot\text{cm}_{\text{ox}}^{-2}$ at pH = 13 and the same overpotential); unfortunately, the authors did not provide any comments on this behavior. Concerning perovskite oxides, Wattiaux *et al.* studied the pH effect on La_{1-x}Sr_xFeO_{3-y} electrodes in alkaline solution ($13 \leq \text{pH} \leq 14.5$) [162]; the authors showed that the OER-rate displays a first-order dependency with respect to the OH⁻ concentration at potentials $\geq 1.65 \text{ V}_{\text{RHE}}$, while being second order at $E \leq 1.50 \text{ V}_{\text{RHE}}$, but again failed to provide an explanation for this observations.

Three decades later, Shao-Horn and co-workers studied different oxide perovskites at pH 7 [160], and demonstrated that all of these materials display lower OER activity and stability at this pH than in alkaline medium (i.e., pH = 13). This poorer stability was related to a greater extent of cation leaching in neutral electrolyte, possibly consistent with the increased Tafel slope at high overpotentials featured by these oxides at pH = 7 (displayed in Figure 7). Thus, this study [160] emphasizes the need for perovskite oxides with enhanced activity and (cation loss) stability at neutral pHs.

A larger number of reports on the pH effect have been carried out on single Mn-, Co- or Ni-oxides [163-168], which in all cases suffer from an OER activity decrease at lower pH values. To justify this effect, some authors proposed that OH⁻ plays a critical role in promoting the OER on the catalyst surface [164,166], while a study dealing with Co-oxide demonstrated that the formation of a more active β -CoOOH phase was particularly favored at higher pHs [163]. Toshihiro *et al.* proposed that the Mn³⁺ would act as a water oxidation precursor, and that the control of this cation's disproportionation and comproportionation efficiencies at neutral pH was crucial to the oxide's OER-activity [168]. Beyond these specificities, the majority of these studies suggest that the decrease of the oxides' OER-activity in neutral and acid media is caused by the instability of their active phase in these environments [165,167,168].

Cation/anion effects.– Electrolyte components can significantly influence the activity of a given electrocatalyst, even if they are seldom regarded as being directly involved in the catalytic process of interest. As an example, the influence of cations and anions on the oxygen reduction activity of Pt-electrodes has been widely studied [169-171], but equivalent studies dealing with their effects on the OER-kinetics are still rare. Ganassin *et al.* [172] grew Ir-oxide films on Ir(111) and observed a decrease

of their OER performance upon transitioning from 0.1 M HClO_4 to 0.05 M H_2SO_4 ; the authors related this behavior to a delay in the oxidation of the metallic surface and a corresponding shift of the OER towards more positive potentials, induced by the presence of $\text{HSO}_4^- / \text{SO}_4^{2-}$ anions. In a resembling study, Owe *et al.* [173] reported that the OER activity of IrO_2 increases with the average electronegativity of the anions, in the order $\text{ClO}_4^- > \text{HSO}_4^- > \text{H}_2\text{PO}_4^-$, and proposed that larger electronegativities (cf. ClO_4^-) would lead to greater charge repulsive forces and correspondingly lower anion adsorption coverages on the catalyst's surface. Similar results have been reported by Franco *et al.* [174] concerning the OER-activity of $\beta\text{-PbO}_2$ in sulfuric or perchloric acids and their mixtures. In contrast to HSO_4^- and H_2PO_4^- anions, F^- was reported to enhance the OER catalytic activity of $\alpha\text{-MnO}_2$ in 1 M KOH electrolyte [175], whereby the presence of 8 mM KF lead to a 1.6-fold increase of the OER-current that the authors related to the F^- -induced formation of a more active (Mn^{3+}) phase.

Regarding cation effects, Suntivich *et al.* [176] compared the OER-activity of $\text{Ba}_{0.5}\text{Sr}_{0.5}\text{Co}_{0.8}\text{Fe}_{0.2}\text{O}_3$ and rutile IrO_2 in Li^+ -, Na^+ - and K^+ -containing electrolyte and found that the presence of Li^+ reduced the activity of both electrocatalysts. The authors proposed that this effect might result from the impact of the cation on the energy of the rate-determining intermediate, whereby the weakest interaction of K^+ with OH_{ad} would result in its weaker impact on the surfaces' OER-activity [170].

Catalyst surface related effects

The descriptor-based analysis discussed above and used as the basis for the Volcano-plot in Figure 5a considers well-defined, model electrocatalyst surfaces [177];⁽²⁴⁾ however, one must bear in mind that the experimental picture can be far more complicated by inhomogeneities in the catalyst's surface morphology and within the particle size. Additionally, it is extremely challenging to establish structure-activity relations for the OER, because the catalyst surface systematically undergoes transformation processes (e.g., into oxy-hydroxide surface layers or through partial dissolution) under OER-conditions.

~~Structure and particle size effect.– Drawing meaningful relations between the structure of surfaces with well defined crystallographic orientations and their OER-activity is extremely challenging due to the likely reconstruction of the surface at the high potentials at which the oxygen evolution proceeds. Thus, tremendous experimental effort is still needed to build.~~ Despite these difficulties arising from the reconstruction of the catalyst surface, epitaxial rutile IrO_2 and RuO_2 films with a (100) orientation were found to possess a greater OER-activity than ~~that~~ those with the (110) orientation [178], possibly due to the enhanced active site density ~~on~~ of the (100) surface. Interestingly, the (110) orientation in Co_3O_4 nanocrystals also contains more active phase (Co^{3+}) and features a greater OER activity than the (001) plane [179]. Moreover, a recent study on strontium ruthenate (SrRuO_3) single-crystal thin films reported that their OER-activity decreases in the order (111) > (110) > (001), while their stability increases in the same order [180]; as we will discuss in the next paragraph, this stability-activity relation might provide a new direction in the design of stable and active materials.

The required transition towards nanoscale catalysts with a higher active surface area has led to several reports that claim an increase of the OER activity of metal-based catalyst (e.g., RuO_2 , Co_3O_4) upon decreasing their particle size [181-186]. However, the explanations for this observation vary among different studies. Jirkovsky *et al.* proposed that, for RuO_2 electrodes, the edges separating the

(110) and (100) faces were the preferential sites for O₂ evolution [182], and showed that these edges were absent from particles larger than 20 nm. Esswein *et al.* also reported an increase of the OER activity of Co₃O₄ nanoparticles with their surface area (determined by N₂-sorption porosimetry) [181], but it remains unclear whether this observation arises from a mere increase of the surface roughness or from actual differences in surface orientation and corresponding reactivity. In contrast with these results, the OER activity of Ru_{0.8}Co_{0.2}O_{2-x} was reported to increase with the particle size [183].

In the particular case of Ru, a major issue related to the use of nanoscale catalysts is their poor stability; as an example, NPs with diameters of 4 ± 1 nm were reported to completely dissolve during the first anodic scan [187]. Other studies have noted an increase of the Tafel slope for nanoparticle sizes below a critical value [188], suggesting the existence of an optimum particle size; this appears to apply to RuO₂ nanoparticles (with 2 < diameter < 9 nm) [189], for which a maximum OER activity is observed at ≈ 3 – 5 nm, and whose stability can be improved by applying a pre-oxidation treatment.

Surface Modification.— Although most OER catalysts are based on crystalline (mixed-) metal oxides, several reports have hinted at the possibility of achieving better OER-activities by using amorphous surfaces [190-193]. Indeed, an initially crystalline Co₃O₄ thermally treated under H₂ and air displayed an enhanced OER-activity that was related to its surface-amorphization [193], which yields high amounts of hydrated Co²⁺ that can be easily oxidized to active Co⁴⁺ during the OER process. Additionally, density functional theory (DFT) calculations by Rossmeisl and co-workers predicted that the incorporation of Ni or Co to ruthenia would lower the *OH and *OOH adsorption energies on the oxide surfaces and bring the difference between the surface binding energies of O* and HO* ($\Delta G_{O^*} - \Delta G_{HO^*}$) significantly closer to that of the “perfect catalyst” (whereby $\eta = 0$ V, Figure 8) [194]. Subsequent experiments partially confirmed this predicted enhancement of the OER-activity upon modification of ruthenia with Ni and Co [152,195,196], but the effects were less significant than expected. Petrykin *et al.* [196] suggested that the inhomogeneous incorporation of Ni onto Ru_{1-x}Ni_xO_{2-δ} would result in the formation of surface Ni-rich regions that were related to the increase in OER-activity of Ru_{1-x}Ni_xO_{2-δ}. In the case of the bimetallic Ir-Ni oxide surface, the leaching of Ni atoms during the OER in 0.1 M HClO₄ would promote the formation of reactive surface hydroxyl groups, which might be considered as a descriptor for the OER activity [152].

Surface chemical state/active site for the OER.— As briefly discussed above, the oxidation state of the active metal surface during the OER plays a crucial role on its catalytic behavior. In this respect, the surface of RuO₂ (which is generally acknowledged as the material displaying the highest OER-activity, particularly in acid) tends to form a hydrated oxide layer upon immersion in aqueous medium, whereby the extent of surface oxidation depends on the physico-chemical properties of the material [153,197]. A combined XPS and electrochemical study proposed that Ru is in a VI+ oxidation state prior to oxygen evolution, and it becomes further oxidized into a VIII+ when oxygen evolution takes place. The resulting RuO₄ then either dissociates into oxygen and the initial hydrous Ru(VI)-oxide (therefore closing the OER- cycle) or dissolves in the electrolyte [198] – explaining the poor stability of RuO₂ under OER conditions.

In contrast to this behavior, IrO₂ features a better stability along with an acceptable OER-activity. Another study combining XPS and electrochemistry reported that IrO₂ undergoes a series of deprotonation steps prior to the OER that lead to a decrease of the photoemission intensity of the O1s signal related to hydroxide’s oxygen bond, along with a simultaneous increase of the signal

related to lattice-bound oxygen [199]. The proposed OER-mechanism starts from an hydrous oxide with Ir in a III+ valence state which, upon deprotonation, leads to tetravalent Ir; two subsequent deprotonation steps bring Ir into an unstable VI+ intermediate oxidation state (IrO_3) where oxygen is split off [199]. Recent *in-situ* X-ray absorption spectroscopy (XAS) measurements [200] have showed that at $\approx 1 \text{ V}_{\text{RHE}}$ Ir is in a IV+ oxidation state that increases during the anodic scan and reaches a value between V+ and VI+ in the oxygen evolution region, with Ir in the III+ and V+ states coexisting at potentials $> 1.3 \text{ V}_{\text{RHE}}$ [200]. On the other hand, this XAS study was performed on an electrodeposited thin film, and thus this hypothesized simultaneity of III+ and V+ oxidation states could alternatively be related to probing of bulk vs. surface atoms.

Looking beyond noble metals, nickel is one of the most promising transition metal catalysts for the OER in alkaline media. Continuous potential cycling across the Ni(II)/Ni(III) (i.e., $\text{Ni(OH)}_2/\text{NiOOH}$) redox transition results in the growth of a Ni(OH)_2 surface layer and a simultaneous improvement of the OER activity [143,154]. On the basis of results on electrodeposited nickel oxides, Bode *et al.* [201,202] suggested the existence of two limiting discharged phases, $\alpha\text{-Ni(OH)}_2$ and $\beta\text{-Ni(OH)}_2$ (with oxidation states of 2+ and 2.2+, respectively), and two limiting charged phases, $\beta\text{-NiOOH}$ (oxidation state 3+) and the $\gamma\text{-NiOOH}$ (oxidation state 3.5-3.7+). $\alpha\text{-Ni(OH)}_2$ is significantly hydrated and poorly crystalline, and can be oxidized to $\gamma\text{-NiOOH}$, whereas $\beta\text{-Ni(OH)}_2$ is mainly anhydrous and crystalline, and can be oxidized to $\beta\text{-NiOOH}$. Ageing of $\alpha\text{-Ni(OH)}_2$ in a strong base leads to its gradual transform into $\beta\text{-Ni(OH)}_2$, while $\beta\text{-NiOOH}$ can be converted into $\gamma\text{-NiOOH}$ upon overcharging at elevated potentials. A sketch of this so-called “Bode cycle” is showed in Figure 9 [154]; we note in passing that, despite the general validity of this oxidation state and phase transformation scheme, the physico-chemical properties of NiO_2 surfaces at different potentials can widely vary depending on the electrode processing and history [154].

Interestingly, Fe-doped NiO generally displays a higher OER activity than pure NiO, and recent DFT calculations and *in-situ* XAS measurements suggest that the active metal phase in this NiFeOOH is the Fe, and not the Ni [203,204]. Additionally, the incorporation of Fe^{3+} into the nickel oxy-hydroxide lattice would lead to a close-to-optimal adsorption energy for the binding of reaction intermediates on Fe sites, accounting the high OER activity of the bimetallic material [205].

Perovskite oxides are another class of compounds with high OER activity in alkaline environment. In the ABO_3 perovskite structure, the A-site is occupied by an alkaline earth element (e.g., Ca, Ba or Sr, or rare earth elements like La or Pr), while the OER-active B-site is occupied by a transition metal in 6-fold coordination to the oxygen atoms [143]. The possibility for cation substitution at the A- and/or B-sites (which in terms leads to the formation of electrons/holes or oxygen vacancies) results in a plethora of possible compositions and correspondingly tunable material properties, including electrocatalytic activity, electronic conductivity, and (electro)chemical stability. However, this wide variety of compositions renders the univocal identification of the surface oxidation state of the perovskite’s active B-site (which can additionally be affected by the A site cation) extremely difficult. Practically speaking, the majority of OER activity descriptors actually refer to bulk material properties [147,148,206,207] that, as discussed in the introduction, can be theoretically correlated to the surface adsorption energy of the key reaction intermediates [150] (and extensively reviewed, e.g., in Ref. [143]). Unfortunately, the experimental validation of these reactivity trends is additionally complicated by the large particle size (and correspondingly low surface area) of most perovskite oxides, which hinders the study of surface properties when bulk characterization techniques (like *in-situ* XAS) are used.

Irreversible surface changes upon OER.— The majority of the investigated metal oxide catalysts have been found to undergo substantial corrosion/modification upon OER, including dissolution of metal cations [208-210] and structural and compositional changes of their surface with a loss of long-range crystalline order [211,212]. Furthermore, a lot of attention has recently been devoted to the relation between OER-activity and catalyst stability, which has been proven for various noble metal catalysts [208,209,180] and highlights the continuous evolution of their surface during the OER [180,208,213-215]. Among these works, a theoretical study by our group [215] has identified the instability of the oxygen anion in the metal oxide lattice as the driving force for the dissolution and structural changes reported in numerous experimental studies, and concluded that this effect would prevent the formation of a thermodynamically stable metal oxide state under oxygen evolution conditions, irrespectively of the electrolyte pH. While verifying the nature of the processes occurring during the OER remains a major experimental challenge, several studies on oxide catalysts have reported the appearance of corrosion processes simultaneously with the OER onset. As an example of this, Change *et al.* proposed that the dissolution of RuO_2 is triggered by the potential-dependent change of ruthenium's valence state, whereby Ru IV+ is inactive but stable, and a higher oxidation state implies a greater activity but also instability [214].

Support, substrate and additive effects.— Several studies have envisaged a possible interaction between the catalyst and its support/substrate, which can consist of a noble metal or a high surface area carbon. Yeo *et al.* [216] observed a modification of the OER activity of monolayers-thick cobalt oxide galvanostatically deposited on different metal substrates, with Au leading to an OER activity ≈ 40 fold greater than that of bulk cobalt oxide. The authors suggested that substrates of increasing electronegativity would facilitate the oxidation of the supported catalyst layer, implying that the preferred oxidation state for the OER on Co-oxide would be IV+, instead of III+ [216]. Resembling OER-activity enhancement effects have been reported for manganese oxides supported on Au [217], for which XAS measurements have shown that the increase in activity also correlates with the higher oxidation state of Mn (IV+ instead II+) [218]. DFT calculations have shown that the addition of Au to manganese- or cobalt-based oxides (either on their surface or used as a substrate) can lead to a decrease of the OER overpotential by 100-300 mV or 100 mV, respectively. In this case, though, theory predicts that the Au would act as a hydrogen acceptor site that helps to stabilize the $^*\text{OOH}$ reaction intermediates, lowering the overall overpotential [219].

Besides these noble metal substrates, carbon-based supports/additives are often added to partially-insulating oxides in order to enhance their electronic conductivity; however, in sight of their often-beneficial effects on the OER-activity, these carbon-based additives have additionally been formulated along with oxides which do not suffer from these intrinsic conductivity limitations. As an example of this, single oxide catalysts such as CoO_x [220-222] or perovskite oxides [223-225] have been reported to feature an improvement of their OER-activity upon addition of carbon. XAS measurements on Co_3O_4 spinel [220] and $\text{Ba}_{0.5}\text{Sr}_{0.5}\text{Co}_{0.8}\text{Fe}_{0.2}\text{O}_3$ perovskite [161] have demonstrated that the processing of these materials with carbon induces a change in the catalyst's electronic structure, which is believed to be responsible for the enhanced activity of the oxide/carbon composites. These results point out the importance of correlating physico-chemical catalyst properties measured *in-situ* with their OER-activity, since material processing and operando conditions can substantially change the (surface) state of the oxide catalyst.

The Electroreduction of CO₂

The electrochemical reduction of carbon dioxide into gases and liquid chemicals/fuels has gathered increasing attention since the seminal studies of Hori and collaborators [226,227], who first demonstrated the electroreduction of CO₂ to methane and ethylene on polycrystalline Cu [228,229]. While the research efforts devoted to this vast topic have yet to result in the development of efficient, cost-competitive co-electrolysis devices, a significant degree of advancement has been achieved concerning the understanding of the mechanism of the various reactions pathways at play; as we will discuss in the remaining of this section, the selectivity of these steps towards particular products strongly depends on interfacial parameters related to catalyst surface and electrolyte properties, for which better insight and fine-tuning are already leading to significant (and greatly needed) improvements in catalyst performance and selectivity. We purposely leave aside in this discussion the electroreduction of CO₂ in (partially or completely) non-aqueous solvents, of undeniable fundamental interest but that we do not envisage as transferable into an operating device due to complications related to the complementing counterelectrode (oxidation) reaction. If the latter were to consist of the evolution of O₂ from added water, the high potentials required for this purpose would likely imply the simultaneous oxidation of the organic electrolyte component; additionally, the resulting O₂ would permeate to the cathode side and get reduced into O₂^{•-}, likely problematic in sight of its extreme reactivity with most organic solvents, which has in terms hindered the development of aprotic metal/air batteries [4, 230-232].

Within this problematic, Figure 10 displays an extended reaction scheme partially inspired by the overall CO₂-reduction mechanism recently proposed by Koper and coworkers [233], which largely succeeds at convening experimental observations with computational predictions. The reduction of CO₂ starts with the thermodynamically unfavorable transfer of one electron to form CO₂^{•-} [234,235] which, when weakly adsorbed (e.g., on Sn, Pb or Hg electrodes), abstracts a proton from a neighboring water molecule and gets further reduced to HCOO⁻/HCOOH [236]. As we will discuss in further detail below, recent DFT-calculations by Nørskov *et al.* [237] have proposed that this formate pathway also leads to the subsequent production of methanol on RuO₂ (which, on the other hand, possibly gets reduced at the potentials associated to this reaction) [238].

~~On the other hand~~ Alternatively, when the initial adsorption of the CO₂ molecule takes place on a stronger-binding substrate, its subsequent reduction proceeds all the way to carbon monoxide. Recent computational [239] and experimental [240] studies have proposed that the binding energy of this CO on the metal surface can be correlated to the CO₂-reduction activity through a Volcano-like relation (following Sabatier's principle); thus, in Figure 11 we have plotted the CO-binding energies of several stepped metal surfaces (computed in Ref. [241]) against their corresponding CO₂-reduction activities, expressed as the potential at which a partial CO₂-reduction current of 1 mA·cm_{surface}⁻² is reached, and averaged from various experimental reports [236,240,242-246] dealing with polycrystalline surfaces (see Figure legend for details). Weak CO-adsorption on Zn, Ag and Au leads to the desorption of this product, with increasing CO-binding energies among these metals resulting in an improvement of their catalytic performance that reaches its maximum for Au. The metals on the opposite side of the Volcano plot are characterized by their strong CO-binding energy and their added ability to adsorb hydrogen on their surface; upon CO₂-reduction, the resulting H_{ads} reacts with CO₂ to yield strongly bound CO_{ads} [226], which poisons their surface and causes the evolution of minute amounts of CH₄ (on Ni) or only H₂ (cf. Pt, Ir, Rh and Fe, which are therefore absent from Figure 11) [226,236]. We note in passing that palladium's ability to yield CO and formate [226]

renders it an exception to this general behavior; however, the extent to which the absorption of hydrogen into the Pd-lattice (concomitant to the operation at such low potentials) may affect palladium's CO-adsorption strength and product selectivity remains unclear, and we have therefore opted to leave Pd outside of Figure 11. Future studies should be devoted to clarify this effect, e.g., by determining the CO₂-reduction activity of Pd-adlayers of known thickness deposited on an inactive substrate [78]. In principle, metallic hydrides should be able to provide 'subsurface' hydrogen to the CO₂^{•-} state and therefore positively affect the kinetics and selectivity of the CO₂ reduction reaction.

Finally, the unique capability of Cu to yield hydrocarbons and alcohols is motivated by the moderate surface binding of CO, which is widely regarded as the key intermediate in the electrochemical reduction of CO₂ on Cu [229,247]. Thus, numerous groups have opted to substitute CO₂ with CO in their studies in an attempt to decrease their complexity while drawing meaningful conclusions from their work. As we will discuss below, the combination of this approach with recent computational studies has proved invaluable in formulating the C1- (i.e., to CH₄ and MeOH) and C2- (to C₂H₄ and EtOH) pathways featured in Figure 10.

Prior to this detailed discussion of the interfacial parameters that govern the CO₂-reduction mechanism in aqueous media, we revisit the main activity descriptors quantifiers presented in the literature. Since in most cases the reduction of CO₂ results in a variety of products, the performance of different electrocatalytic surfaces is often compared on the basis of the *partial current* devoted to the reduction into a certain product at a given potential, $i_{\text{product}}(E)$. This magnitude is in terms estimated from the molar flux of that product ($\dot{n}_{\text{product}}(E)$) detected through the analytical tool of choice (e.g., gas chromatography), using Faraday's law:

$$i_{\text{product}}(E) = n \cdot F \cdot \dot{n}_{\text{product}}(E) \quad [5]$$

whereby n represents the number of electrons exchanged in the electrochemical reaction (see Table 1) and F is the Faraday constant (96,485 C·mol⁻¹·s⁻¹). On the basis of this $i_{\text{product}}(E)$ and the total current measured at the same potential, $i_{\text{total}}(E)$, one can additionally derive the product's *Faradaic efficiency* (FE, often expressed as a percentage) by simply dividing both magnitudes:

$$\text{FE}_{\text{product}}(E) = i_{\text{product}}(E) / i_{\text{total}}(E) \quad [6]$$

Electrolyte-related effects

The nature and composition of the electrolyte can influence the CO₂-reduction activity and selectivity through multiple effects [229,248], including the adsorption of anions and/or cations on the electrode surface, changes in the surface wettability and pH, or through ion-pairing interactions with reactants and products. Thus, the effect of these variables on the reaction pathway [248-252] is further commented in the following.

pH effects.— The improved HER-kinetics observed on all metal surfaces in acid medium and discussed above results in a poor selectivity for the reduction of CO₂ when the reaction is performed in media with high proton concentrations. On the other hand, the carbonation of alkaline electrolytes upon contact with carbon dioxide (triggered by the equilibrium $\text{CO}_2 + \text{OH}^- \rightleftharpoons \text{HCO}_3^-$) practically impedes the use of media which set a high operational pH. Instead, CO₂-reduction is most often performed in quasi-neutral conditions, typically by using buffer solutions for which the pH additionally shifts upon

saturation with CO₂ (according to the carbonation formulated above). As an example of this electrolyte pH effect, CO₂ electroreduction on an Ag electrode yielded FE_{CO} > 85 % and $i_{CO} \approx 40$ mA/cm² at pH = 10, as compared to FE_{CO} $\approx$ 75 % and $i_{CO} \approx 30$ mA·cm_{geom}⁻² at pH = 7 and only FE_{CO} $\approx$ 40 % and $i_{CO} \approx 15$ mA·cm_{geom}⁻² at pH = 4. These data were obtained in a flow cell with an overall potential of 3.0 V (i.e., vs. the anodic OER), using a phosphate buffer (0.5 M K₂HPO₄ and 0.5 M KH₂PO₄) as the electrolyte and adjusting the pH by addition of 10 M KOH or 10 M H₃PO₄ [249]. The use of the alkaline buffer with a lower proton concentration lead to a partial suppression of the HER, and thus more surface sites available for the adsorption and subsequent reduction of CO₂ into CO [253,254].

Beyond this bulk pH effect, the consumption of protons associated to the CO₂-reduction and H₂-evolution reactions formulated in Table 1 is known to results in an increase of the surface pH even when the reaction is performed in a buffered solution [24,226,255]. Gupta *et al.* quantified the extent of this surface pH shift on the basis of the pH of the bulk electrolyte, its buffer strength and the local current density and corresponding diffusion layer thickness [256]; upon applying these corrections to the results reported by Hori *et al.* [229] for the reduction of CO₂ on polycrystalline Cu in 0.1 M KHCO₃, the authors discerned a shift towards the formation of less-hydrogenated products at higher local pH values. Additionally, the resemblance in the corrected Tafel slopes for methane and ethylene production from CO₂ was rationalized in terms of the (partially) common pathways depicted in Fig. 10. These results emphasize the ~~importance~~ importance of this approach for unveiling the reaction mechanisms, and the need to extend its use to current studies in which materials with different degrees of dispersion (and correspondingly different local currents and reactant concentrations) are being compared.

Finally, the effect of the pH on the formation of C1- and C2-products (i.e., methane vs. ethylene, respectively) on Cu electrodes has also been discussed in several studies [257-259]. Following the seminal work of Hori *et al.* [257], the pH-dependency observed for the methane-formation pathway has been related to a rate determining step involving the transfer of an electron and a proton in recent experimental [260] and computational [259] studies that suggest that CHO_{ads} is the key intermediate. On the contrary, ethylene formation is pH-independent [257] (i.e., its rate determining step does not involve a hydrogen atom), and instead appears to proceed through a CO-dimer that constitutes the key intermediate in the required C-C coupling [258,260].

Cation/anion effects.— The overall CO₂-reduction current is significantly affected by the size and charge of the supporting electrolyte cation, with CO₂-reduction currents on Cu increasing upon transitioning from Na⁺ to La³⁺ [252]. The nature of the cation was also shown to greatly influence the product distribution and current efficiencies, whereby C₂H₄ formation on Cu was enhanced by the cation radius, in the order Li⁺ < Na⁺ < K⁺ $\approx$ Cs⁺ [261]. Such effects are often rationalized on the basis of the cation's hydration ability, which in terms determines its adsorption on the electrode surface [248,262]. Larger cations (e.g., K⁺, Rb⁺ or Cs⁺) with a weaker hydration shell have more chances to directly adsorb on the electrode surface, while smaller, strongly hydrated cations (like Li⁺ and Na⁺) display a weaker adsorption. On the other hand, anionic species, (e.g., Cl⁻, Br⁻, I⁻) tend to adsorb strongly onto the electrode surface and preferentially affect the CO₂ reduction rate, to promote instead the evolution of hydrogen [250].

Electrolyte impurities.— Hori *et al.* [250] showed that the CO₂-reduction activity and stability of Cu electrodes greatly depends on the quality of the chemical reagents used to prepare the electrolyte solutions, since these can contain heavy metal impurities (e.g., Fe²⁺ and Zn²⁺) that may deposit on the

metal surface and affect its selectivity. Similar deactivation effects as those observed on Cu have also been reported on polycrystalline Au [263], therefore concluding that this behavior is not caused by intermediates and/or products of the CO₂-reduction. It is also worth noting that this impurity-related “stability issues” can be temporarily circumvented by increasing the surface area of the working electrode; this may explain the improved activity and stability of oxide-derived Au electrodes reported in Ref. [245], thereby related to a greater stabilization of the CO₂^{•-} intermediate on these surfaces. This extent may be verified by systematically performing these electrochemical studies in pre-electrolysed solutions (using, e.g., the procedure outlined in Ref. [250]) in which the current efficiency has been showed to remain stable within the course of the CO₂-reduction measurement.

Catalyst-surface effects

From single-crystal studies to nanoparticles.– Hoshi *et al.* studied the reduction of CO₂ to CO on Pd [264] and Ag [265] low-index single crystals, and in both cases reported ≈ 2 -5 fold larger CO-currents on the (110) plane as compared to the (111) and (100) orientations. While these short reports did not provide further insight on these reactivity trends, it is interesting to note that the topmost surface atoms in the stepped (110) plane have a coordination number (CN = 7) smaller than those of the (111) and (100) surfaces (with CN = 9 and 8, respectively). Interestingly, this lower CN-value is also equal to that of Au(211), which has recently been related to an optimal CO-binding strength and the correspondingly improved CO-selectivity of Au-nanoparticles [266] and nanowires [267], as further discussed below.

As for the production of hydrocarbons and alcohols on Cu-electrodes, the elucidation of the separated reaction pathways towards C1- and C2-products originally postulated by Hori and collaborators [257,283] was greatly aided by experiments with Cu-single crystals performed by the same group [268] and, more recently, by Schouten and coworkers [269,270]. In brief, as summarized in Figure 10, the formation of methane favored on (111) terraces proceeds through a *COH intermediate that also yields minor amounts of MeOH (in this case through a kinetically disadvantageous *CHO isomer) [271]. On the other hand, ethylene formation on Cu(100) is believed to proceed through a CO-dimer [258,272,273] that gets reduced to surface-adsorbed acetaldehyde, CH₂CHO*; again, the selectivity of this intermediate towards C₂H₄ vs. EtOH appears to be dictated by the surface crystallographic orientation, whereby planes with low coordination numbers (and correspondingly greater adsorption strengths) favor the production of the alcohol over the gas [274].

Beyond the fundamental understanding gained by the single crystal studies discussed above, the envisaged transition towards realistic CO₂-electroreduction devices implementing highly-dispersed catalysts has motivated a lot of recent studies dealing with the performance of such materials. Within this context, the electroreduction of CO₂ on Au-based catalysts has gathered a lot of interest, partially because the resulting mixture of CO and H₂ (i.e., *syngas*) offers alternative pathways for synthetic chemistry [25,275]. As discussed above, Zhu and coworkers prepared Au-nanoparticles [266] and nanowires [267] of various diameters and lengths (4-10 and 15-500 nm, respectively) and reported that their CO-selectivities [FE_{CO} (-0.5V_{RHE}) $\approx$ 80-90 %] scaled with the content of low-coordinated surface sites; according to their DFT-calculations, these active centers would display an enhanced adsorption strength of the *COOH intermediate and intermediate moderate binding of the CO-product. The same reasoning was followed by Mistry *et al.* [275] to explain the selectivity values and H₂/CO ratios of samples consisting of size-selected, $\approx$ 1-8 nm nanoparticles supported on glassy

carbon electrodes. In this case, however, the authors reported FE_{CO} -values of only ≈ 20 -40 % at a much lower potential of $-1.2 V_{RHE}$ at which the competing HER was enhanced by the abundance of under-coordinated surface sites in the smaller Au-particles. Additionally, Feng and collaborators [276] have recently reported $FE_{CO}(-0.5 V_{RHE})$ values spanning between ≈ 20 and ≈ 90 % for Au-nanoparticles (≈ 20 -40 nm in diameter) supported on carbon nanotubes. These selectivity differences could not be solely explained on the basis of the catalysts' electrochemical surface area; instead, the authors found a linear correlation between $i_{CO}(-0.4 V_{RHE})$ and the grain boundary surface density, suggesting that these defects are particularly active for the selective reduction of CO_2 to CO.

Looking beyond Au, a number of recent studies by the group of Jiao have focused on the reduction of CO_2 on alternative (and partially) CO-selective metals like Ag [242,277] and Zn [243]. Electrodes based on nanoporous Ag [242,277] or Ag-nanoparticles [242] yielded i_{CO} vs. E curves with Tafel slopes (TS's) of only $\approx 60 \text{ mV}\cdot\text{dec}^{-1}$, in stark contrast with the ≈ 120 -140 $\text{mV}\cdot\text{dec}^{-1}$ observed for polycrystalline Ag [242,277,278]. The authors related this lower slope to an intrinsic difference in the reaction mechanism for the nanomaterials vs. the polycrystalline surface; on the latter, the rate determining step (RDS) would be the initial reduction of CO_2 to $CO_2^{\bullet-}$ [229,235], while on the former the RDS would correspond to the subsequent protonation of this radical into $*COOH$. Interestingly, the same group [243] also reported a ≈ 2 -fold difference in Tafel slopes for the reduction to CO on Zn-dendrites vs. polycrystalline Zn (with TS ≈ 100 vs. $\approx 250 \text{ mV}\cdot\text{dec}^{-1}$, and $FE_{CO}(-1 V_{RHE}) \approx 70$ vs. $\approx 30\%$, respectively). In this case, however, the apparent differences in reactivity were justified on the basis of the ≈ 90 -fold larger roughness factor (RF) of the dendrites. We note by passing that this mere RF-difference should not lead to the change in TS-values observed in Ref. [243]; nevertheless, as pointed by the same authors [242] and further discussed below, the rigorous assessment of mechanistic properties on the basis of Tafel plots requires corrections for RF-values, local pH shifts [256] and reactant transport properties that are hardly fulfilled in most of the existing literature.

Finally, the effect of increasing the surface area of copper on its CO_2 -reduction activity has also received recent attention. Tang *et al.* [279] compared the catalytic behaviors of polycrystalline, sputter-roughened and nanoparticle-covered Cu-electrodes, and observed that the production of CO and C_2H_4 increased with the surface roughness [i.e., for Cu-NPs, $FE_{CO}(-1.1 V_{RHE}) \approx FE_{C_2H_4}(-1.1 V_{RHE}) \approx 40$ %]. As discussed above, these results can be rationalized on the basis of the mechanism in Fig. 10b, whereby the formation of ethylene proceeds preferentially on undercoordinated Cu-planes (more abundant in roughened surfaces) through an intermediate CO-dimer [272,273]. Reske and coworkers [280] prepared size-selected Cu-nanoparticles supported on glassy carbon with diameters ≈ 2 -15 nm; at $-1.1 V_{RHE}$, all electrodes yielded CO and H_2 as the major products independently from the Cu-particle size, along with faradic efficiencies of only ≈ 10 and ≈ 5 % for CH_4 and C_2H_4 , respectively. The high H_2 -yields [$FE_{H_2}(-1.1 V_{RHE}) \approx 60$ %] were related to an increase of the binding strength of H_{ads} and CO_2 on the low-coordination sites in the nanoparticles, which would favor H_2 -evolution while being detrimental to the subsequent reduction of CO to hydrocarbons. Interestingly, these reactivity trends are not fully consistent with the results of Baturina *et al.* [281], who tested ≈ 10 -100 nm diameter Cu-NPs on various carbons supports and reported $FE(-2 V_{RHE})$ values of ≈ 40 % for C_2H_4 and CH_4 formation. The latter was proposed to result from a contribution of H_2 evolved by the carbon support, in a slip-over effect that, to the best of our knowledge, constitutes one of the only examples of a surface-induced effect on the products selectivity reported in the literature.

Importance of the surface oxidation state.— The reduction of CO_2 on copper oxides has been the subject of numerous studies since the seminal work of Frese [282], who first reported significant

MeOH-yields on thermally oxidized copper electrodes. Qualitatively similar results were recently obtained by Le and coworkers [283], who prepared Cu-oxides by anodization, thermal oxidation and electrodeposition and observed (initial) FEs of up to 38 % at $\approx -0.5 V_{\text{RHE}}$. Recent DFT-calculations have related this preferred selectivity for MeOH vs. CH_4 to copper's surface oxidation state [284], whereby the surface hydroxides in Cu_2O would favor methanol formation, while methane gas would be produced on Cu^0 . On the other hand, the identification of CH_3O^* as the reaction's selectivity determining intermediate in this recent computational work [284] would disagree with other theoretical and experimental studies [233,271] that have related the methanol vs. methane yields to $^*\text{CHO}$ - vs. $^*\text{COH}$ -adsorbates occurring at an earlier stage of the mechanism (cf. Fig. 10d).

On top of these uncertainties regarding the reaction mechanism, it also remains unclear whether the initial surface-oxidized state of these materials can be maintained at the low potentials intrinsic to the reduction of CO_2 [279,283]. In this respect, *in-situ* Raman spectroscopy measurements [285] in 0.1 M KHCO_3 on electrodeposited Cu_2O films showed that their surfaces were fully reduced after only 200 seconds at $-0.99 V_{\text{RHE}}$. Contradictorily, a depth-profiling, Auger spectroscopy study of qualitatively similar materials revealed the presence of Cu_2O in the near surface after two hours of electrolysis at $\approx -1.3 V_{\text{RHE}}$ [286]. Moreover, the authors of Ref. [285] found that the reduction of CO_2 yielded mostly ethylene and ethanol, but no MeOH was reported, while in Ref. [278] [286] ethylene production was again enhanced but no alcohols whatsoever were detected. This last product distribution is consistent with the results of Kas *et al.* [287], who also observed significant ethylene yields [$\text{FE}_{\text{C}_2\text{H}_4}(-1.1 V_{\text{RHE}}) \approx 25 \%$] on preferentially-oriented Cu_2O films with no significant alcohol formation.

These discrepancies in the nature and distribution of CO_2 -reduction products catalyzed by (reduced) Cu-oxides also extend to the studies of Kanan and collaborators. In their first report on this topic, electrochemically reduced thermal oxides [244] yielded high FEs of $\approx 40\%$ for CO and formate at $-0.5 V_{\text{RHE}}$, along with FEs $< 10 \%$ for ethylene and ethane formation at $-0.9 V_{\text{RHE}}$ and (again) no methanol formation. Subsequently, the same group studied the reduction of CO on the same thermally-prepared Cu_2O -electrodes, yet now reduced by heat-treatment in the presence of H_2 [288]; the authors observed FEs of $\approx 20\text{-}30\%$ for the formation of acetate and ethanol at only $-0.3 V_{\text{RHE}}$, and later concluded [289] that these unique product selectivity was directly related to the presence and density of grain boundaries on the reduced materials. On the other hand, these last studies dealing with the reduction of carbon monoxide [288,289] were performed in an alkaline electrolyte (0.1 M KOH) of constant and high pH; thus, the selectivity results reported in those works should not be affected by the shifts in surface pH observed in quasi-neutral media, which have been related to the product distribution in Refs. [285] and [287].

The reaction picture becomes increasingly complicated when considering that many of the studies cited above have reported severe surface reconstruction during CO_2 -reduction [244,285,287] (consistent with single crystal behavior [290,291]), which further complicates the common interpretation of their results. This lack of consensus concerning the exact nature and distribution of the reaction products extends to other works dealing with alternative, initially oxidized metals like Sn [292], Pb [293] or Au [294], in which product distributions unequivocally different from those observed on the corresponding reduced surfaces are reported but the stability is not specifically assessed. Therefore, more systematic studies are needed in order to determine the role and interplay of roughness factor, surface oxidation state [285], local pH [287] and surface orientation/defects [289] on these reactivity trends. Here, the combination of techniques capable of

providing *in-situ* information about the time-evolution of surface oxidation state and particle morphology during CO₂-reduction (like synchrotron-assisted X-ray photoelectron and absorption spectroscopies, along with small angle X-ray scattering) could provide greatly needed insight into these effects.

To finalize this section, we briefly discuss the reduction of CO₂ on RuO₂, which has also been reported to lead to significant CH₃OH-yields [e.g., $FE_{CH_3OH}(-0.2 V_{RHE})=30\%$ in Ref. [294]]. In this case, however, the reaction is believed to proceed through the formate-formation mechanism schematized in Figure 10b [237], which would agree with the large amounts of formic acid observed experimentally [238,295]. Additionally, as in the case of the copper oxides surfaces discussed above, the oxide RuO₂ surface would be (at least) partially reduced at the low potentials required for CO₂-reduction [296]; again, further studies would be needed to clarify the extent of this state and its subsequent effect on the product selectivity and stability.

Surface modification.— Extensive investigation of the electroreduction of CO₂ on AuCu alloys with different Au/Cu ratios has showed that their activity and selectivity compared to pure Au and Cu surfaces can be tuned by controlling the alloys' structural and electronic properties [290-294]. In particular, Au₃Cu was found to have the highest mass activity for CO production [292], which was related to its enhanced ability to provide additional binding sites for *COOH while featuring weak *CO-binding (thus favoring its desorption as CO(g)) [297-301]. Cu-Ag alloys with various atomic ratios were investigated as well [302]; the alloy with a Cu/Ag ratio of 28/72 featured the highest selectivity for the formation of C2 compounds such as CH₃CHO, C₂H₅OH, and C₂H₄ (with FEs of $\approx 24\%$, $\approx 17\%$ and $\approx 13\%$, respectively, at $-0.6 V_{RHE}$ in CO₂-saturated 0.1 M KHCO₃ buffer) [302]. Cu-Pt alloys have also been investigated, and an optimum Cu/Pt element atomic ratio of 3:1 was found for the reduction of CO₂ to CH₄ [303]. These results were rationalized on the basis of DFT calculations by Peterson *et al.*, who suggest that the selectivity-determining step for CH₄ formation on Cu is the protonation of adsorbed CO* to form adsorbed HCO* (i.e., $CO^* + H^+ + e^- \rightarrow HCO^*$) [304]; thus, with its outstanding activity for hydrogen evolution, the presence of Pt in the alloy surface would play a synergetic role and facilitate the protonation of adsorbed CO* to yield CH₄ [303]. On the other hand, more recent computational works [271] and well-established experimental observations [229] have concluded that the formation of methane proceeds through a *COH intermediate, instead of the *CHO proposed in Ref. 304 (cf. Fig. 10d), so the results in Ref. [303] should be revised on the basis of this (more plausible) reaction mechanism.

Alloys of Pt with other transition metals are also of potential interest for CO₂-reduction, since this alloying is known to modify the binding energies of H*, CO* and other intermediates and may promote platinum's poor activity and selectivity for CO₂ reduction. As an example of these effects, a Pt-Ru alloy displayed improved selectivity towards methanol production than compared to pure Pt ($FE_{MeOH}(-0.03 V_{RHE}) = 75\%$, vs. 7.5 % for pure Pt), likely due to the decrease in CO-poisoning imparted by Ru atoms, which in terms lead to an easier desorption of carbonaceous species [305]. Additionally, theoretical work has showed that among 34 stable binary alloys, six may be capable of reducing CO into methanol [306]; in Figure 12, the computed binding energies of the *CHO and *COH intermediates resulting from the first proton/electron transfer (i.e., $\Delta G(*CHO/*COH)$) is plotted against the corresponding CO-bonding energies. The most active surface is expected to be PtIn₂(111), followed by PtHg₂(201), PtPb₄(001), PdBi₂(111), and IrSn₂(111), with theoretical onset potentials for the reduction of CO of -0.67 , -0.69 , -0.75 , -0.95 , and $-1.08 V_{RHE}$, respectively (as compared to $-0.71 V_{RHE}$ for the reduction of CO on Cu). Furthermore, these alloy surfaces were also predicted to be

more selective for the formation of methanol than copper is for the reduction of CO₂ to hydrocarbons.

Doped catalysts.— the modification of the surface binding sites with doping elements is a promising approach to improve CO₂-electroreduction. Carbon-based materials including B-doped diamond [307], N-doped graphitic carbon [308] and cobalt complex modified diamond [309] were found to convert CO₂ to C1 products. In the case of the N-doped graphitic carbon (NCNT) [308], the combination of N-doping and a polyethylenimine (PEI) overlayer lead to a FE_{HCOO}⁻(-1.95 V_{RHE}) ≈ 87% at a current density of 9.5 mA·cm_{geom}⁻² in 0.1 M KHCO₃, whereas in the absence of PEI these values dropped to ≈ 5 % and 1.3 mA·cm_{geom}⁻² at the same potential, respectively [308]. This beneficial PEI overlayer is believed to provide a stabilizing environment for CO₂^{•-} through H-bonding with its N-based surface functionalities (i.e. predominantly pyrrolic and pyridinic nitrogen, with surface concentrations of 63 and 24 at %, respectively) which, as schematized in Figure 13 [308], would increase the CO₂ concentration on the electrode surface. The results of these studies open a perspective on a new promising class of materials which, on top of displaying a high efficiency for the electroreduction of CO₂ in aqueous media, are inexpensive and can be made following uncomplicated procedures.

Conclusions and Perspectives

Following this exhaustive review of the literature dealing with (co-)electrolyzer reactions, we now revisit the main interfacial aspects in which research directions are common to all three processes. Having defined these, we finalize this manuscript by providing some hints that we hope may lead to the development of better performing catalytic systems.

Prior to discussing actual interfacial electrocatalysis effects, though, we emphasize again the need for adequate electrochemical setups in order to rigorously assess kinetic parameters for all three reactions. This aspect is probably less pressing for the OER, for which the combination of sluggish kinetics and unlimited reactant (H₂O) transport allows for the use of well-established RDE-voltammetry protocols. As we have extensively discussed above, the HER constitutes a far more complicated case, since the extremely fast kinetics brought along by the combination of PGM-surfaces and acid media can only be assessed with a limited number of mass-transport free setups (like the H₂-pump or SECM). In the case of the reduction of CO₂, complications principally arise from the required *online* coupling of electrochemistry and analytic techniques, which often results in ill-defined reactant- and product-transport and hinders the comparison between results acquired on different (and most often custom-made) setups.

The subsequent comparison of the kinetic parameters derived from these measurements on the basis of values normalized with respect to the catalysts' active surface (e.g., i_0 in mA·cm_{metal}⁻²) is further complicated by the often challenging quantification of their electrochemical area. This aspect is particularly critical in the case of the metal oxides often used for OER-catalysis, whose roughness cannot be assessed on the basis of the charge associated to a given surface adsorption process, as it is customarily done for PGMs. Thus, other quantities derived from double-layer capacitance, N₂-sorption porosimetry or transmission electron microscopy should consider the intrinsic limitations of these techniques when drawing conclusions about the surface-specific activities of the corresponding materials.

Moving on to electrolyte-related effects, the pH of the reaction medium appears as the most pressing parameter, not only because it can limit the range of applicable (i.e., stable) materials, but also in sight of its great impact on the surface-specific activity of the catalysts used in each device. In this respect, PEME's highly acidic operative conditions result in extremely fast HER-rates on all PGM-surfaces, and the corresponding possibility of implementing ultra-low metal loadings that (in sight of the lack of particle-size effects) could take advantage of the smallest possible particles. On the other hand, IrO₂ currently appears as the only reliable catalyst for the complementing OER, and more efforts should be devoted to the design of novel catalyst morphologies (aiming at maximizing its dispersion) and/or to the development of alternative, Ir-free materials. Transitioning towards alkaline media would bring a solution to this issue, but more studies should deal with the stability of the transition metal oxides applicable in AEMEs upon carbonation of the alkaline membrane (and corresponding pH-shift towards quasi-neutral values). Additionally, one must bear in mind that the HER in alkaline and neutral media is orders of magnitude slower than in acid even on the most active PGMs, ultimately implying the need for greater PGM-loadings and a possible cost limitation to this technology. Thus, more research efforts should be devoted to understand the reason for this marked pH effect, as well as to the preparation of PGM-free HER-catalysts with activities comparable to that of Pt. Finally, the possible substitution of the HER with the reduction of CO₂ in a carbonated, AEME-inspired co-electrolysis cell would result in quasi-neutral operative pHs that would significantly shift in the vicinity of the catalyst surface. The implications of this effect on the kinetic parameters derived in most of the existing literature should be assessed using electrochemical setups (and corresponding analytic techniques) with well-defined electrode geometries and transport modes (i.e., precise diffusion layer thicknesses). Beyond these fundamental considerations, we believe that there is an urgent need for a rigorous assessment of the technological feasibility and economic implications of this co-electrolysis concept, as it has already been done for other (battery-based) energy storage technologies [4,310].

Regarding interfacial effects related to the catalyst surface, we recognize a need for an unambiguous determination of its oxidation state under *operando* conditions, particularly in the case of CO₂-reduction and OER-catalysts. While *in-situ* XAS would appear as a proper technique to shed light on these effects, its bulk nature translates into the need for small nanoparticles (ideally with diameters ≤ 5 nm) in order to draw meaningful, surface-related conclusions from its results. Unfortunately, the synthesis of such small NPs poses a challenge by of its own, especially in the case of transition metals (like Cu or Ni) and their oxides (or perovskites) and considering the need for (unsupported) nanoparticles free of surface-adsorbed organics. As for the HER/HOR equilibrium, the ongoing development of X-ray emission techniques that may be sensitive to the hydrogen adsorbed on the PGM-surface (H_{ads}) could prove crucial in unveiling its involvement in the reaction mechanism, and possibly in understanding the HER's strong pH-dependency.

While it is somehow adventurous to hint at research directions that may lead to significant catalytic activity improvements, tuning the adsorption strength of key intermediates through alloying with other metals appears as a plausible strategy, particularly in the case of CO₂-reduction and HER-catalysts. On the other hand, the alkaline and quasi-neutral pHs of interest for these reactions may trigger the segregation of the alloying element towards the surface [311], in terms causing a loss of activity with time. Alternatively, CO₂-reduction electrocatalysts are already benefiting from the addition of protonable N-functionalites that stabilize CO₂^{•-} through H-bonding, and whose effect on the reaction selectivity deserves further attention. Finally, the possibility of fine-tuning the electronic properties of perovskite oxides renders them a particularly appealing OER-catalytic system, especially

if their durability under neutral pH conditions can be corroborated and synthetic means leading to greater catalyst dispersions can be refined.

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References

- [1] S. Chu, A. Majumdar, *Nature* 488 (2012) 294-303.
- [2] F. Steinke, P. Wolfrum, C. Hoffmann, *Renew. Energy* 50 (2013) 826-832.
- [3] N. Konno, S. Mizuno, H. Nakaji, Y. Ishikawa, *SAE Int. J. Alt. Power.* 4 (2015) 123-129.
- [4] O. Gröger, H. A. Gasteiger, J.-P. Suchsland, *J. Electrochem. Soc.* 162 (2015) A2605-A2622.
- [5] F. N. Büchi, M. Hofer, C. Peter, U. D. Cabalzar, J. Bernard, U. Hannesen, T. J. Schmidt, A. Closset, P. Dietrich, *RSC Adv.* 4 (2014) 56139-56146.
- [6] S. Schiebahn, T. Grube, M. Robinus, V. Tietze, B. Kumar, D. Stolten, *Int. J. Hydrogen Energy* 40 (2015) 4285-4294.
- [7] M. Götz, J. Lefebvre, F. Mörs, A. McDaniel Koch, F. Graf, S. Bajohr, R. Reimert, T. Kolb, *Renew. Energy* 85 (2016) 1371-1390.
- [8] K. Zeng, D. Zhang, *Prog. Energy Comb. Sci.* 36 (2010) 307-326.
- [9] M. Felgenhauer, T. Hamacher, *Int. J. Hydrogen Energy* 40 (2015) 2084-2090.
- [10] M. Ruth, F. Joseck, “Hydrogen Threshold Cost Calculation (DOE Hydrogen Program Record nr. 11007)” (accessed 01/26/2016), http://hydrogen.energy.gov/pdfs/11007_h2_threshold_costs.pdf
- [11] Daily Pt- and Ir-prices (accessed 01/26/2016), <http://www.platinum.matthey.com/>.
- [12] C. K. Mittelsteadt, *ECS Trans.* 69 (2015) 205-211.
- [13] M. Carmo, D. L. Fritz, J. Mergel, D. Stolten, *Int. J. Hydrogen Energy* 38 (2013) 4901-4934.
- [14] E. B. Anderson, K. E. Ayers, L. Dalton, M. Schiller, in *Proceedings of the ASME 2014 12th International Conference on Fuel Cell Science, Engineering and Technology*, available online at <http://proceedings.asmedigitalcollection.asme.org/proceeding.aspx?articleid=1920886> (accessed 01/26/2016).
- [15] A. Rabis, P. Rodríguez, T. J. Schmidt, *ACS Catal.* 2 (2012) 864-890.
- [16] P. C. K. Vesborg, T. F. Jaramillo, *RSC Adv.* 2 (2012) 7933-7947.
- [17] K. A. Lewinski, D. F. van der Vliet, S. M. Luopa, *ECS Trans.* 69 (2015) 893-917.
- [18] J. R. Varcoe, P. Atanassov, D. R. Dekel, A. M. Herring, M. A. Hickner, P. A. Kohl, A. R. Kucernak, W. E. Mustain, K. Nijmeijer, K. Scott, T. Xu, L. Zhuang, *Energy Environ. Sci.* 7 (2014) 3135-3191.
- [19] H. Yanagi, K. Fukuta, *ECS Trans.* 16 (2008) 257-262.

- [20] C. C. Pavel, F. Cecconi, C. Emiliani, S. Santiccioli, A. Scaffidi, S. Catanorchi, M. Comotti, *Angew. Chem. Int. Ed.* 53 (2014) 1378-1381.
- [21] K. E. Ayers, E. B. Anderson, C. B. Capuano, M. Niedzweicki, M. Hickner, C.-Y. Wang, Y. Len, W. Zhou, *ECS Trans.* 45 (2013) 121-130.
- [22] K. E. Ayers, E. B. Anderson, K. T. Dreier, K. W. Harrison, *ECS Trans.* 50 (2013) 35-46.
- [23] H.-R. Jhong, S. Ma, P. J. A. Kenis, *Curr. Op. Chem. Eng.* 2 (2013) 191-199.
- [24] D. Pletcher, *Electrochem. Commun.* 61 (2015) 97-101.
- [25] J. Durst, A. Rudnev, A. Duttaby, Y. Fu, J. Herranz, V. Kaliginedi, A. Kuzume, A. A. Permyakova, Y. Paratcha, P. Broekmann, T. J. Schmidt, *Chimia* 69 (2015) 769-776.
- [26] M. Breiter, in *Handbook of Fuel Cells: Fundamentals, Technology and Applications, Vol. 2*, W. Vielstich, A. Lamm, and H. A. Gasteiger, Editors, p. 361, John Wiley & Sons, New York (2003)
- [27] K. J. Vetter, *Electrochemical Kinetics: Theoretical and Experimental Aspects*, p. 516, Academic Press, New York (1967).
- [28] K. Krischer, E.R. Savinova in *Handbook of Heterogeneous Catalysis*, G. Ertl, H. Knözinger, F. Schüth, and J. Weitkamp, Editors, p. 1873, Wiley-VCH, Chichester (2009).
- [29] B. Conway, B. Tilak, *Electrochim. Acta* 47 (2002) 3571-3594.
- [30] A. Lasia, in *Handbook of Fuel Cells: Fundamentals, Technology and Applications*, W. Vielstich, H. A. Gasteiger, A. Lamm and Harumi Yokokawa Editors, John Wiley & Sons (2010).
- [31] W. Sheng, H. A. Gasteiger, Y. Shao-Horn, *J. Electrochem. Soc.* 157 (2010) B1529-B1536.
- [32] J. Durst, C. Simon, F. Hasché, H. A. Gasteiger, *J. Electrochem. Soc.* 162 (2015) F190-F203.
- [33] P. J. Rheinländer, J. Herranz, J. Durst, H. A. Gasteiger, *J. Electrochem. Soc.* 161 (2014) F1-F10.
- [34] M. Auinger, I. Katsounaros, J. C. Meier, S. O. Klemm, P. U. Biedermann, A. A. Topalov, M. Rohwerder, K. J. J. Mayrhofer, *Phys. Chem. Chem. Phys.* 13 (2011) 16384-16394.
- [35] I. Katsounaros, J. C. Meier, S. O. Klemm, A. A. Topalov, P. U. Biedermann, M. Auinger, K. J. J. Mayrhofer, *Electrochem. Commun.* 13 (2011) 634-637.
- [36] J. Zheng, Y. Yan, B. Xu, *J. Electrochem. Soc.* 162 (2015) F1470-F1481.
- [37] C. C. McCrory, S. Jung, I. M. Ferrer, S. M. Chatman, J. C. Peters, T. F. Jaramillo, *J. Am. Chem. Soc.* 137 (2015) 4347-4357.
- [38] K. C. Neyerlin, W. Gu, J. Jorne, H. A. Gasteiger, *J. Electrochem. Soc.* 154 (2007) B631-B635.
- [39] C. M. Zalis, D. Kramer, A. R. Kucernak, *Phys. Chem. Chem. Phys.* 15 (2013) 4329-4340.
- [40] J. Zhou, Y. Zu, A. J. Bard, *J. Electroanal. Chem.* 491 (2000) 22-29.
- [41] C.G. Zoski, *J. Phys. Chem. B* 107 (2003) 6401-6405.
- [42] B. Łosiewicz, M. Popczyk, in *Solid State Phenomena, Vol. 228*, p. 333, Trans. Tech. Publ. (2015).
- [43] E. A. Franceschini, G. I. Lacconi, H. R. Corti, *Electrochim. Acta* 159 (2015) 210-218.
- [44] A. Kellenberger, N. Vasilcsin, W. Brandl, N. Duteanu, *Int. J. Hydrog. Energy* 32 (2007) 3258-3265.
- [45] B. Pierozynski, T. Mikolajczyk, I. M. Kowalski, *J. Power Sources* 271 (2014) 231-238.
- [46] A. Lasia, A. Rami, *J. Electroanal. Chem.* 294 (1990) 123-141.
- [47] J. Jakšić, M. Vojnović, N. Krstajić, *Electrochim. Acta* 45 (2000) 4151-4158.
- [48] F. Paloukis, S. Zafeiratos, V. Drakopoulos, S. G. Neophytides, *Electrochim. Acta* 53 (2008) 8015-8025.
- [49] A. Pătru, P. Antitomaso, R. Sellin, N. Jerez, P. L. Taberna, F. Favier, *Int. J. Hydrog. Energy* 38 (2013) 11695-11708.
- [50] W. Martínez, A. Fernández, U. Cano, *Int. J. Hydrog. Energy*, 35 (2010) 8457-8462.
- [51] X. Qian, T. Hang, S. Shanmugam, M. Li, *ACS Appl. Mater. Interf.* 7 (2015) 15716-15725.
- [52] M. Domínguez-Crespo, E. Ramírez-Meneses, V. Montiel-Palma, A. T. Huerta, H. D. Rosales, *Int. J. Hydrog. Energy* 34 (2009) 1664-1676.

- [53] M. E. Lyons, M. P. Brandon, *Int. J. Electrochem. Sci.* 3 (2008) 1386 - 1424.
- [54] R. Šimpraga, B. Conway, *Electrochim. Acta* 43 (1998) 3045-3058.
- [55] A. Kellenberger, N. Vasilcsin, W. Brandl, *J. Solid State Electrochem.*, 11 (2007) 84-89.
- [56] S. Fletcher, *J. Solid State Electrochem.* 13 (2009) 537-549.
- [57] J. Kubisztal, A. Budniok, A. Lasia, *Int. J. Hydrog. Energy* 32 (2007) 1211-1218.
- [58] I. Herraiz-Cardona, E. Ortega, L. Vázquez-Gómez, V. Pérez-Herranz, *Int. J. Hydrog. Energy* 37 (2012) 2147-2156.
- [59] I. Herraiz-Cardona, C. González-Buch, C. Valero-Vidal, E. Ortega, V. Pérez-Herranz, *J. Power Sources* 240 (2013) 698-704.
- [60] T. Shinagawa, A. T. Garcia-Esparza, K. Takanabe, *Sci. Rep.* 5 (2015) 13801
- [61] J. Durst, A. Siebel, C. Simon, F. Hasche, J. Herranz, H. A. Gasteiger, *Energy Environ. Sci.* 7 (2014) 2255-2260.
- [62] S. Rausch, H. Wendt, *J. Electrochem. Soc.* 143 (1996) 2852-2862.
- [63] R. Šimpraga, G. Tremiliosi-Filho, S. Qian, B. Conway, *J. Electroanal. Chem.* 424 (1997) 141-151.
- [64] A. Lasia, *J. Electroanal. Chem.* 454 (1998) 115-121.
- [65] I. Herraiz-Cardona, E. Ortega, J.G. Antón, V. Pérez-Herranz, *Int. J. Hydrog. Energy* 36 (2011) 9428-9438.
- [66] M. Domínguez-Crespo, A. Torres-Huerta, B. Brachetti-Sibaja, A. Flores-Vela, *Int. J. Hydrog. Energy* 36 (2011) 135-151.
- [67] R. Parsons, *Trans. Faraday Soc.* 54 (1958) 1053-1063.
- [68] L. L. Krishtalik, *Advances in Electrochemistry and Electrochemical Engineering*, Interscience, New York, 1970.
- [69] S. Trasatti, *J. Electroanal. Chem.* 39 (1972) 163-184.
- [70] J. K. Nørskov, T. Bligaard, A. Logadottir, J. Kitchin, J. Chen, S. Pandalov, U. Stimming, *J. Electrochem. Soc.* 152 (2005) J23-J26.
- [71] W. Schmickler, S. Trasatti, *J. Electrochem. Soc.* 153 (2006) L31-L32.
- [72] E. Skúlason, V. Tripkovic, M. E. Björketun, S. Gudmundsdottir, G. Karlberg, J. Rossmeisl, T. Bligaard, H. Jónsson, J. K. Nørskov, *J. Phys. Chem. C* 114 (2010) 18182-18197.
- [73] P. Quaino, F. Juarez, E. Santos, W. Schmickler, Beilstein J. Nanotec. 5 (2014) 846-854.
- [74] J. Greeley, T. F. Jaramillo, J. Bonde, I. Chorkendorff, J. K. Nørskov, *Nat. Mater.* 5 (2006) 909-913.
- [75] J. Greeley, J. K. Nørskov, L. A. Kibler, A. M. El-Aziz, D. M. Kolb, *ChemPhysChem.* 7 (2006) 1032-1035.
- [76] W. Sheng, M. Myint, J. G. Chen, Y. Yan, *Energy Environ. Sci.* 6 (2013) 1509-1512.
- [77] J. Rossmeisl, K. Chan, R. Ahmed, V. Tripkovic, M. Bjorketun, *Phys. Chem. Chem. Phys.* 15 (2013) 10321-10325.
- [78] S. Henning, J. Herranz, H. A. Gasteiger, *J. Electrochem. Soc.* 162 (2015) F178-F189.
- [79] J. O. M. Bockris, K.N. Reddy, *Modern Electrochemistry*, Plenum Press, New York (1970).
- [80] J. Durst, A. Siebel, P.J. Rheinlader, J. Herranz, F. Hasché, M. Hanzlik, H. A. Gasteiger, HOR/HER on Pt Electrodes - Acid vs. Alkaline - Mechanism, Activity and Particle Size Effects, in *226th Meeting of The Electrochemical Society*, Cancun, Mexico, 2014.
- [81] W. Sheng, Z. Zhuang, M. Gao, J. Zheng, J. G. Chen, Y. Yan, *Nat. Commun.* 6 (2015) 5848.
- [82] D. Strmcnik, M. Uchimura, C. Wang, R. Subbaraman, N. Danilovic, D. Van der Vilet, A. P. Paulikas, V. Stamenkovic, N. Markovic, *Nat. Chem.* 5 (2013) 300-306.
- [83] R. Subbaraman, D. Tripkovic, D. Strmcnik, K.-C. Chang, M. Uchimura, A. P. Paulikas, V. R. Stamenkovic, N. M. Markovic, *Science* 334 (2011) 1256-1260.

- [84] N. Danilovic, R. Subbaraman, D. Strmcnik, A.P. Paulikas, D. Myers, V. R. Stamenkovic, N.M. Markovic, *Electrocatalysis* 3 (2012) 221-229.
- [85] N. Danilovic, R. Subbaraman, D. Strmcnik, V. R. Stamenkovic, N. M. Markovic, *J. Serbian Chem. Soc.* 78 (2013) 2007-2015.
- [86] J. Zheng, Z. Zhuang, B. Xu, Y. Yan, *ACS Catal.* 5 (2015) 4449-4455.
- [87] Y. Wang, G. Wang, G. Li, B. Huang, J. Pan, Q. Liu, J. Han, L. Xiao, J. Lu, L. Zhuang, *Energy Environ. Sci.* 8 (2015) 177-181.
- [88] K. Schouten, M. van der Niet, M. Koper, *Phys. Chem. Chem. Phys.* 12 (2010) 15217-15224.
- [89] M. J. van der Niet, N. Garcia-Araez, J. Hernández, J. M. Feliu, M. Koper, *Catal. Today* 202 (2013) 105-113.
- [90] N. M. Markovic, T. J. Schmidt, B. N. Grgur, H. A. Gasteiger, R. J. Behm, P. N. Ross, *J. Phys. Chem. B* 103 (1999) 8568-8577.
- [91] E. Skúlason, G. S. Karlberg, J. Rossmeisl, T. Bligaard, J. Greeley, H. Jónsson, J. K. Nørskov, *Phys. Chem. Chem. Phys.* 9 (2007) 3241-3250.
- [92] J. Rossmeisl, K. Chan, E. Skúlason, M. E. Björketun, V. Tripkovic, *Catal. Today* 262 (2015) 36-40.
- [93] A. Gorczyca, V. Moizan, C. Chizallet, O. Proux, W. Del Net, E. Lahera, J. L. Hazemann, P. Raybaud, Y. Joly, *Angew. Chem. Int. Ed.* 126 (2014) 12634-12637.
- [94] M. Teliska, W. E. O'Grady, D. E. Ramaker, *J. Phys. Chem. B* 108 (2004) 2333-2344.
- [95] D. E. Ramaker, C. Roth, *ChemElectroChem* 2 (2015) 1582-1594.
- [96] S. Mukerjee, J. McBreen, *J. Electrochem. Soc.* 143 (1996) 2285-2294.
- [97] A. Lasia, *J. Electroanal. Chem.* 562 (2004) 23-31.
- [98] B. Łosiewicz, R. Jurczakowski, A. Lasia, *Electrochim. Acta* 56 (2011) 5746-5753.
- [99] B. Łosiewicz, R. Jurczakowski, A. Lasia, *Electrochim. Acta* 80 (2012) 292-301.
- [100] N. García-Araez, V. Climent, J. M. Feliu, *Electrochim. Acta* 54 (2009) 966-977.
- [101] T. J. Schmidt, U. A. Paulus, H. A. Gasteiger, R. J. Behm, *J. Electroanal. Chem.* 508 (2001) 41-47.
- [102] N. M. Markovic, H. A. Gasteiger, P. N. Ross, *J. Phys. Chem.* 99 (1995) 3411-3415.
- [103] N. M. Markovic, H. A. Gasteiger, B. N. Grgur, P. N. Ross, *J. Electroanal. Chem.* 467 (1999) 157-163.
- [104] N. M. Markovic, P. N. Ross, *Surf. Sci. Rep.* 45 (2002) 117-229.
- [105] R. Subbaraman, D. Strmcnik, A. P. Paulikas, V. R. Stamenkovic, N. M. Markovic, *ChemPhysChem*. 11 (2010) 2825-2833.
- [106] R. Subbaraman, D. Strmcnik, V. R. Stamenkovic, N. M. Markovic, *J. Phys. Chem. C* 114 (2010) 8414-8422.
- [107] J. Zhang, B. A. Litteer, F. D. Coms, R. Makharia, *J. Electrochem. Soc.* 159 (2012) F287-F293.
- [108] J. Eller, J. Roth, F. Marone, M. Stambanoni, A. Wokaun, F. N. Büchi, *J. Power Sources* 245 (2014) 796-800.
- [109] S. Chen, A. Kucernak, *J. Phys. Chem. B* 108 (2004) 13984-13994.
- [110] V. Bagotzky, N. Osetrova, *J. Electroanal. Chem.* 43 (1973) 233-249.
- [111] C. Zalitis, J. Sharman, E. Wright, A. Kucernak, *Electrochim. Acta* 176 (2015) 763-776.
- [112] D. Strmcnik, K. Kodama, D. van der Vliet, J. Greeley, V. R. Stamenkovic, N. M. Markovic, *Nat. Chem.* 1 (2009) 466-472.
- [113] J. Olivares-Ramirez, M. Campos-Cornelio, J. U. Godinez, E. Borja-Arco, R. Castellanos, *Int. J. Hydrog. Energy* 32 (2007) 3170-3173.
- [114] B. Conway, H. Angerstein-Kozłowska, M. Sattar, B. Tilak, *J. Electrochem. Soc.* 130 (1983) 1825-1836.

- [115] A. Morozan, V. Goellner, A. Zitolo, E. Fonda, B. Donnadieu, D. Jones, F. Jaouen, *Phys. Chem. Chem. Phys.* 17 (2015) 4047-4053.
- [116] Y. Petrov, J.-P. Schosger, Z. Stoyanov, F. de Bruijn, *Int. J. Hydrog. Energy* 36 (2011) 12715-12724.
- [117] T. J. Schmidt, P. N. Ross Jr, N. M. Markovic, *J. Electroanal. Chem.* 524 (2002) 252-260.
- [118] J. Perez, E. R. Gonzalez, H. M. Villullas, *J. Phys. Chem. B* 102 (1998) 10931-10935.
- [119] G. Brisard, N. Bertrand, P. N. Ross, N. M. Marković, *J. Electroanal. Chem.* 480 (2000) 219-224.
- [120] D. Floner, C. Lamy, J.-M. Leger, *Surf. Sci.* 234 (1990) 87-97.
- [121] J. Durst, C. Simon, A. Siebel, P. J. Rheinländer, T. Schuler, M. Hanzlik, J. Herranz, F. Hasché, H. A. Gasteiger, *ECS Trans.* 64 (2014) 1069-1080.
- [122] F. Maillard, S. Pronkin, E. R. Savinova, in *Fuel Cell Catalysis: a Surface Science Approach*, M.T.M. Koper (Ed.), p. 507, John Wiley & Sons, Inc., New York (2009).
- [123] D. Buceta, M. Blanco, M. López-Quintela, M. Vukmirovic, *J. Electrochem. Soc.* 161 (2014) D3113-D3115.
- [124] T. Fujitani, I. Nakamura, T. Akita, M. Okumura, M. Haruta, *Angew. Chem. Int. Ed.* 121 (2009) 9679-9682.
- [125] Z. Grubač, M. Metikoš-Huković, R. Babić, *Int. J. Hydrog. Energy* 38 (2013) 4437-4444.
- [126] B. Łosiewicz, A. Budniok, E. Rówiński, E. Łągiewka, A. Lasia, *Int. J. Hydrog. Energy* 29 (2004) 145-157.
- [127] V. Ganesh, V. Lakshminarayanan, *Electrochim. Acta* 49 (2004) 3561-3572.
- [128] I. Brown, S. Sotiropoulos, *J. Appl. Electrochem.* 30 (2000) 107-111.
- [129] M. McArthur, L. Jorge, S. Coulombe, S. Omanovic, *J. Power Sources* 266 (2014) 365-373.
- [130] I. Bianchi, E. Guerrini, S. Trasatti, *Chem. Phys.* 319 (2005) 192-199.
- [131] D. Chanda, J. Hnát, A.S. Dobrota, I. A. Pašti, M. Paidar, K. Bouzek, *Phys. Chem. Chem. Phys.* 17 (2015) 26864-26874.
- [132] I. Paseka, J. Velicka, *Electrochim. Acta* 42 (1997) 237-242.
- [133] T. Burchardt, *Int. J. Hydrog. Energy* 25 (2000) 627-634.
- [134] Z. Wei, A. Yan, Y. Feng, L. Li, C. Sun, Z. Shao, P. Shen, *Electrochem. Commun.* 9 (2007) 2709-2715.
- [135] M. Ledendecker, S. Krick Calderón, C. Papp, H. P. Steinrück, M. Antonietti, M. Shalom, *Angew. Chem. Int. Ed.* 127 (2015) 12538-12542.
- [136] Y. Pan, W. Hu, D. Liu, Y. Liu, C. Liu, *J. Mater. Chem. A* 3 (2015) 13087-13094.
- [137] A. Laursen, K. Patraju, M. Whitaker, M. Retuerto, T. Sarkar, N. Yao, K. Ramanujachary, M. Greenblatt, G. Dismukes, *Energy Environ. Sci.* 8 (2015) 1027-1034.
- [138] A. Han, S. Jin, H. Chen, H. Ji, Z. Sun, P. Du, *J. Mater. Chem. A* 3 (2015) 1941-1946.
- [139] A.B. Laursen, S. Kegnaes, S. Dahl, I. Chorkendorff, *Energy Environ. Sci.* 5 (2012) 5577-5591.
- [140] T. F. Jaramillo, K. P. Jørgensen, J. Bonde, J. H. Nielsen, S. Horch, I. Chorkendorff, *Science* 317 (2007) 100-102.
- [141] H.I. Karunadasa, E. Montalvo, Y. Sun, M. Majda, J.R. Long, C.J. Chang, *Science* 335 (2012) 698-702.
- [142] E. L. Warren, J. R. McKone, H. A. Atwater, H. B. Gray, N. S. Lewis, *Energy Environ. Sci.* 5 (2012) 9653-9661.
- [143] E. Fabbri, A. Habereeder, K. Waltar, R. Kötz, T. J. Schmidt, *Catal. Sci. Technol.* 4 (2014) 3800-3821.
- [144] J. O. M. Bockris, *J. Chem. Phys.* 24 (1956) 817-817.
- [145] J. Rossmesl, Z. W. Qu, H. Zhu, G. J. Kroes, J. K. Nørskov, *J. Electroanal. Chem.* 607 (2007) 83-89.
- [146] J. O. M. Bockris, T. Otagawa, *J. Electrochem. Soc.* 131 (1984) 290-302.

- [147] J. Suntivich, K. J. May, H. A. Gasteiger, J. B. Goodenough, Y. Shao-Horn, *Science* 334 (2011) 1383-1385.
- [148] X. Cheng, E. Fabbri, M. Nachtegaal, I. E. Castelli, M. El Kazzi, R. Haumont, N. Marzari, T. J. Schmidt, *Chem. Mater.* 27 (2015) 7662-7672
- [149] I. C. Man, H.-Y. Su, F. Calle-Vallejo, H. A. Hansen, J. I. Martínez, N. G. Inoglu, J. Kitchin, T. F. Jaramillo, J. K. Nørskov, J. Rossmeisl, *ChemCatChem* 3 (2011) 1159-1165.
- [150] F. Calle-Vallejo, O. A. Díaz-Morales, M. J. Kolb, M. T. M. Koper, *ACS Catal.* 5 (2015) 869-873.
- [151] M. S. Burke, L. J. Enman, A. S. Batchellor, S. Zou, S. W. Boettcher, *Chem. Mater.* 27 (2015) 7549-7558.
- [152] T. Reier, Z. Pawolek, S. Cherevko, M. Bruns, T. Jones, D. Teschner, S. Selve, A. Bergmann, H. N. Nong, R. Schlogl, K. J. J. Mayrhofer, P. Strasser, *J. Am. Chem. Soc.* 137 (2015) 13031-13040.
- [153] M. E. G. Lyons, S. Floquet, *Phys. Chem. Chem. Phys.* 13 (2011) 5314-5335.
- [154] R. L. Doyle, I. J. Godwin, M. P. Brandon, M. E. G. Lyons, *Phys. Chem. Chem. Phys.* 15 (2013) 13737-13783.
- [155] G. R. Meseck, E. Fabbri, T. J. Schmidt, S. Seeger, *Adv. Mater. Interfaces* 2 (2015) 1500216.
- [156] C. C. L. McCrory, S. Jung, J. C. Peters, T. F. Jaramillo, *J. Am. Chem. Soc.* 135 (2013) 16977-16987.
- [157] R. Mohamed, E. Fabbri, P. Levecque, R. Kotz, T. J. Schmidt, O. Conrad, *ECS Trans.* 58 (2014) 9-18.
- [158] R. Mohamed, X. Cheng, E. Fabbri, P. Levecque, R. Kotz, O. Conrad, T. J. Schmidt, *J. Electrochem. Soc.* 162 (2015) F579-F586.
- [159] Y. Lee, J. Suntivich, K. J. May, E. E. Perry, Y. Shao-Horn, *J. Phys. Chem. Lett.* 3 (2012) 399-404.
- [160] B. H. Han, M. Risch, Y. L. Lee, C. Ling, H. F. Jia, Y. Shao-Horn, *Phys. Chem. Chem. Phys.* 17 (2015) 22576-22580.
- [161] E. Fabbri, M. Nachtegaal, X. Cheng, T. J. Schmidt, *Adv. Energy Mater.* 5 (2015).
- [162] A. Wattiaux, J. C. Grenier, M. Pouchard and P. Hagenmuller, *J Electrochem Soc.* 134 (1987) 1714-1718.
- [163] C. W. Tung, Y. Y. Hsu, Y. P. Shen, Y. X. Zheng, T. S. Chan, H. S. Sheu, Y. C. Cheng, H. M. Chen, *Nat. Commun.* 6 (2015) 8106.
- [164] I. M. Sadiek, A. M. Mohammad, M. E. El-Shakre, M. S. El-Deab, *Int. J. Hydrogen Energy.* 37 (2012) 68-77.
- [165] J. B. Raoof, F. Chekin, V. Ehsani, *B. Mater Sci.* 38 (2015) 135-140.
- [166] A. M. Mohammad, M. I. Awad, M. S. El-Deab, T. Okajima, T. Ohsaka, *Electrochim. Acta* 53 (2008) 4351-4358.
- [167] F. Chekin, H. Tahermansouri, M. R. Besharat, *J. Solid State Electrochem.* 18 (2014) 747-753.
- [168] T. Toshihiro, H. Kazuhito, N. Ryuhei, *J. Am. Chem. Soc.* 134 (2012) 1519-1527.
- [169] Q. G. He, X. F. Yang, W. Chen, S. Mukerjee, B. Koel, S. W. Chen, *Phys. Chem. Chem. Phys.* 12 (2010) 12544-12555.
- [170] D. Strmcnik, K. Kodama, D. van der Vliet, J. Greeley, V. R. Stamenkovic, N. M. Markovic, *Nat. Chem.* 1 (2009) 466-472.
- [171] S. Thomas, Y. E. Sung, H. S. Kim, A. Wieckowski, *J. Phys. Chem-US.* 10 (1996) 11726-11735.
- [172] A. Ganassin, V. Colic, J. Tymoczko, A. S. Bandarenka, W. Schuhmann, *Phys. Chem. Chem. Phys.* 17 (2015) 8349-8355.
- [173] L.-E. Owe, M. Tsympkin, S. Sunde, *Electrochim. Acta.* 58 (2011) 231-237.
- [174] D. V. Franco, L. M. Da Silva, W. F. Jardim and J. F. C. Boodts, *J. Brazil. Chem. Soc.* 17 (2006) 746-757.
- [175] I. Hwang, E. Ahn, Y. Tak, *Int. J. Electrochem. Sci.* 9 (2014) 5454-5466.
- [176] J. Suntivich, E. E. Perry, H. A. Gasteiger, Y. Shao-Horn, *Electrocatalysis* 4(2013) 49-55.
- [177] I. C. Man, H. Y. Su, F. Calle-Vallejo, H. A. Hansen, J. I. Martinez, N. G. Inoglu, J. Kitchin, T. F. Jaramillo, J. K. Nørskov, J. Rossmeisl, *ChemCatChem* 3 (2011) 1159-1165.
- [178] K. A. Stoerzinger, L. Qiao, M. D. Biegalski, Y. Shao-Horn, *J. Phys. Chem. Lett.* 5 (2014) 1636-1641.
- [179] Y. X. Zhang, F. Ding, C. Deng, S. Y. Zhen, X. Y. Li, Y. F. Xue, Y. M. Yan, K. N. Sun, *Catal. Commun.* 67 (2015) 78-82.

- [180] S. H. Chang, N. Danilovic, K. C. Chang, R. Subbaraman, A. P. Paulikas, D. D. Fong, M. J. Highland, P. M. Baldo, V. R. Stamenkovic, J. W. Freeland, J. A. Eastman, N. M. Markovic, *Nat. Commun.* 5 (2014) 4191.
- [181] A. J. Esswein, M. J. McMurdo, P. N. Ross, A. T. Bell, T. D. Tilley, *J. Phys. Chem. C* 113 (2009) 15068-15072.
- [182] J. Jirkovsky, H. Hoffmannova, M. Klementova, P. Krtil, *J. Electrochem. Soc.* 153 (2006) E111-E118.
- [183] J. Jirkovsky, M. Makarova, P. Krtil, *Electrochem. Commun.* 8 (2006) 1417-1422.
- [184] K. Jin, A. Chu, J. Park, D. Jeong, S. E. Jerng, U. Sim, H. Y. Jeong, C. W. Lee, Y. S. Park, K. D. Yang, G. K. Pradhan, D. Kim, N. E. Sung, S. H. Kim, K. T. Nam, *Sci Rep-Uk*, 5 (2015) Doi:10.1038/srep10279.
- [185] K. Macounova, J. Jirkovsky, M. V. Makarova, J. Franc, P. Krtil, *J. Solid State Electrochem.* 13 (2009) 959-965.
- [186] E. Rasten, G. Hagen, R. Tunold, *Electrochim. Acta* 48 (2003) 3945-3952.
- [187] T. Reier, M. Oezaslan, P. Strasser, *ACS Catal.* 2 (2012) 1765-1772.
- [188] E. Guerrini, S. Trasatti, *Russ. J. Electrochem.* 42 (2006) 1017-1025.
- [189] E. A. Paoli, F. Masini, R. Frydendal, D. Deiana, C. Schlaup, M. Malizia, T. W. Hansen, S. Horch, I. E. L. Stephens, I. Chorkendorff, *Chem. Sci.* 6 (2015) 190-196.
- [190] R. D. L. Smith, M. S. Prevot, R. D. Fagan, Z. P. Zhang, P. A. Sedach, M. K. J. Siu, S. Trudel, C. P. Berlinguette, *Science* 340 (2013) 60-63.
- [191] E. Tsuji, A. Imanishi, K.-i. Fukui, Y. Nakato, *Electrochim. Acta* 56 (2011) 2009-2016.
- [192] Y. Qiu, L. Xin, W. Z. Li, *Langmuir* 30 (2014) 7893-7901.
- [193] X. Leng, Q. C. Zeng, K. H. Wu, I. R. Gentle, D. W. Wang, *RSC Adv.* 5 (2015) 27823-27828.
- [194] N. B. Halck, V. Petrykin, P. Krtil, J. Rossmeisl, *Phys. Chem. Chem. Phys.* 16 (2014) 13682-13688.
- [195] R. G. González-Huerta, G. Ramos-Sánchez, P. B. Balbuena, *J. Power Sources* 268 (2014) 69-76.
- [196] V. Petrykin, Z. Bastl, J. Franc, K. Macounova, M. Makarova, S. Mukerjee, N. Ramaswamy, I. Spirovova, P. Krtil, *J. Phys. Chem. C* 113 (2009) 21657-21666.
- [197] M. E. G. Lyons, L. D. Burke, *J. Chem. Soc., Faraday Trans.* 83 (1987) 299-321.
- [198] R. Kötz, H. J. Lewerenz, S. Stucki, *J. Electrochem. Soc.* 130 (1983) 825-829.
- [199] R. Kötz, H. Neff, S. Stucki, *J. Electrochem. Soc.* 131 (1984) 72-77.
- [200] A. Minguzzi, O. Lugaresi, E. Achilli, C. Locatelli, A. Vertova, P. Ghigna, S. Rondinini, *Chem Sci.* 5 (2014) 3591-3597.
- [201] H. Bode, K. Dehmelt, J. Witte, *Z. Anorg. Allg. Chem.* 366 (1969) 1-21.
- [202] H. Bode, K. Dehmelt, J. Witte, *Berich. Bunsen. Gesell.* 67 (1963) 839-839.
- [203] O. Diaz-Morales, I. Ledezma-Yanez, M. T. M. Koper, F. Calle-Vallejo, *ACS Catal.* 5 (2015) 5380-5387.
- [204] J. Landon, E. Demeter, N. İnoğlu, C. Keturakis, I. E. Wachs, R. Vasić, A. I. Frenkel, J. R. Kitchin, *ACS Catal.* 2 (2012) 1793-1801.
- [205] J. R. Swierk, S. Klaus, L. Trotochaud, A. T. Bell, T. D. Tilley, *J. Phys. Chem. C* 119 (2015) 19022-19029.
- [206] Y. Matsumoto, S. Yamada, T. Nishida, E. Sato, *J. Electrochem. Soc.* 127 (1980) 2360-2364.
- [207] A. Grimaud, K. J. May, C. E. Carlton, Y.-L. Lee, M. Risch, W. T. Hong, J. Zhou, Y. Shao-Horn, *Nat. Commun.* 4 (2013) 2439.
- [208] S. Cherevko, A. R. Zeradjanin, A. A. Topalov, N. Kulyk, I. Katsounaros, K. J. J. Mayrhofer, *ChemCatChem* 6 (2014) 2219-2223.
- [209] S. Cherevko, S. Geiger, O. Kasian, N. Kulyk, J.-P. Grote, A. Savan, B. R. Shrestha, S. Merzlikin, B. Breitbach, A. Ludwig, K. J. J. Mayrhofer, *Catal. Today* 262 (2016) 170-180.
- [210] N. Hodnik, P. Jovanovič, A. Pavlišič, B. Jozinović, M. Zorko, M. Bele, V. S. Šelih, M. Šala, S. Hočevar, M. Gaberšček, *J. Phys. Chem. C* 119 (2015) 10140-10147.
- [211] K. J. May, C. E. Carlton, K. A. Stoerzinger, M. Risch, J. Suntivich, Y. L. Lee, A. Grimaud, Y. Shao-Horn, *J. Phys. Chem. Lett.* 3 (2012) 3264-3270.
- [212] M. Risch, A. Grimaud, K. J. May, K. A. Stoerzinger, T. J. Chen, A. N. Mansour, Y. Shao-Horn, *J. Phys. Chem. C* 117 (2013) 8628-8635.

- [213] N. Danilovic, R. Subbaraman, K.-C. Chang, S. H. Chang, Y. J. Kang, J. Snyder, A. P. Paulikas, D. Strmcnik, Y.-T. Kim, D. Myers, V. R. Stamenkovic, N. M. Markovic, *J. Phys. Chem. Lett.* 5 (2014) 2474-2478.
- [214] S. H. Chang, J. G. Connell, N. Danilovic, R. Subbaraman, K.-C. Chang, V. R. Stamenkovic, N. M. Markovic, *Faraday Discuss.* 176 (2014) 125-133.
- [215] T. Binninger, R. Mohamed, K. Waltar, E. Fabbri, P. Levecque, R. Kötz, T. J. Schmidt, *Sci. Reps.* 5 (2015) 12167.
- [216] B. S. Yeo, A. T. Bell, *J. Am. Chem. Soc.* 133 (2011) 5587-5593.
- [217] Y. Gorlin, C.-J. Chung, J. D. Benck, D. Nordlund, L. Seitz, T.-C. Weng, D. Sokaras, B. M. Clemens, T. F. Jaramillo, *J. Am. Chem. Soc.* 136 (2014) 4920-4926.
- [218] L. C. Seitz, T. J. P. Hersbach, D. Nordlund, T. F. Jaramillo, *J. Phys. Chem. Lett.* 6 (2015) 4178-4183.
- [219] R. Frydendal, M. Busch, N. B. Halck, E. A. Paoli, P. Krtil, I. Chorkendorff, J. Rossmeisl, *ChemCatChem* 7 (2015) 149-154.
- [220] Y. Y. Liang, Y. G. Li, H. L. Wang, J. G. Zhou, J. Wang, T. Regier, H. J. Dai, *Nat. Mater.* 10 (2011) 780-786.
- [221] S. Mao, Z. Wen, T. Huang, Y. Hou, J. Chen, *Energy Environ. Sci.* 7 (2014) 609-616.
- [222] X. Lu, C. Zhao, *J. Mater. Chem. A* 1 (2013) 12053-12059.
- [223] W. Bian, Z. Yang, P. Strasser, R. Yang, *J. Power Sources.* 250 (2014) 196-203.
- [224] K. Nishio, S. Molla, T. Okugaki, S. Nakanishi, I. Nitta, Y. Kotani, *J. Power Sources.* 298 (2015) 236-240.
- [225] W. G. Hardin, J. T. Mefford, D. A. Slanac, B. B. Patel, X. Q. Wang, S. Dai, X. Zhao, R. S. Ruoff, K. P. Johnston, K. J. Stevenson, *Chem Mater.* 26 (2014) 3368-3376.
- [226] Y. Hori, in *Modern Aspects of Electrochemistry*, Nr. 42, Eds. C. Vayenas et al, Springer, New York, 2008.
- [227] Y. Hori, in *Handbook of Fuel Cells – Fundamentals, Technology and Applications*, Eds. W. Vilestich, H. A. Gasteiger, A. Lamm, and H. Yokokawa, John Wiley & Sons, 2010.
- [228] Y. Hori, K. Kikuchi, S. Suzuki, *Chem. Lett.* (1985) 1695-1698.
- [229] Y. Hori, A. Murata, R. Takahashi, *J. Chem. Soc., Faraday Trans. I* 85 (1989) 2309-2326.
- [230] J. Herranz, A. Garsuch, H. A. Gasteiger, *J. Phys. Chem. C* 116 (2012) 19084-19094.
- [231] K. U. Schwenke, S. Meini, X. Wu, H. A. Gasteiger, M. Piana, *Phys. Chem. Chem. Phys.* 15 (2013) 11830-11839.
- [232] K. U. Schwenke, J. Herranz, H. A. Gasteiger, M. Piana, *J. Electrochem. Soc.* 162 (2015) A905-A914.
- [233] R. Kortlever, J. Shen, K. J. P. Schouten, F. Calle-Vallejo, M. T. M. Koper, *J. Phys. Chem. Lett.* 6 (2015) 4073-4082.
- [234] E. Lamy, L. Nadjo, J.-M. Savéant, *J. Electroanal. Chem.* 78 (1977) 403-407.
- [235] A. Gennaro, A. A. Isse, M.-G. Severin, E. Vianello, I. Bhugun, J.-M. Savéant, *J. Chem. Soc., Faraday Trans.* 92 (1996) 3963-3968.
- [236] Y. Hori, H. Wakabe, T. Tsukamoto, O. Koga, *Electrochim. Acta* 39 (1994) 1833-1839.
- [237] M. Karamad, H. A. Hansen, J. Rossmeisl, J. K. Nørskov, *ACS Catal.* 5 (2015) 4075-4081.
- [238] N. Spataru, K. Tokuhito, C. Terashima, T. N. Rao, A. Fujishima, *J. Appl. Electrochem.* 33 (2003) 1205-1210.
- [239] A. A. Peterson, J. K. Nørskov, *J. Phys. Chem. Lett.* 3 (2012) 251-258.
- [240] K. P. Kuhl, T. Hatsukade, E. R. Cave, D. N. Abram, J. Kibsgaard, T. F. Jaramillo, *J. Am. Chem. Soc.* 136 (2014) 14107-14113.
- [241] T. Jiang, D. J. Mowbray, S. Dobrin, H. Falsig, B. Hvolbæk, T. Bligaard, J. K. Nørskov, *J. Phys. Chem. C* 113 (2009) 10548-10553.

- [242] J. Rosen, G. S. Hutchins, Q. Lu, S. Rivera, Y. Zhou, D. G. Vlachos, F. Jiao, *ACS Catal.* 5 (2015) 4293-4299.
- [243] J. Rosen, G. S. Hutchins, Q. Lu, R. V. Forest, A. Moore, F. Jiao, *ACS Catal.* 5 (2015) 4586-4591.
- [244] C. W. Li, M. W. Kanan, *J. Am. Chem. Soc.* 134 (2012) 7231-7234.
- [245] Y. Chen, C. W. Li, M. W. Kanan, *J. Am. Chem. Soc.* 134 (2012) 19969-19972.
- [246] Y. Hori, A. Murata, K. Kikuchi, S. Suzuki, *J. Chem. Soc., Chem. Commun.* (1987) 728.
- [247] J. J. Kim, D. P. Summer, K. W. Frese, *J. Electroanal. Chem.* 245 (1988) 223-244.
- [248] A. Murata, Y. Hori, *Bull. Chem. Soc. Jpn.* 64 (1991) 123-127.
- [249] B. Kim, S. Ma, H.-R. Jhong, P. J. A. Kenis, *Electrochim. Acta* 166 (2015) 271-276.
- [250] Y. Hori, H. Konishi, T. Futamura, A. Murata, O. Koga, H. Sakurai, K. Oguma, *Electrochim. Acta* 50 (2005) 5354-5369.
- [251] R. Kortlever, K. H. Tan, Y. Kwon, M. T. M. Koper, *J. Solid State Electrochem.* 17 (2013) 1843-1849.
- [252] A. Schizodimou, G. Kyriacou, *Electrochim. Acta* 78 (2012) 171-176.
- [253] J. J. Wu, F.G. Risalvato, P. P. Sharma, P. J. Pellechia, F. S. Ke, X. D. Zhou, *J. Electrochem. Soc.* 160 (2013) F953-F957.
- [254] C. Delacourt, P. L. Ridgway, J. B. Kerr, J. Newman, *J. Electrochem. Soc.* 155 (2008) B42-B49.
- [255] D. T. Whipple, E. C. Finke, P. J. A. Kenis, *Electrochem. Solid State Lett.* 13 (2010) D109-D111.
- [256] N. Gupta, M. Gattrell, B. MacDougall, *J. Appl. Electrochem.* 36 (2006) 161-172.
- [257] Y. Hori, R. Takahashi, Y. Yoshinami, A. Murata, *J. Phys. Chem. B* 101 (1997) 7075-7081.
- [258] M. Gattrell, N. Gupta, A. Co, *J. Electroanal. Chem.* 594 (2006) 1.
- [259] A. A. Peterson, F. Abild-Pedersen, F. Studt, J. Rossmeisl, J. K. Nørskov, *Energy Environ. Sci.* 3 (2010) 1311-1315.
- [260] K. J. P. Schouten, Y. Kwon, C. J. M. van der Ham, Z. Qin, M. T. M. Koper, *Chem. Sci.* 2 (2011) 1902-1909.
- [261] G. Kyriacou, A. Anagnostopoulos, *J. Appl. Electrochem.* 23 (1993) 483-486.
- [262] S. Kaneco, H. Katsumata, T. Suzuki, K. Ohta, *Electrochim. Acta* 51 (2006) 3316-3321.
- [263] R. Kedzierzawski, J. Augustynski, *J. Electrochem. Soc.* 141 (1994) L58-L60.
- [264] N. Hoshi, M. Noma, T. Suzuki, and Y. Hori, *J. Electroanal. Chem.* 421 (1997) 15-18.
- [265] N. Hoshi, M. Kato, and Y. Hori, *J. Electroanal. Chem.* 440 (1997) 283-286.
- [266] W. Zhu, R. Michalsky, Ö. Metin, H. Lv, S. Guo, C. J. Wright, X. Sun, A. A. Peterson, and S. Sun, *J. Am. Chem. Soc.* 135 (2013) 16833-16836.
- [267] W. Zhu, Y.-J. Zhang, H. Zhang, H. Lv, Q. Li, R. Michalsky, A. A. Peterson, and S. Sun, *J. Am. Chem. Soc.* 136 (2014) 16132-16135.
- [268] Y. Hori, I. Takahashi, O. Koga, and N. Hoshi, *J. Phys. Chem. B* 106 (2002) 15-17.
- [269] K. J. P. Schouten, Z. Qin, E. Pérez Gallent, and M. T. M. Koper, *J. Am. Chem. Soc.* 134 (2012) 9864-9867.
- [270] K. J. P. Schouten, E. Pérez Gallent, and M. T. M. Koper, *ACS Catal.* 3 (2013) 1292-1295.
- [271] X. Nie, M. R. Esopi, M. J. Janik, and A. Asthagiri, *Angew. Chem. Int. Ed.* 52 (2013) 2459-2462.
- [272] F. Calle-Vallejo and M. T. M. Koper, *Angew. Chem. Int. Ed.* 125 (2013) 7423.
- [273] J. H. Montoya, C. Shi, K. Chan, and J. K. Nørskov, *J. Phys. Chem. Lett.* 6 (2015) 2032-2037.
- [274] I. Ledezma-Yanez, E. Pérez Gallent, M. T. M. Koper, and F. Calle-Vallejo, *Catal. Today* 262 (2016) 90-94.
- [275] H. Mistry, R. Reske, Z. Zeng, Z.-J. Zhao, J. Greeley, P. Strasser, B. Roldan Cuenya, *J. Am. Chem. Soc.* 136 (2014) 16473-16476.
- [276] X. Feng, K. Jiang, S. Fan, and M. W. Kanan, *J. Am. Chem. Soc.* 137 (2015) 4606-4609.

- [277] Q. Lu, J. Rosen, Y. Zhou, G. S. Hutchings, Y. C. Kimmel, J. G. Chen, F. Jiao, *Nat. Commun.* 5 (2014) 3242.
- [278] T. Hatsukade, K. P. Kuhl, E. R. Cave, D. N. Abram, T. F. Jaramillo, *Phys. Chem. Chem. Phys.* 16 (2014) 13814-13819.
- [279] W. Tang, A. A. Peterson, A. S. Varela, Z. P. Jovanov, L. Bech, W. J. Durand, S. Dahl, J. K. Nørskov, I. Chorkendorff, *Phys. Chem. Chem. Phys.* 14 (2012) 76-81.
- [280] R. Reske, H. Mistry, F. Behafarid, B. Roldand Cuenya, P. Strasser, *J. Am. Chem. Soc.* 136 (2014) 6978-6986.
- [281] O. A. Baturina, Q. Lu, M. A. Padilla, L. Xin, W. Li, A. Serov, K. Artyushkova, P. Atanassov, F. Xu, A. Epshteyn, T. Brintlinger, M. Schuette, G. E. Collins, *ACS Catal.* 4 (2014) 3682-3695.
- [282] K. W. Frese, *J. Electrochem. Soc.* 138 (1991) 3338-3344.
- [283] A.M. Le, M. Ren, Z. Zhang, P. T. Sprunger, R. L. Kurtz, J. C. Flake, *J. Electrochem. Soc.* 158 (2011) E45-E49.
- [284] Y.-J. Zhang, A. A. Peterson, *Phys. Chem. Chem. Phys.* 17 (2015) 4505-4515.
- [285] D. Ren, Y. Deng, A. D. Handoko, C. S. Chen, S. Malkhandi, B. S. Yeo, *ACS Catal.* 5 (2015) 2814-2821.
- [286] A.D. Kim, S. Lee, J. D. Ocon, B. Jeong, J. K. Lee, J. Lee, *Phys. Chem. Chem. Phys.* 17 (2015) 824-830.
- [287] R. Kas, R. Kortlever, A. Milbrat, M. T. M. Koper, G. Mul, J. Baltrusaitis, *Phys. Chem. Chem. Phys.* 16 (2014) 12194-12201.
- [288] C. W. Li, J. Ciston, M. W. Kanan, *Nature* 508 (2014) 504-510.
- [289] A. Verdaguer-Casadevall, C. W. Li, T. P. Johansson, S. B. Scott, J. T. McKeown, M. Kumar, I. E. L. Stephens, M. W. Kanan, I. Chorkendorff, *J. Am. Chem. Soc.* 137 (2015) 9808-9811.
- [290] Y.-G. Kim, J. H. Baricuatro, A. Javier, J. M. Gregoire, M. P. Soriaga, *Langmuir* 30 (2014) 15053-15056.
- [291] T. M. T. Huynh, P. Broekmann, *ChemElectroChem* 1 (2014) 1271-1274.
- [292] Y. Chen, M. W. Kanan, *J. Am. Chem. Soc.* 134 (2012) 1986-1989.
- [293] C. H. Lee, M. W. Kanan, *ACS Catal.* 5 (2015) 465-469.
- [294] A.J. P. Popic, M. L. Avramov-Ivic, N. B. Vukovic, *J. Electroanal. Chem.* 421 (1997) 105-110.
- [295] A. Bandi, *J. Electrochem. Soc.* 137 (1990) 2157-2160.
- [296] E. R. Kötz, S. Stucki, *J. Appl. Electrochem.* 17 (1987) 1190-1197.
- [297] W. Zhao, L. Yang, Y. Yin, M. Jin, *J. Mater. Chem. A* 2 (2014) 902-906.
- [298] J. Christophe, T. Doneux, C. Buess-Herman, *Electrocatal.* 3 (2012) 139-146.
- [299] D. Kim, J. Resasco, Y. Yu, A. M. Asiri, P. Yang, *Nat. Commun.* 5 (2014) 4948.
- [300] F. Jia F, X. Yu, L. Zhang *J. Power Sources* 252 (2014) 85-89.
- [301] P. Hirunsit, *J. Phys. Chem. C* 117 (2013) 8262-8268.
- [302] S. Ishimaru, R. Shiratsuchi, G. Nogami, *J. Electrochem. Soc.* 147 (2000) 1864-1867.
- [303] X. Guo, Y. Zhang, C. Deng, X. Li, Y. Xue, Y.-M. Yan, and K. Sun, *Chem. Commun.* 51 (2015) 1345-1348.
- [304] M. Nakamura, T. Kobayashi, N. Hoshi, *Surf. Sci.* 605 (2011) 1462-1465.
- [305] S. Shironita, K. Karasuda, K. Sato, M. Umeda, *J. Power Sources* 240 (2013) 404-410.
- [306] M. Karamad, V. Tripkovic, J. Rossmeisl, *ACS Catal.* 4 (2014) 2268-2273.
- [307] K. Nakata, T. Ozaki, C. Terashima, A. Fujishima, Y. Einaga, *Angew. Chem., Int. Ed.* 53 (2014) 871-874.
- [308] S. Zhang, P. Kang, S. Ubnoske, M. K. Brennaman, N. Song, R. L. House, J. T. Glass, T. J. J. Meyer, *J. Am. Chem. Soc.* 136 (2014) 7845-7848.

- [309] S. A. Yao, R. E. Ruther, L. Zhang, R. A. Franking, R. J. Hamers, J. F. Berry, *J. Am. Chem. Soc.* 134 (2012) 15632-15635.
- [310] K. G. Gallagher, S. Goebel, T. Greszler, M. Mathias, W. Oelerich, D. Eroglu, V. Srinivasan, *Energy Environ. Sci.*, 7 (2014) 1555-1563.
- [311] K. J. J. Mayrhofer, K. Hartl, V. Juhart, M. Arenz, *J. Am. Chem. Soc.* 131 (2009) 16348–16349.

Table 1. Summary of the electrochemical half-reactions at play at the anode and cathodes of (co-)electrolysis cells, along with their corresponding reversible potential values (at standard conditions and 25 °C). Note that all reactions are arbitrarily formulated in the acid form, i.e., with H^+ (instead of H_2O) as the hydrogen source.

Device Electrode	Reaction	E_{rev} [V _{RHE}]
(Co-) Electrolyzer anode	$H_2O \rightleftharpoons \frac{1}{2}O_2 + 2H^+ + 2e^-$	1.23
Electrolyzer cathode	$2H^+ + 2e^- \rightleftharpoons H_2$	0.00
Co-electrolyzer cathode	$CO_2 + 8H^+ + 8e^- \rightleftharpoons CH_4 + 2H_2O$	− 0.17
	$2CO_2 + 12H^+ + 12e^- \rightleftharpoons C_2H_4 + 4H_2O$	− 0.08
	$CO_2 + 2H^+ + 2e^- \rightleftharpoons CO + H_2O$	0.11
	$CO_2 + H^+ + 2e^- \rightleftharpoons HCOO^-$	0.25
	$CO_2 + 6H^+ + 6e^- \rightleftharpoons CH_3OH + H_2O$	− 0.02
	$CO_2 + 12H^+ + 12e^- \rightleftharpoons C_2H_5OH + 3H_2O$	0.09

Table 2. Summary of literature-compiled exchange current density (i_0) values for the HER at $T = 293$ K and $p_{\text{H}_2} \approx 1$ atm on Pt, Ir, Rh, Pd, Au, Ni and Cu surfaces at low and high electrolyte pH.

Surface	pH	i_0 [mA·cm _{metal} ⁻²]	Reference
Pt	0 – 1	90 ± 1 †	[32,40]
	13	$(6 \pm 2) \cdot 10^{-1}$ †	[31,33]
Ir	0 – 1	30 ± 15 †	[32,41]
	13	$4 \cdot 10^{-1}$ *	[61]
Rh	0 – 1	5 ± 2 *	[32]
	13	$2 \cdot 10^{-1}$ *	Unpublished work
Pd	0	1 *	[32]
	13	$5 \cdot 10^{-2}$ †	[61,76, 78]
Au	0	$(3 \pm 2) \cdot 10^{-4}$ §	[79]
	13	$2 \cdot 10^{-4}$ §	Unpublished work
Cu	1	$4 \cdot 10^{-3}$ §	[69]
	13	$(1.6 \pm 1.0) \cdot 10^{-3}$ §	[31]
Ni	1	$6.3 \cdot 10^{-3}$ §	[69]
	13	$(8 \pm 2) \cdot 10^{-3}$ §	[31]

Values (averaged, when applicable) from measurements on carbon-supported nanoparticles, * polycrystalline electrodes[§] or both kinds of surfaces. †

Table 3. Proposed OER-mechanisms [144,145] arbitrarily formulated in the acid form (whereby the equivalent pathways at play in alkaline media can be obtained by adding an OH[−] group at each side of the partial proton-bearing equations). Note that asterisks (‘*’) represent catalytic surface sites.

Electrochemical Oxide Pathway [144]	Four-step Pathway [145]
$* + \text{H}_2\text{O} \rightarrow *\text{OH} + \text{H}^+ + \text{e}^-$	$* + \text{H}_2\text{O} \rightarrow *\text{OH} + \text{H}^+ + \text{e}^-$
$*\text{OH} \rightarrow *\text{O} + \text{H}^+ + \text{e}^-$	$*\text{OH} \rightarrow *\text{O} + \text{H}^+ + \text{e}^-$
$2 *\text{O} \rightarrow 2* + \text{O}_2$	$*\text{O} + \text{H}_2\text{O} \rightarrow *\text{OOH} + \text{H}^+ + \text{e}^-$
	$*\text{OOH} \rightarrow * + \text{O}_2 + \text{H}^+ + \text{e}^-$

Figure 1. Arrhenius plot summarizing the temperature-dependence of the HOR/HER exchange current density (i_0) values on Pt electrodes estimated with different experimental approaches. Reprinted with permission from Reference [31]. Reprinted from Reference [32] and licensed under CC BY 4.0. Note that the References quoted on the Figure can be found in the original work by Durst and coworkers [32], and do not correspond to the equivalent numbers in this manuscript.

Figure 2. Exchange current density (i_0) values on monometallic surfaces taken from Table 2 and reported as a function of the hydrogen binding energy (ΔE_H) calculated in Ref. [69] the corresponding H-adsorption energy (ΔG_{H^*} , estimated as $\Delta E_H + 0.24$ eV). The lines represent the kinetic model derived in the work of Nørskov *et al.* [70].

Figure 3. Schematic drawings illustrating entropy and enthalpy changes (left) and the entropic barrier changes (right) along the reaction path for the HER at low and high pH. The first step corresponds to the transition of the proton from the aqueous electrolyte bulk (H_{aq}^+) to the outer Helmholtz plane (H_{OHP}^+), followed by the formation of surface adsorbed hydrogen (H^*). ~~Reproduced with permission from Ref. [91].~~ Reprinted from Reference [92], with permission from Elsevier.

Figure 4. Hydrogen oxidation/evolution polarization curves (20 mV s^{-1} , 2500 rpm) recorded on Pt(100) (dashed line), Pt(111) (dash-dotted line) and Pt(110) (solid line) single crystals, in rotating disk electrode configuration and H_2 -saturated 0.1 M KOH at 275 K (a) or 333 K (b). The dotted line in (a) represent the theoretical HOR polarization curve for a purely diffusion controlled reaction. Reproduced with permission from Ref. [114]. Reproduced from Reference [117] with inclusion of color codes, with permission from Elsevier.

Figure 5. Volcano-like relations between several possible descriptors and the OER-activity of LaBO₃ perovskites (with B = Ti, Cr, Mn, etc.). In (a) the computed OER-overpotential (η_{OER} , equivalent to the onset potential) is related to the formation energy of a bulk oxide ($\Delta G_{\text{form, bulk}}$) [150] or to the difference between the energy states of surface-adsorbed *O and *OH intermediates ($\Delta G_{\text{O}^*}^0 - \Delta G_{\text{OH}^*}^0$) [149]. In (b), a second Volcano plot correlates experimental OER-activity values to the filling of the e_g -orbitals [147] or to the binding energy of an adsorbed *OH intermediate ($E_{\text{binding}}(*\text{OH})$) [146].

Figure 6. Schematic representation of the proposed mechanism of surface-transformation of Fe-doped NiO upon electrochemical conditioning. After the OER, the surface (oxy)hydroxide phase is composed of disordered stacks of single atomic sheets of metal cations. Reproduced with permission from Reference [148]. Reprinted with permission from Reference [151]. Copyright 2015 American Chemical Society.

Figure 7. Tafel plots for the OER on LaNiO_3 , LaCoO_3 , $\text{Ba}_{0.5}\text{Sr}_{0.5}\text{Co}_{0.8}\text{Fe}_{0.2}\text{O}_3$ (BSCF) and $\text{PrBaCo}_2\text{O}_5$ (PBCO) at pH 7 and 13 (from RDE-voltammetry in O_2 -saturated 0.4 M NaH_2PO_4 + 0.6 M Na_2SO_4 or 0.1 M KOH, respectively; $0.25 \text{ mg}_{\text{oxide}} \cdot \text{cm}_{\text{geom}}^{-2}$, 1,600 rpm, $10 \text{ mV} \cdot \text{s}^{-1}$). Reproduced with permission from Reference [156]. Reproduced from Ref. [160] with permission from the PCCP Owner Societies.

Figure 8. Free energy diagram based on DFT calculations of the four OER steps on conventional, Ni- or Co-modified ruthenia, as well as an hypothetical “perfect catalyst”. The modified ruthenia catalysts have significantly stronger binding in S_3 , which is the potential limiting step for the OER on RuO_2 . Reproduced with permission from Reference [190]. Reproduced from Ref. [194] with permission from the PCCP Owner Societies.

Figure 9. Schematic representation of the Bode cycle for the Ni(II)/Ni(III) redox couple on the surface of the Ni (oxy)hydroxide layer. Reproduced with permission from Reference [151]. Reproduced from Ref. [154] with permission from the PCCP Owner Societies.

Figure 10. Tentative, overall reaction mechanism for the electroreduction of CO_2 into formate and methanol (a, b), carbon monoxide (c), methane and methanol (d), and ethylene and ethanol (e). The asterisk (*) represents an active surface site.

Figure 11. Volcano-plot displaying the relation between the binding energy of CO (theoretical values for stepped surfaces from Ref. [240]) and the catalytic activity of the corresponding metals, expressed as the potential required to reach a CO_2 -reduction current of $1 \text{ mA cm}^{-2}_{\text{metal}}$ (disregarding formate production, which does not proceed through a CO-intermediate, cf. Fig. 10). The activity values were averaged from experimental reports dealing with polycrystalline Zn [236,240,264], Ag [236,240,263], Au [236,240,275,278] Cu [236,240,258], and Ni [236] surfaces; note that a roughness factor of $1 \text{ cm}^2_{\text{metal}} \cdot \text{cm}^{-2}_{\text{geom}}$ was assumed for all the surfaces in these studies, and that the activity values extracted from Ref. [236] were extrapolated by assuming a Tafel slope of 150 mV dec^{-1} . The vertical grey line marks the equilibrium between surface-adsorbed and gaseous CO at a partial pressure of 1% [239], whereby CO desorption or adsorption are expected to its right or left, respectively. Blue and red lines are mere guides to the eye.

Figure 12. Relation between the computed free binding energies of $^*\text{CHO}$ or $^*\text{COH}$ intermediates and the corresponding binding energies for $^*\text{CO}$ on various bimetallic surfaces. The green and blue triangles represent data points for intermetallic surfaces that bind or do not bind CO , respectively. The red circle stands for Cu (111). The red and blue lines are linear fits to data for the intermetallic compounds and pure transition metals, respectively. The overpotential is given by the vertical distance of each point from the diagonal. Reprinted with permission from Reference [299]. Reprinted with permission from Reference [306]. Copyright 2014 American Chemical Society.

Figure 13. Proposed mechanism at play upon CO_2 reduction on polyethylenimine-functionalized, nitrogen-doped carbon nanomaterials. Reprinted with permission from Reference [301]. Reprinted with permission from Reference [308]. Copyright 2014 American Chemical Society.

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