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Prospects of Value-Added Chemicals and Hydrogen via Electrolysis

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Cost is a major drawback that limits the industrial-scale hydrogen production through water electrolysis. The overall cost of this technology can be decreased by coupling the electrosynthesis of value-added chemicals at the anode side with electrolytic hydrogen generation at the cathode. This Minireview provides a directory of anodic oxidation reactions that can be

combined with cathodic hydrogen generation. The important parameters for selecting the anodic reactions, such as choice of catalyst material and its selectivity towards specific products are elaborated in detail. Furthermore, various novel electrolysis cell architectures for effortless separation of value-added products from hydrogen gas are described.

1. Introduction

Electrical energy collected from green sources is presently available, but the challenges related to its storage and conversion need to be overcome. Hydrogen is a promising alternative to conventional fuels due to its high energy density.^[1] Storing energy as hydrogen could be the solution for intermittent power supply from solar- and wind-energy provision systems. The electrolytic production of hydrogen, for which electricity splits water into hydrogen and oxygen, is presently considered expensive for industrial-scale applications. In a recent study,^[2] it was shown that the cost of hydrogen generated from renewable electricity is presently 3.23 € kg⁻¹ and needs to be further decreased to 2.50 € kg⁻¹ to become competitive with industrial-scale steam reforming.

Besides storing energy, other important materials we use today on a large scale are obtained from fossil fuels. In a broader context one can imagine that a further development not only for alternative fuels but also for basic commodities needs to happen at the same time. Electrosynthesis is currently

a growing field, driven by the need of identifying alternative ways to synthesize chemicals without using complex and expensive catalysts, without additional separation steps required among others, and with minimal impact on the environment.

A concept taking all this into consideration will combine both, electrosynthesis of high-value chemicals in one half cell with the hydrogen evolution as the counter reaction.^[3–6] This in turn can be considered from two perspectives, either by integrating cathodic hydrogen production as a side reaction into oxidative electrosynthesis systems or/and by incorporating oxidative synthesis of certain chemicals instead of oxygen into water electrolysis system. In classical water electrolysis the oxygen evolution reaction (OER) is the major bottleneck due to its sluggish kinetics and the produced oxygen is simply discarded. Simultaneous development of technologies that can combine the cathodic hydrogen evolution reaction (HER), and hence the sustainable generation of a fuel, with the anodic formation of valuable chemicals instead of the oxygen will lead to a substantial decrease of costs. More than this, such systems could push forward the transition from fossil-based resources to green solutions. Accordingly, this work aims to review the reactions that can potentially replace the OER and make the electrolytic hydrogen production more cost efficient.


2. Key Challenges for Alternative Oxidation Reactions


In this section we briefly summarize the parameters that need to be considered when selecting different anodic reactions instead of OER. In general, for electrocatalytic reactions an optimal balance between reaction kinetics, faradaic efficiency (FE) and selectivity needs to be established.^[7] Moreover, several important criteria that need to be considered are the following:

- 1) Low overpotential of the oxidation reaction
- 2) High selectivity of the catalyst towards the desired product

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- 3) Selection of the optimal electrolyte composition
- 4) Simplicity of the product separation

In electrocatalytic reactions the overpotential is mainly governed by the electrocatalyst activity, which mainly depends on its surface structure and composition.^[8–11] Furthermore, in recent studies the rate of the reaction is shown to be largely influenced by the so-called spectator species in the electrolyte.^[12–15] Thus, the composition of the solution needs to be carefully tailored. Finally, the organic value-added compound should not be in the gaseous phase for effortless separation from hydrogen gas.^[16] Most importantly, the new anodic reactant should be abundant and cheap. In an ideal system, waste products would be converted into value-added chemicals. For instance, many bio-residual products require additional costs for disposal (e.g., glycerol, cellulose), which means that one could potentially use a zero-cost resource as starting material. Thus, catalysts that perform a selective reaction should be further investigated even if the envisaged current densities are

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not reached yet, since further engineering processes could be used to generate performant electrodes, which can address the high current-density demand. Last but not the least, life cycle assessments need to be conducted for promising laboratory systems.

Several reactions that satisfy the aforementioned parameters, such as oxidation of different alcohols, peroxide synthesis, and amine and nitrile production are discussed in more detail in the following subsections.

2.1. Selective electrooxidation of oxygenated compounds

Alcohol electrooxidation in the context of energy conversion and storage was largely explored as anodic reaction in direct alcohol fuel cells. The full oxidation of different alcohols at overpotentials lower than 1.23 V [note that all potentials in this article are referred against reversible hydrogen electrode (RHE), if not noted differently] is possible on Pt- and Pd-based electrocatalysts;^[17] however, due to catalyst poisoning current densities lower than 10 mAcm⁻² are usually reported. Thus, the electrocatalyst plays a crucial role in alcohol conversion. Several non-Pt group electrocatalysts, mainly based on Ni^[18] or Co,^[19] enabled high current densities during alcohol electrooxidation at much higher potentials than on Pt-based catalysts. This makes alcohol electrooxidation one of the obvious reactions that can be used at the anode as the counter reaction for the cathodic HER while maintaining a low cell voltage.^[20]

Recently, the generation of hydrogen assisted by alcohol electrooxidation was possible at lower voltages compared to water electrolysis and the concept was described as “electrochemical reforming” or “chemical-assisted HER”.^[21] Full conversion of ethanol to CO₂ can occur, but also more complex compounds like ethyl acetate were reported as oxidation products with 95% yield and a 98% FE on Co₂O₃ at 1.44 V.^[22]

The energetic benefit of generating hydrogen at the cathode while producing a chemical compound at the anode through the electrooxidation of biomass alcohols was described first in 2010, indicating that up to 92% less energy is required to produce hydrogen using an aqueous ethanol electrolyzer compared to an alkaline electrolyzer.^[23] The concept was explored also in a proton electrolyte membrane (PEM) electrolysis cell,^[24] and a special design of the anode allowed the electrochemical reforming to be run at similar current densities as the traditional PEM water electrolysis.^[25] Several fundamental studies were performed to establish activity–structure relationships using model C₃ alcohols (1-propanol; 2-propanol; 1,2 or 1,3-propanediol) aiming to understand glycerol electrooxidation. Different activity trends were observed depending on the electrocatalyst,^[26,27] but no selectivity data were presented. A significant contribution to the alcohol electrooxidation field was made by the Koper group investigating electrooxidation of a multitude of alcohols over Au as electrocatalyst; they established the relationship between alcohol p*K*_a value and electrocatalytic activity.^[28] Although the low potential required for the alcohol conversion has a clear benefit on the overall energy consumption, the challenge lies in conducting the reaction selectively with the formation of either single

product or several easily separable products. To the best of our knowledge, no selectivity correlations based on the alcohol structure were described. Therefore, in the next paragraph we will focus on alcohols that have economical and chemical potential to be used as reactant for the anodic reaction based on their availability as well as the generated products via their electrooxidation. A summary of the products with high industrial relevance and their starting alcohols are presented in Figure 1.

Taking in consideration that H_2 production via water electrolysis can be presently run at $A\text{cm}^{-2}$ current densities, an ideal replacement reaction for OER would still allow similar current

densities to be achieved. However, the majority of organic oxidation reactions are performed at lower current densities, so increasing the yield of the anodic reaction is envisaged. In a recent study, high selectivity and high yields were observed for the conversion of a series of derived benzyl alcohols obtained in flow cells using a Ni cathode and a carbon anode, with currents up to 800 mA being applied to perform the reaction.^[29] Depending on the solubility of the generated product, the addition of acetonitrile or ionic surfactants was required in some cases to facilitate the homogeneity of the reaction environment. The selectivity of the reaction depends on the alcohol type, higher selectivity being reported for benzylic alcohols

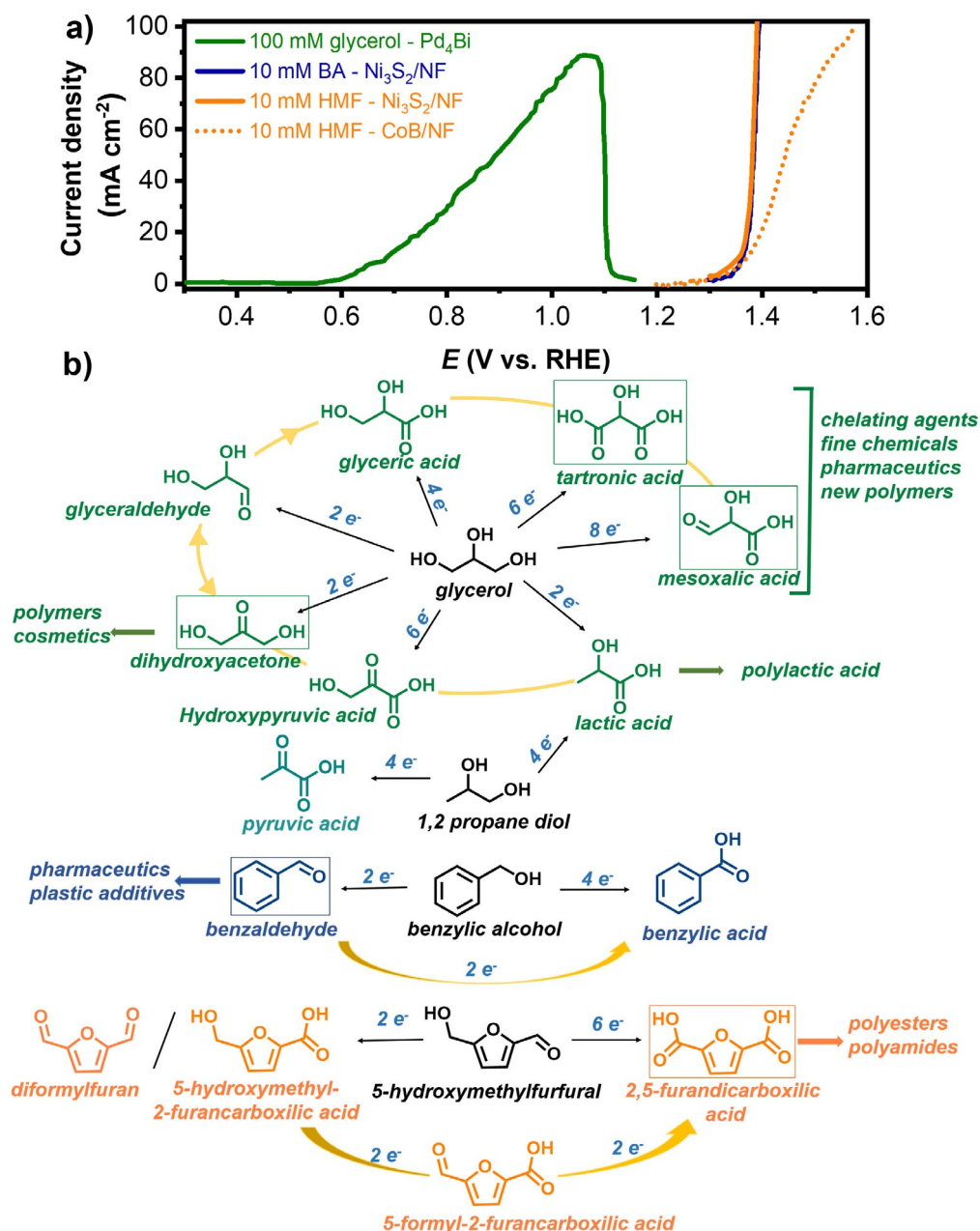


Figure 1. a) Linear sweep voltammograms recorded in the presence of 100 mM glycerol on Bi_4Pt nanoparticles (green) (adapted with permission from Ref. [33]), 10 mM benzylic alcohol on $\text{Ni}_3\text{S}_2/\text{NF}$ (dark blue) (adapted with permission from Ref. [37]), and 10 mM HMF on $\text{Ni}_3\text{S}_2/\text{NF}$ (orange—solid line) (adapted with permission from Ref. [37]) and on CoB/NF (orange—dot line) (adapted with permission from Ref. [40]). b) Overview of alcohol electrooxidation reactions and important target products and their application domain.

over the allylic ones.^[29] Complex CoCuN-based electrodes having a hierarchical structure allowed also the conversion of benzylic alcohol to benzaldehyde with high selectivity.^[30]

Although selectivity can be partially controlled in the case of aromatic alcohols, where electronic effects contribute, for example, to the stabilization of aldehydes, selectivity control becomes more challenging for multiple aliphatic alcohols. An excellent platform chemical currently available in high quantities is glycerol due to the increased production of biodiesel, which generates glycerol as by-product. The disposal of glycerol involves additional costs, therefore using glycerol electrooxidation as paired anodic reaction for HER will have additional economic benefit. By partial oxidation of glycerol, depending on the degree of oxidation, compounds such as glyceraldehyde, dihydroxyacetone, glyceric acid, hydroxypyruvic acid, tartronic acid, glycolic acid, glyoxylic acid, or 1,3-propanediol can be obtained, all of them being relevant in several industries such as: food additives, pharmaceuticals, personal care products, or polymers (Figure 1b). Despite all efforts in developing highly selective electrocatalysts, most of the reports are showing the formation of mixtures of the mentioned compounds. One interesting element for designing selective catalysts for glycerol electrooxidation is Bi. Bi has shown to modulate the selectivity of Pt group metal (PGM) catalysts for glycerol electrooxidation, thus being a very important co-catalyst for the generation of specific value-added product. Although Pt can be used to convert glycerol to CO₂ by breaking the C–C bond at low overpotentials, it was shown that the addition of Bi to Pt/C systems prevents C–C breaking and leads to a highly selective formation of dihydroxyacetone.^[31,32] Besides, PtBi is also a very active HER electrocatalyst in acidic environments.

Alloying Pd with Bi while simultaneously inducing a porous structure leads to a class of PdBi catalysts that shows up to four times higher current densities than Pd-only electrocatalysts. Current densities close to 90 mA cm⁻² were reported for Pd_xBi electrocatalysts and, depending on the applied potential, the selective conversion of glycerol to dihydroxyacetone, glyceraldehyde or hydroxypyruvate was possible in alkaline environment.^[33] Glyceraldehyde and hydroxypyruvate are very important intermediates for the further generation of lactic acid and 1,3-propanediol, two essential building blocks for polymers. Reports regarding the synthesis of lactic acid via the glycerol electrooxidation are limited,^[34] however, the glyceraldehyde or dihydroxyacetone generation without further oxidation is essential for determining the reaction pathway.^[34] If a higher oxidation state of glycerol is achieved and glyceric acid is formed, the formation of lactic acid is no longer possible. The catalytic system formed from dicobalt octacarbonyl and 1,2-bis(diphenylphosphino)ethane could change the ratio between lactic acid and glycolic acid during glycerol electrooxidation in an alkaline environment. The formation of lactic acid was possible at low current densities (1.8 mA cm⁻²) at 60 °C whereas glyceric acid formed at higher current densities (8.8 mA cm⁻²) at room temperature. As byproducts oxalic, tartronic, glycolic and formic acid were reported.^[34]

Another important biomass-derived alcohol is 1,2-propanediol. A selectivity of 98% for lactate was reported for 1,2-pro-

panediol electrooxidation using a Rh/C anode in an alkaline environment.^[35] The same catalyst did not show the same high selectivity in the glycerol electrooxidation. These results highlight that there is no universal substrate that can be used to generate all needed products concomitant with hydrogen as well as no unique catalyst that can convert all alcohols; however, there are many options and identifying the optimal substrate/catalyst pair is essential for the hydrogen generation at industrially relevant current densities.

Furan dicarboxylic acid (FDCA) is another important monomer for polymer synthesis, which can be synthesized via electrooxidation of hydroxy methyl furfural (HMF), a biomass product. HMF exhibits an increased complexity in the structure since it contains an aldehyde and one hydroxyl group; because of this it has a low chemical stability in an alkaline environment. The low-oxidation products of HMF are 5-hydroxymethyl-2-furancarboxylic acid (HMFCFA) or dialdehyde 2,5-diformylfuran (DFF), which both can be further oxidized to 5-formyl-2-furancarboxylic acid (FFCA), generating FDCA in the next step (Figure 1b).^[36–38] Despite the presence of multiple functional groups in the HMF molecule, the high-oxidation products of HMF are independent of the reaction pathway. Hierarchically porous Ni electrodes showed a clear advantage in HMF electrooxidation, 50 mA cm⁻² current densities were recorded with 220 mV less voltage compared to water oxidation.^[36] Moreover, Ni-based electrocatalysts such as Ni₃S₂^[37] or NiP_y^[39] immobilized on Ni foam by drop casting^[39] or direct growth^[37] were efficiently used for converting HMF to FDCA with high FE. Current densities up to hundreds of mA cm⁻² were reported for both catalysts at potentials lower than 1.4 V,^[37] making HMF oxidation a promising anodic counter reaction for cathodic HER. In another study, Co-based electrocatalysts^[38,40] showed 100% conversion of HMF to FDCA with 90% FE but at higher overpotentials than the Ni-based electrocatalysts.

2.2. H₂O₂ synthesis via water electrooxidation

To date, the synthesis of H₂O₂ is widely based on the catalytic reduction of oxygen in the so-called anthraquinone process, which lacks in terms of sustainability, involves scarce catalysts, and suffers from high energy consumption.^[41] H₂O₂ can be considered being one of the most important inorganic commodity chemicals with a steadily increasing demand, which requires further built-up of the respective energy-demanding peroxide plants. Therefore, methods need to be elaborated to make the industrial-scale synthesis of H₂O₂ more energy efficient while reducing the amount of waste products. The electrosynthesis of H₂O₂ has been proven to be a sustainable alternative to the aforementioned synthetic route. For example, an efficient and selective generation of H₂O₂ by oxygen reduction has been reported in several studies.^[42] However, typical catalysts achieving high activity and selectivity are based on scarce elements, such as nanostructured PtHg or PdAu alloys.^[42,43]

In recent years, the electrooxidation of water has been established as another versatile alternative to the classical reaction paths as it not only enables the two-electron oxidation of water to H₂O₂ using sustainable electricity but also features the

simultaneous generation of H₂ at the complementary electrode, providing a more cost-efficient system. However, to achieve high efficiencies, competitive reactions such as the OER have to be suppressed effectively, which demands a high selectivity of the catalysts involved.

Early studies by MacFarlane and co-workers identified MnO_x as a promising catalyst for the electrocatalytic oxidation of water.^[44] MnO_x thin films, electrodeposited on Au substrate, showed low overpotentials for the generation of H₂O₂ in aqueous butyl ammonium bisulfate (BAS) and hydrated BAS ionic liquid (BAS-IL) electrolyte. Notably, at low overpotentials reasonably high current densities ($\approx 1 \text{ A cm}^{-2}$ at 0.15 V) were only observed in alkaline BAS-based electrolyte (pH 10) whereas at

neutral pH as well as in NaOH solution (pH 10) no significant current density was observed, as seen in Figure 2a. Theoretical calculations indicate that in alkaline BAS, the peroxide is stabilized by an ethylamine complex formed in the electrolyte, explaining the increase in activity (Figure 2b).

A useful tool to gain principle understanding of such reactions and, in turn, improve the electrocatalytic efficiency of the process, are theoretical studies based on density functional theory (DFT) calculations. For instance, Nørskov and co-workers employed DFT to rate the efficiency of different metal oxide catalysts (TiO₂, SnO₂, WO₃, and BiVO₄) towards water electrooxidation, combined with an experimental validation of the theoretical results.^[45] Here, weak *OH free energies are of particular

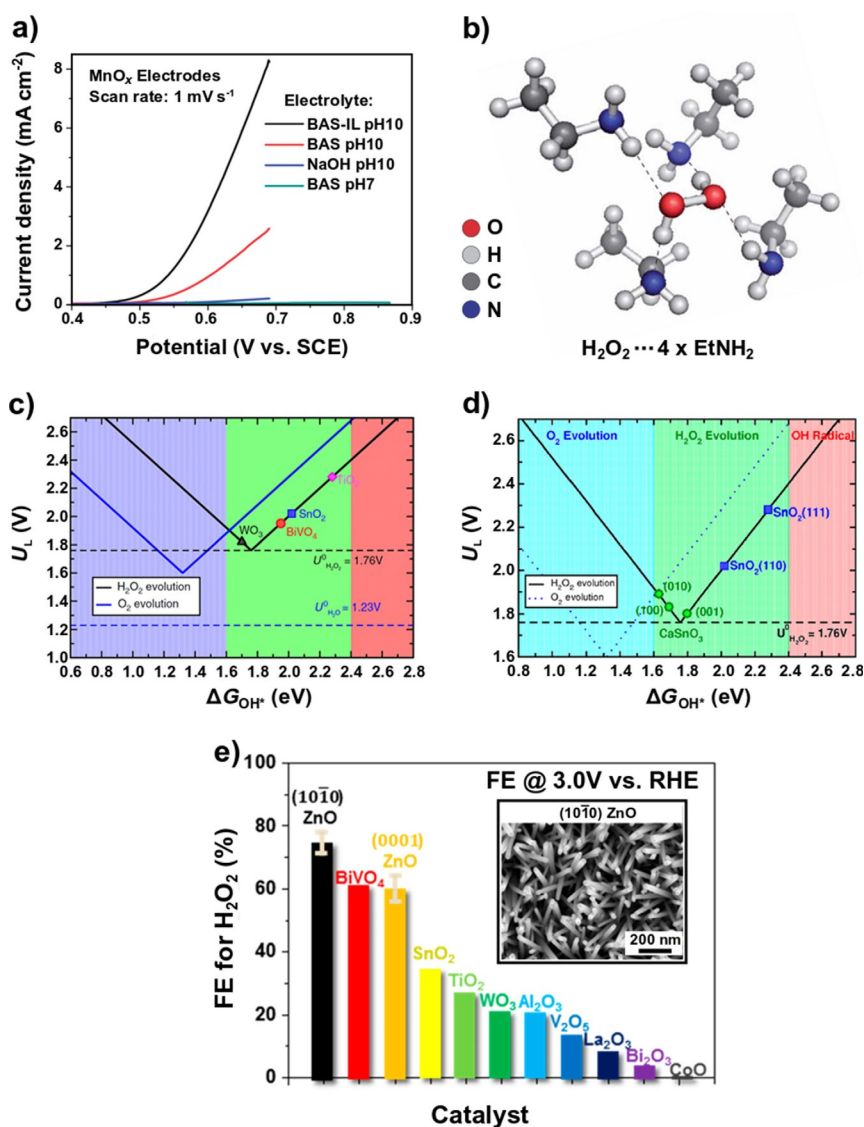


Figure 2. a) Polarization curves of MnO_x thin film electrocatalyst, recorded in different electrolytes. Adapted with permission from Ref. [44]. Copyright Royal Society of Chemistry. b) Corresponding stabilization of H₂O₂ through the formation of an ethylamine complex in BAS electrolyte. Adapted with permission from Ref. [44]. Copyright Royal Society of Chemistry. c) Theoretical Volcano plot, indicating that weak *OH binding preferably leads to H₂O₂ evolution rather than O₂ evolution. Comparing four different metal oxide electrocatalysts, WO₃ and BiVO₄ are placed closest to the top of the Volcano plot. Adapted with permission from Ref. [45] (under CC BY 4.0 license). d) Theoretical Volcano plot indicating that low-index facets are responsible for a high activity of nanostructured CaSnO₃ towards the electrooxidation of water. Adapted with permission from Ref. [47]. Copyright American Chemical Society. e) FE of different state-of-the-art water electrooxidation catalysts, indicating superior activity of ZnO, depending on the surface facet. The inset shows a typical scanning electron microscopy image of the synthesized ZnO nanorods. Adapted with permission from Ref. [48]. Copyright American Chemical Society.

relevance as they lead to a preference of the 2-electron pathway rather than the 4-electron formation of O_2 while also strongly influencing the reaction overpotential. Accordingly, WO_3 and $BiVO_4$ are placed closest to the top of the corresponding theoretical Volcano plot (Figure 2c). Comparing the investigated materials experimentally, WO_3 showed the lowest onset potential whereas $BiVO_4$ exhibited the highest amount of H_2O_2 generated with highest FE ($\approx 70\%$ at 3.1 V). Remarkably, this can be further increased by illumination in photoelectrochemical applications, which confirms previous results on the photoelectrochemical water splitting by Fuku and Sayama.^[46] However, with regard to industrial applications, the poor dissolution stability of $BiVO_4$ in non-neutral electrolytes has to be noted as a main drawback, which is owed to the contained vanadium.

Screening for more stable catalysts, Park et al. proposed $CaSnO_3$ nanoparticles as a promising alternative to $BiVO_4$, which reduces the reaction overpotential from ≈ 0.34 to ≈ 0.23 V at a current density of 0.2 mA cm^{-2} while also exhibiting a higher FE (76% at 3.2 V). From DFT calculations they concluded that in particular low-index facets, such as the $CaSnO_3$ (001) facet, are responsible for the high activity and selectivity (Figure 2d).^[47]

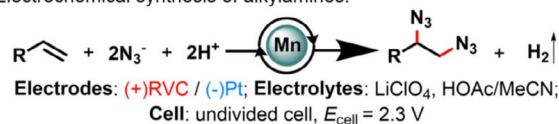
Similarly, recent studies report that tailoring surface facets has a beneficial impact on the water electrooxidation performance of ZnO-based electrocatalysts.^[48] Herein, synthesized ZnO nanoparticles showed a low overpotential of 0.04 V at a current density of 0.1 mA cm^{-2} . As depicted in Figure 2e, ZnO can outperform other state-of-the-art catalysts in terms of FE; however, the orientation of the surface facets indeed has a crucial influence on its performance. Overall, especially the environmental safety of ZnO has to be emphasized, for example, compared to catalysts such as $CaSnO_3$, which is highly toxic, and thus there is a high probability that its further application will be hindered.

The described electrocatalysts have high potential to become an economically viable solution to produce H_2O_2 . Regarding this process, the applicability of non-precious metal catalysts combined with the complementary generation of other valuable products, such as H_2 , have to be highlighted, especially compared to the alternative electrochemical path via the oxygen electroreduction.

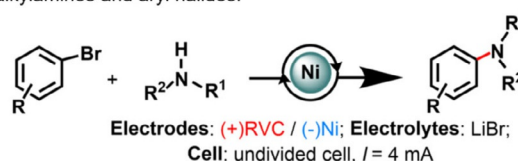
2.3. Electrocatalytic amine/ nitrile generation

A valuable group of chemicals widely used in medicinal and chemical industry are amines. Nowadays, anodic electrooxidative C–N formation coupled with cathodic formation of hydrogen has been developed as a more direct and sustainable synthetic approach in comparison to traditional processes. One of the main challenges is to identify an efficient catalyst for the formation of C–N bonds. So-called redox-active catalysts are shown to be promising candidates, where the catalyst initially forms active metal azidyl (M–N₃) complex, which then reacts with the carbon atom (see Figure 3a). Mostly, transition-metal complexes (such Cu-, Co-, Fe-, and Mn-based complexes) were shown to be an efficient redox-active catalyst, as seen in the

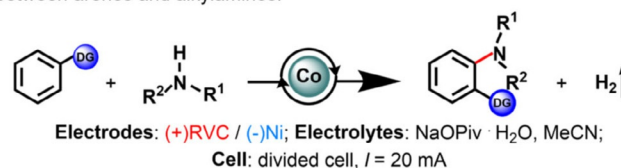
a) Electrochemical synthesis of alkylamines:



b) Electrochemical synthesis of arylamines through cross-coupling between alkylamines and aryl halides:



c) Electrochemical synthesis of arylamines through cross-coupling between arenes and alkylamines:



d) Electrochemical synthesis of nitriles:

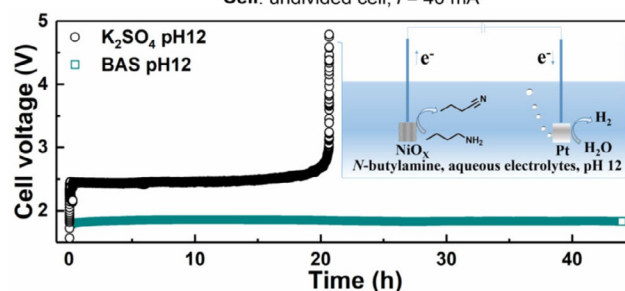
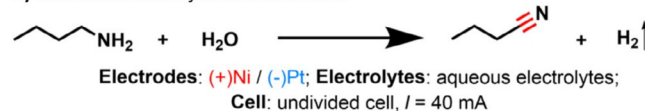


Figure 3. Electrochemical generation of amines and nitriles. a) Proposed electrocatalytic approach for Mn-catalyzed diazidation of alkenes. RVC, Pt, alkene, and Mn salts used as anode, cathode, mediator, substrate and redox mediators. b) Ni-electrocatalyzed amination of aryl halides. c) Electrochemical Co-catalyzed amination of arenes. DG represents directing groups, for detailed information please see Ref. [52]. d) Electrocatalytic generation of *n*-butryronitrile from *n*-butylamine, stability measurements in $0.4\text{ M K}_2\text{SO}_4$ and 0.4 M n -butylamine-containing electrolytes at pH 12 as well as a schematic of the generation of *n*-butryronitrile. The system converting *n*-butylamine to *n*-butryronitrile exhibits both, a reasonable stability and a lower cell voltage as compared to normal aqueous systems. Figures a–d) are adapted with permission from Ref. [49, 51, 52, and 58], respectively. Copyright Wiley.

Figure 3. Recently, Lin and co-workers reported an electrochemical protocol for alkylamine synthesis (Figure 3a).^[49] The electrolysis system consists of a robust graphite anode, namely reticulated vitreous carbon (RVC), and a Pt cathode and uses azides and alkenes as reactants. At the anode, azides are oxidized to azidyl radicals, which successively react with the alkene C=C bond in the presence of Mn-based catalyst, forming two new C–N bonds, namely a vicinal diazide. Subsequently, the obtained 1,2-diazide is selectively converted to 1,2-diamine.

Considerable efforts have been made in utilizing electrochemistry to drive the Buchwald–Hartwig–Ullmann-type amination of aryl halides, one of the 20 most frequently used reac-

tions in medicinal chemistry.^[50] For instance, Baran's group presented an electrochemical method to cross-couple alkylamines and aryl halides,^[51] where the formation of C–N bonds can be easily accomplished through catalysis on Ni at room temperature (Figure 3 b). The yield of arylamines was 76% at a constant current of 4 mA for 4.5 h in an undivided cell, with Ni foam and RVC as cathode and anode, respectively. Moreover, the electrochemical synthesis of arylamines through amination of arenes with alkylamines has been reported by both, Lei's^[52] and Ackermann's^[53] groups. In those studies, the cross-coupling between arenes and alkylamines was achieved in a divided cell, containing a Ni foam cathode and RVC anode (Figure 3 c). Under galvanostatic electrolysis at 10 mA for 3 h, the obtained isolated amination yield was about 74%. Hence, combining electrochemical oxidation with an earth-abundant catalyst indeed enables amine synthesis under relatively mild conditions while generating H₂ fuel as a sole byproduct. However, it should be noted that more systematic research needs to be conducted to elaborate the source of H⁺ utilized for H₂ generation, as the majority of these studies do not distinguish between H⁺ coming from the organic substrate or the solvent.

Nitrile compounds are another important class of organic chemicals, which are used for the synthesis of fine chemicals, agrochemicals, and pharmaceuticals.^[54–56] Initially, electrochemical nitrile synthesis has been developed in the 1980s,^[57] and since then significant progress has been achieved.^[58–60] One-pot electrochemical synthesis of nitriles from alcohol was reported by Li's group,^[60] where ammonium acetate and 2,2,6,6-tetramethylpiperidyl-1-oxyl served as the nitrogen source and catalyst, respectively. In another study, Xue et al. reported an effective way to convert *n*-butylamine into *n*-butyronitrile with 95% FE.^[58] Here, a two-electrode system was employed, where Ni(OH)₂/Ni foam was used as anode and a Pt wire served as cathode, and immersed in an aqueous solution of 0.4 M *n*-butylamine as electrolyte (Figure 3 d). The onset potential of the anodic reaction was at 1.3 V, which is significantly lower than that for the OER, resulting in a lower anode overpotential. Furthermore, the catalytic system shows high stability and selectivity, as seen in Figure 3 d. More importantly, the cell voltage required to produce *n*-butyronitrile is much lower compared to a conventional water electrolysis system (Figure 3 d).

3. Decoupling Anode and Cathode Reactions via New Cell Designs

In the conventional electrolyzer architecture, the hydrogen and oxygen gases are produced at the cathode and anode, respectively, which in turn are separated by a membrane, where the H⁺-conducting membrane is utilized in acidic electrolyzers and the OH⁻-conducting membrane is used in alkaline electrolyzers. This typical cell design can lead to several critical challenges when the OER at the anode is replaced by other organic oxidation reactions, such as poisoning of the cathode catalyst, mixing of the organic co-products with hydrogen gas, lower current densities due to the mass-transfer limitations of organic reactants. To overcome these challenges, one solution implies the conduction of the reactions in two separate chambers

by using mediators, as it was already shown for conventional water electrolysis.^[61–64] In this section we provide a short guideline on the cell architectures that can be translated for electrolyzers with various other organic oxidation reactions at the anode side.

A continuous flow cell reactor was recently described for the electrochemical oxidation of various alcohols.^[29] The flow cell reactor, schematically shown in Figure 4 a, uses carbon paper and a Ni plate as anode and cathode, respectively. The oxidation of different types of alcohols (e.g., alkyl-, aryl-, allyl-alcohol) to aldehydes and ketones was successfully carried out in the flow cell reactor without any additional oxidant or media-

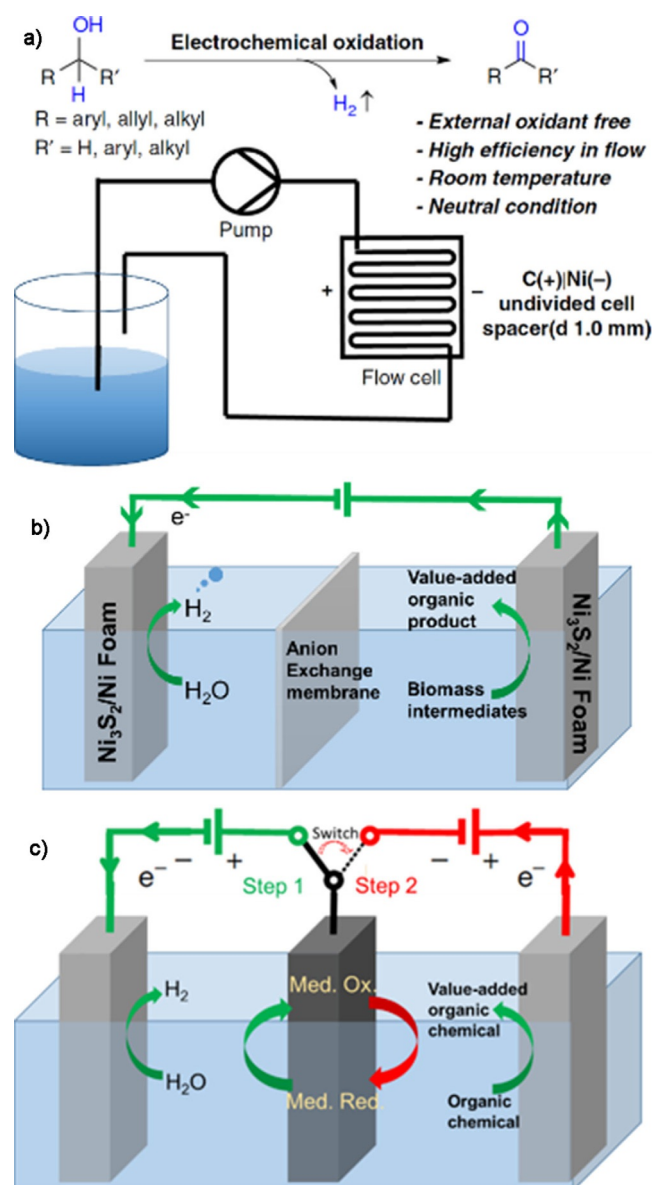


Figure 4. Proposed cell designs for electrocatalytic applications. a) Scheme of an alcohol oxidation reaction in a flow-cell setup. Adapted with permission from Ref. [29]. Copyright Springer Nature. b) Electrolysis cell design adapted with permission from Ref. [37]. Copyright American Chemical Society. c) Proposed schematic of the two-step cell architecture with redox mediator. Step 1 is the H₂ production and oxidation of the mediator; step 2 involves the value-added-chemical production and reduction of the mediator.

tor. Interestingly, no overoxidation of alcohols into carboxylic acids was observed, which makes the methodology highly selective towards aldehydes or ketones. Furthermore, the fuel cell reactor can be used with water as a solvent in the presence of surfactants, which makes the product handling and separation easier. Moreover, selective oxidation of pharmaceutically relevant precursors was conducted in the continuous-flow electrolysis cell to further extend the applicability of the system.

Figure 4b depicts an example of an electrolyzer producing value-added organic products at the anode side while producing hydrogen gas at the cathode.^[37] This type of two-compartment cell design was successfully implemented in production of various high-value chemicals with reduced cell voltage and prevented mixing of the products with hydrogen gas.^[37] Another way of decoupling the anode and cathode reactions is by utilizing redox mediators. Figure 4c shows a schematic of a cell architecture utilizing a redox mediator, in which the process proceeds by two steps. By adjusting the nature of the mediator, this cell design can be transformed for selected reactions, for example, alcohol oxidation or peroxide, nitrile, and amine production. Certainly, several important parameters need to be considered, such as electrolyte composition and the potential of the oxidation reaction compared to the redox potential of the mediator material.

4. Conclusions and Perspectives

In this work, we summarized several important aspects of simultaneously producing valuable chemical together with hydrogen gas. The most important parameters for choosing anodic reactions were elaborated with the directory of possible oxidation reactions. By taking these key examples, we believe that an electrochemical strategy for organic synthesis represents an exciting area where a simple, effective, and environmentally friendly production of valuable products can be realized. Additionally, the cost of hydrogen generation can be considerably reduced as more value-added organic compounds are obtained instead of oxygen at the anode. Since most of the commonly used organic chemicals are in the liquid phase, separation of the products from hydrogen gas will be straightforward. Furthermore, we outlined some of the new cell architectures that might be suitable for conducting the anodic and cathodic reactions in separate compartments. Taken together, this Minireview will serve as a guideline for developing future electrolysis systems assisted by electrosynthesis of various organic chemicals aiming to push forward the use of renewable resources at low cost for a carbon-free society. The concept of combining different anodic and cathodic important reactions can go beyond hydrogen production. Synthesis of CO via CO₂ electroreduction concomitant with production of lactic acid via 1,2-propanediol electrooxidation was recently reported,^[65] highlighting the increased interest of the scientific community for generating new alternative processes based on renewable energy.

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Conflict of interest

The authors declare no conflict of interest.

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- [1] D. Elliott, *Nat. Energy* **2016**, *1*, 15003.
- [2] G. Glenk, S. Reichelstein, *Nat. Energy* **2019**, *4*, 216–222.
- [3] B. You, G. Han, Y. Sun, *Chem. Commun.* **2018**, *54*, 5943–5955.
- [4] B. You, Y. Sun, *Acc. Chem. Res.* **2018**, *51*, 1571–1580.
- [5] Y. Xu, B. Zhang, *ChemElectroChem* **2019**, *6*, 3214.
- [6] Y. Yuan, A. Lei, *Acc. Chem. Res.* **2019**, *52*, 3309–3324.
- [7] B. Garlyyev, J. Fichtner, O. Piqué, O. Schneider, A. S. Bandarenka, F. Calle-Vallejo, *Chem. Sci.* **2019**, *10*, 8060–8075.
- [8] J. Fichtner, B. Garlyyev, S. Watzele, H. A. El-Sayed, J. Schwaemmlein, W. Li, F. Maillard, L. Dubau, J. Michalicka, J. Macak, A. W. Holleitner, A. S. Bandarenka, *ACS Appl. Mater. Interfaces* **2019**, *11*, 5129–5135.
- [9] S. Anantharaj, S. R. Ede, K. Sakthikumar, K. Karthick, S. Mishra, S. Kundu, *ACS Catal.* **2016**, *6*, 8069–8097.
- [10] Z. W. Seh, J. Kibsgaard, C. F. Dickens, I. B. Chorkendorff, J. K. Nørskov, T. F. Jaramillo, *Science* **2017**, *355*, eaad4998.
- [11] B. Garlyyev, K. Kratzl, M. Rück, J. Michalicka, J. Fichtner, J. M. Macak, T. Kratky, S. Günther, M. Cokoja, A. S. Bandarenka, A. Gagliardi, R. A. Fischer, *Angew. Chem. Int. Ed.* **2019**, *58*, 9596; *Angew. Chem.* **2019**, *131*, 9697.
- [12] S. C. Lai, S. E. Kleijn, F. T. Öztürk, V. C. van Rees Vellinga, J. Koning, P. Rodriguez, M. T. Koper, *Catal. Today* **2010**, *154*, 92–104.
- [13] B. Garlyyev, S. Xue, S. Watzele, D. Scieszka, A. S. Bandarenka, *J. Phys. Chem. Lett.* **2018**, *9*, 1927–1930.
- [14] B. Garlyyev, S. Xue, M. D. Pohl, D. Reinisch, A. S. Bandarenka, *ACS Omega* **2018**, *3*, 15325–15331.
- [15] S. Xue, B. Garlyyev, S. Watzele, Y. Liang, J. Fichtner, M. D. Pohl, A. S. Bandarenka, *ChemElectroChem* **2018**, *5*, 2326.
- [16] Y. Huang, X. Chong, C. Liu, Y. Liang, B. Zhang, *Angew. Chem. Int. Ed.* **2018**, *57*, 13163; *Angew. Chem.* **2018**, *130*, 13347.
- [17] G. M. Alvarenga, H. M. Villullas, *Curr. Opin. Electrochem.* **2017**, *4*, 39–44.
- [18] T.-H. Ko, K. Devarayan, M.-K. Seo, H.-Y. Kim, B.-S. Kim, *Sci. Rep.* **2016**, *6*, 20313.
- [19] D. Hassen, S. A. El-Safty, K. Tsuchiya, A. Chatterjee, A. Elmarakbi, M. A. Shenashen, M. Sakai, *Sci. Rep.* **2016**, *6*, 24330.
- [20] C. Coutanceau, S. Baranton, *WIREs Energy Environ.* **2016**, *5*, 388–400.
- [21] L. Chen, J. Shi, *J. Mater. Chem. A* **2018**, *6*, 13538–13548.
- [22] L. Dai, Q. Qin, X. Zhao, C. Xu, C. Hu, S. Mo, Y. O. Wang, S. Lin, Z. Tang, N. Zheng, *ACS Cent. Sci.* **2016**, *2*, 538–544.
- [23] V. Bambagioni, M. Bevilacqua, C. Bianchini, J. Filippi, A. Lavacchi, A. Marchionni, F. Vizza, P. K. Shen, *ChemSusChem* **2010**, *3*, 851–855.
- [24] A. Caravaca, A. de Lucas-Consuegra, A. B. Calcerrada, J. Lobato, J. L. Valverde, F. Dorado, *Appl. Catal. B* **2013**, *134–135*, 302–309.
- [25] Y. X. Chen, A. Lavacchi, H. A. Miller, M. Bevilacqua, J. Filippi, M. Innocenti, A. Marchionni, W. Oberhauser, L. Wang, F. Vizza, *Nat. Commun.* **2014**, *5*, 4036.
- [26] N. E. de Souza, J. F. Gomes, G. Tremiliosi-Filho, *J. Electroanal. Chem.* **2017**, *800*, 106–113.

- [27] S. Sun, L. Sun, S. Xi, Y. Du, M. A. Prathap, Z. Wang, Q. Zhang, A. Fisher, Z. J. Xu, *Electrochim. Acta* **2017**, *228*, 183–194.
- [28] Y. Kwon, S. C. Lai, P. Rodriguez, M. T. Koper, *J. Am. Chem. Soc.* **2011**, *133*, 6914–6917.
- [29] D. Wang, P. Wang, S. Wang, Y.-H. Chen, H. Zhang, A. Lei, *Nat. Commun.* **2019**, *10*, 2796.
- [30] J. Zheng, X. Chen, X. Zhong, S. Li, T. Liu, G. Zhuang, X. Li, S. Deng, D. Mei, J.-G. Wang, *Adv. Funct. Mater.* **2017**, *27*, 1704169.
- [31] Y. Kwon, Y. Birdja, I. Spanos, P. Rodriguez, M. T. M. Koper, *ACS Catal.* **2012**, *2*, 759–764.
- [32] A. C. Garcia, Y. Y. Birdja, G. Tremiliosi-Filho, M. T. M. Koper, *J. Catal.* **2017**, *346*, 117–124.
- [33] A. Zalineeva, A. Serov, M. Padilla, U. Martinez, K. Artyushkova, S. Baranton, C. Coutanceau, P. B. Atanassov, *J. Am. Chem. Soc.* **2014**, *136*, 3937–3945.
- [34] C. H. Lam, A. J. Bloomfield, P. T. Anastas, *Green Chem.* **2017**, *19*, 1958–1968.
- [35] M. V. Pagliaro, M. Bellini, M. Bevilacqua, J. Filippi, M. G. Folliero, A. Marchionni, H. A. Miller, W. Oberhauser, S. Caporali, M. Innocenti, F. Vizza, *RSC Adv.* **2017**, *7*, 13971–13978.
- [36] B. You, X. Liu, X. Liu, Y. Sun, *ACS Catal.* **2017**, *7*, 4564–4570.
- [37] B. You, X. Liu, N. Jiang, Y. Sun, *J. Am. Chem. Soc.* **2016**, *138*, 13639–13646.
- [38] N. Jiang, B. You, R. Boonstra, I. M. Terrero Rodriguez, Y. Sun, *ACS Energy Lett.* **2016**, *1*, 386–390.
- [39] S. Barwe, J. Weidner, S. Cychy, D. M. Morales, S. Dieckhöfer, D. Hiltrop, J. Masa, M. Muhler, W. Schuhmann, *Angew. Chem. Int. Ed.* **2018**, *57*, 11460–11464; *Angew. Chem.* **2018**, *130*, 11631–11636.
- [40] J. Weidner, S. Barwe, K. Sliozberg, S. Piontek, J. Masa, U.-P. Apfel, W. Schuhmann, *Beilstein J. Org. Chem.* **2018**, *14*, 1436–1445.
- [41] J. M. Campos-Martin, G. Blanco-Brieva, J. L. G. Fierro, *Angew. Chem. Int. Ed.* **2006**, *45*, 6962–6984; *Angew. Chem.* **2006**, *118*, 7116–7139.
- [42] S. Siahrostami, A. Verdaguer-Casadevall, M. Karamad, D. Deiana, P. Malacrida, B. Wickman, M. Escudero-Escribano, E. A. Paoli, R. Frydendal, T. W. Hansen, I. Chorkendorff, I. E. L. Stephens, J. Rossmeisl, *Nat. Mater.* **2013**, *12*, 1137–1143.
- [43] J. S. Jirkovský, I. Panas, E. Ahlberg, M. Halasa, S. Romani, D. J. Schiffrin, *J. Am. Chem. Soc.* **2011**, *133*, 19432–19441.
- [44] A. Izgorodin, E. Izgorodina, D. R. MacFarlane, *Energy Environ. Sci.* **2012**, *5*, 9496–9501.
- [45] X. Shi, S. Siahrostami, G.-L. Li, Y. Zhang, P. Chakthranont, F. Studt, T. F. Jaramillo, X. Zheng, J. K. Nørskov, *Nat. Commun.* **2017**, *8*, 701.
- [46] K. Fuku, K. Sayama, *Chem. Commun.* **2016**, *52*, 5406–5409.
- [47] S. Y. Park, H. Abroshan, X. Shi, H. S. Jung, S. Siahrostami, X. Zheng, *ACS Energy Lett.* **2019**, *4*, 352–357.
- [48] S. R. Kelly, X. Shi, S. Back, L. Vallez, S. Y. Park, S. Siahrostami, X. Zheng, J. K. Nørskov, *ACS Catal.* **2019**, *9*, 4593–4599.
- [49] N. Fu, G. S. Sauer, A. Saha, A. Loo, S. Lin, *Science* **2017**, *357*, 575–579.
- [50] D. G. Brown, J. Boström, *J. Med. Chem.* **2016**, *59*, 4443–4458.
- [51] C. Li, Y. Kawamata, H. Nakamura, J. C. Vantourout, Z. Liu, Q. Hou, D. Bao, J. T. Starr, J. Chen, M. Yan, P. S. Baran, *Angew. Chem. Int. Ed.* **2017**, *56*, 13088; *Angew. Chem.* **2017**, *129*, 13268.
- [52] X. Gao, P. Wang, L. Zeng, S. Tang, A. Lei, *J. Am. Chem. Soc.* **2018**, *140*, 4195–4199.
- [53] N. Saueremann, R. Mei, L. Ackermann, *Angew. Chem. Int. Ed.* **2018**, *57*, 5090; *Angew. Chem.* **2018**, *130*, 5184.
- [54] T. Wang, N. Jiao, *Nitrogenation Strategy for the Synthesis of N-containing Compounds: Nitrogenation Strategy for the Synthesis of Nitriles* (Ed.: N. Jiao), Springer, Singapore, **2017**.
- [55] M.-X. Wang, *Acc. Chem. Res.* **2015**, *48*, 602–611.
- [56] A. Kleemann, J. Engel, B. Kutscher, D. Reichert, *Pharmaceutical substances: syntheses, patents, applications*, Georg Thieme, Stuttgart, **2001**.
- [57] M. F. Semmelhack, C. R. Schmid, *J. Am. Chem. Soc.* **1983**, *105*, 6732–6734.
- [58] S. Xue, S. Watzel, V. Čolić, K. Brandl, B. Garlyyev, A. S. Bandarenka, *ChemSusChem* **2017**, *10*, 4812.
- [59] R. Matthesen, L. Claes, J. Fransaer, K. Binnemans, D. E. De Vos, *Eur. J. Org. Chem.* **2014**, 6649–6652.
- [60] Z. Fan, X. Yang, C. Chen, Z. Shen, M. Li, *J. Electrochem. Soc.* **2017**, *164*, G54–G58.
- [61] A. Landman, H. Dotan, G. E. Shter, M. Wullenkord, A. Houaijia, A. Maljus, G. S. Grader, A. Rothschild, *Nat. Mater.* **2017**, *16*, 646–651.
- [62] B. Rausch, M. D. Symes, G. Chisholm, L. Cronin, *Science* **2014**, *345*, 1326–1330.
- [63] M. D. Symes, L. Cronin, *Nat. Chem.* **2013**, *5*, 403–409.
- [64] L. Chen, X. Dong, Y. Wang, Y. Xia, *Nat. Commun.* **2016**, *7*, 11741.
- [65] E. Pérez-Gallent, S. Turk, R. Latsuzbaia, R. Bhardwaj, A. Anastasopol, F. Sastre-Calabuig, A. C. Garcia, E. Giling, E. Goetheer, *Ind. Eng. Chem. Res.* **2019**, *58*, 6195–6202.

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