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Upgrading Organic Compounds through the Coupling of Electrooxidation with Hydrogen Evolution

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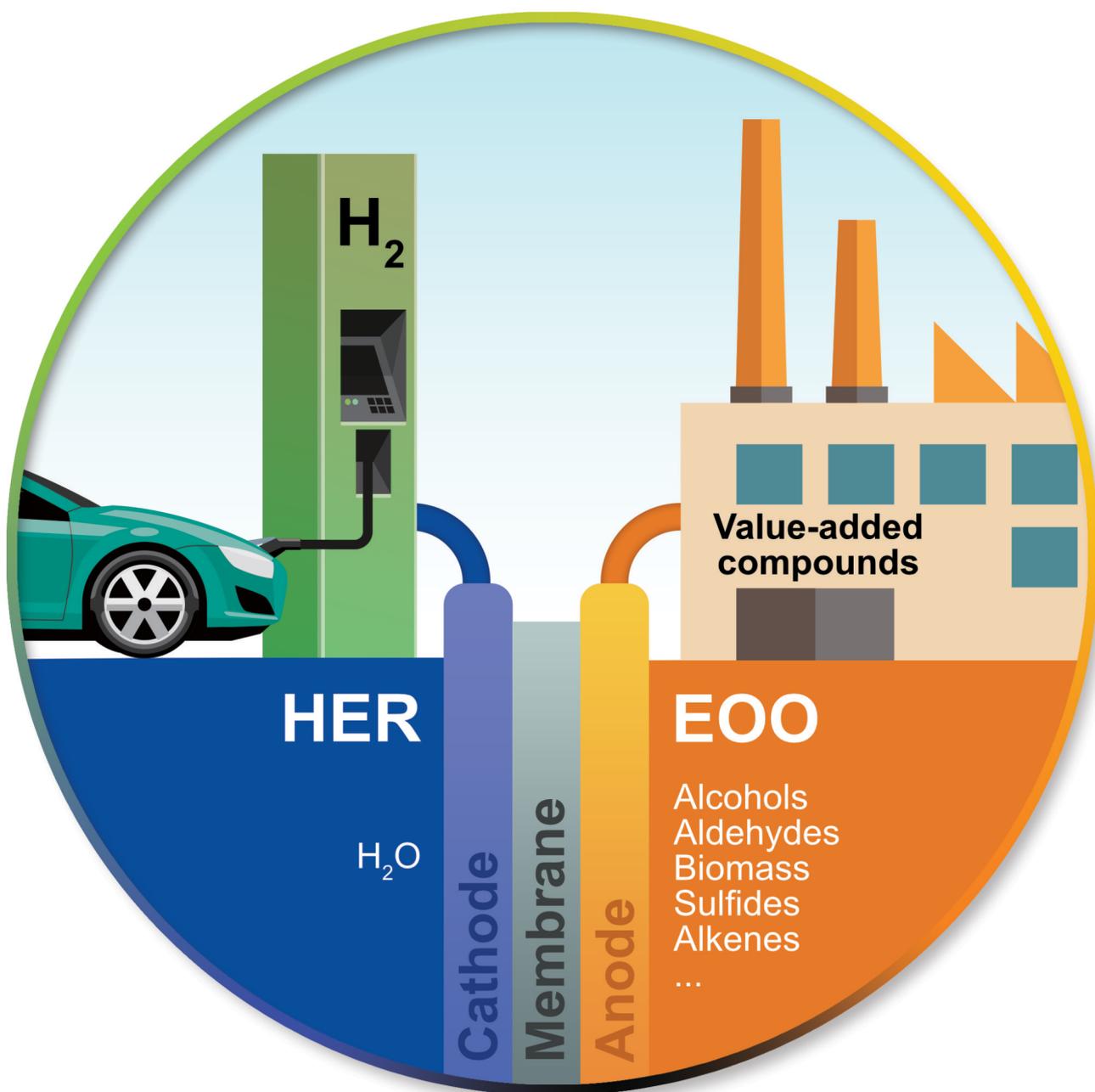
Abstract: The electrocatalytic splitting of water is recognized to be the most sustainable and clean technology for the production of hydrogen (H_2). Unfortunately, the efficiency is seriously restricted by the sluggish kinetics of the oxygen evolution reaction (OER) at the anode. In contrast to the OER, the electrooxidation of organic compounds (EOO) is more thermodynamically and kinetically favorable. Thus, the coupling of the EOO and hydrogen evolution reaction (HER) has emerged as an alternative route, as it can greatly improve the catalytic efficiency for the production of H_2. Simultaneously, value-added organic compounds can be generated on the anode through electrooxidation upgrading. In this Minireview, we highlight the latest progress and milestones in coupling the EOO with the HER. Emphasis is focused on the design of the anode catalyst, understanding the reaction mechanism, and the construction of the electrolyzer. Moreover, challenges and prospects are offered relating to the future development of this emerging technology.

1. Introduction

Growing environmental pollution and the energy crisis has raised great concerns about the exploitation of sustainable energy sources as feasible alternatives to traditional fossil fuels.[1,2] Molecular hydrogen (H_2) has been pursued as a prospective energy carrier, thanks to its high energy density and environmentally friendly properties.[3] Among various H_2 production technologies, electrocatalytic water splitting (e.g. the water electrolyzer) has emerged because of its low cost and zero-carbon emissions.[4,5] The overall water splitting (OWS) reaction in a water electrolyzer incorporates two half-cell reactions: the hydrogen evolution reaction (HER) on the cathode and the oxygen evolution reaction (OER) on the anode[6] (Figure 1a). The thermodynamic equilibrium potential for the HER ($2H^+/H_2$) and OER ($2H_2O/O_2$) is 0 and 1.23 V (vs. the reversible hydrogen electrode (RHE), respectively[7] (Figure 1b). Thus, a theoretical minimum voltage of 1.23 V is needed to promote the OWS. However, additional energy input and highly active electrocatalysts are needed to overcome the kinetic barrier for both the HER and OER. In particular, the extremely sluggish four-electron-transfer OER process on the anode seriously restricts the OWS efficiency,[8] thereby resulting in the need for a high voltage (e.g. >1.6 V) for realizing a meaningful production of H_2 (Figure 1b).

Recently, the electrooxidation of organic compounds (EOOs) has also attracted increasing attention.[9,10] It provides a sustainable pathway that utilizes electricity from renewable energy sources for chemical upgrading,[11] avoiding the use of organic solvents, homogeneous catalysts, and hazardous/poisonous strong oxidants (e.g. H_2O_2, 3-chloro-

perbenzoic acid, peroxy acids, oxone, or iodine) or even the elevated temperatures and pressures used in traditional organic oxidation reactions.[12] Importantly, the EOO is thermodynamically and kinetically favored over the OER, as it has a lower theoretical equilibrium potential (ca. 1.0 V_{RHE}). Thus, coupling the EOO and HER in a hybrid electrolyzer would undoubtedly lower the cell voltage for generating clean H_2 with less energy input. Importantly, value-added compounds can be simultaneously produced on the anode (Figure 1b,c), and these can be further utilized for chemical synthesis, polymer production, and pharmaceutical manufacturing. The last decade has witnessed significant progress in the coupling of the EOO and HER. However, the catalytic activities and cell configurations are still far from sufficient for practical applications.

In this Minireview, we do not intend to be exhaustive, but rather to highlight the latest accomplishments and landmarks in the strategy of integrating the EOO with the HER to realize effective chemical upgrading and H_2 generation. We place particular interest on the EOOs on the anode side, namely, alcohols, biomass-derived compounds (e.g. aldehydes), amines, nitro compounds, sulfides, and alkenes. In each section, key aspects of the catalysts, catalytic activity, structure–performance relationships, reaction mechanism, and electrolyzer configuration will be discussed. Additionally, challenges and perspectives for the future development of EOO-HER systems are provided. Our goal is to provide a state-of-the-art update on the development of efficient EOO-HER systems and to point out the potential of this attractive technology for the future upgrading of organic compounds and H_2 production.

2. Electrooxidation of Organic Compounds Coupled with Hydrogen Evolution

In the past decade, significant achievements have been made in investigating the HER on the cathode of water electrolyzers. By understanding the HER mechanisms and engineering the active sites, various electrocatalysts have been developed that show excellent HER activity comparable to the benchmark Pt/C material. To date, a number of excellent reviews on the HER have already been published, examining both the design of the electrocatalysts and their potential use in practical water electrolyzers.[13–17] Accordingly, in this Minireview, we mainly focus on the anode

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Figure 1. a) Schematic representation showing the water electrolyzer for the HER and OER. b) Schematic representation showing the potential ranges of the OER, EOO, and HER. c) Schematic illustration of the hybrid electrolyzer for coupling the EOO and HER.

electrooxidation reactions, including the reaction type, representative catalysts, catalytic performance, reaction mechanisms, and the construction of the electrolyzer.

2.1. Electrooxidation of Alcohols

Alcohol oxidation is an essential process for the synthesis of value-added aldehydes and organic acids. Coupling the electrooxidation of alcohols and the HER in a hybrid electrolyzer is a brilliant way to upgrade alcohols and simultaneously produce H_2.[18,19] In the last few years, the co-production of formate and H_2 from methanol and water was

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successfully realized in alkaline media. The typical electro-catalysts for the generation of formate on the anode include transition-metal-based materials, such as $Co_xP@NiCo$-LDH,[20] CNFs@NiSe,[21] $Co(OH)_2@HOS/CP$,[22] $Ni(OH)_2/NF$,[23] and NiIr-MOF/NF.[24] Similarly, when coupled with the HER, acetate[25]/ethyl acetate[26] from ethanol, acetone from 2-propanol,[27] benzaldehyde[28]/benzoic acid[29,30] from benzyl alcohol, glycolic acid from ethylene glycol,[31] acrylate from 1,3-propanediol,[32] glycerate/oxalate from glycerol,[33,34] gluconic acid/gluconolactone from glucose[35] and cyclohexanone from cyclohexanol[36] have also been achieved with good efficiencies.

2.2. Electrooxidation of Aldehydes

Aldehydes are also important precursors for the synthesis of valuable organic acids. In the past few decades, great efforts have been paid to convert biomass-derived (e.g. cellulose, hemicellulose, and lignin[37]) compounds containing –CH=O groups, namely, furfural (FUR) and 5-hydroxymethylfurfural (HMF). The oxidation upgrading of FUR and HMF is a sustainable path for the synthesis of valuable materials, solvents, and desired chemicals.[38] Compared to the thermocatalytic process using oxidants (e.g. O_2, H_2O_2)

and even high temperatures/pressures, electrooxidative conversion provides a clean pathway for FUR and HMF upgrading, particularly when coupled with the HER. In 2017, Sun and co-workers realized the electrocatalytic conversion of FUR and the HER using a cost-efficient bifunctional $Ni_2P/Ni/NF$ catalyst.[39] In 1.0 M KOH, the hybrid electrolyzer achieved nearly 100% Faraday efficiencies (FEs) and showed robust stability for the formation of 2-furoic acid and the production of H_2. Such a device needed a cell voltage of 1.48 V to afford a current density of $10\ mA\,cm^{-2}$, which is about 110 mV lower than that of pure OWS (1.59 V). Furthermore, maleic acid can also be produced from FUR on a PbO_2 anode, when coupled to the HER in acid solution (pH 1.0 H_2SO_4).[42]

2,5-Furandicarboxylic acid (FDCA) is one of the valuable products derived from the electrooxidation of HMF and can be used to produce important fine chemicals and polymers.[43] The oxidation of both the alcohol and the aldehyde group in HMF is the key to the generation of FDCA. Figure 2a displays two possible routes (route I and route II) for the formation of FDCA.[44] Route I begins the oxidation of the alcohol group with diformylfuran (DFF) as the first intermediate. Route II generates 5-hydroxymethyl-2-furancarboxylic acid (HMFCA) as the first intermediate by the oxidation of the aldehyde group. The formed DFF
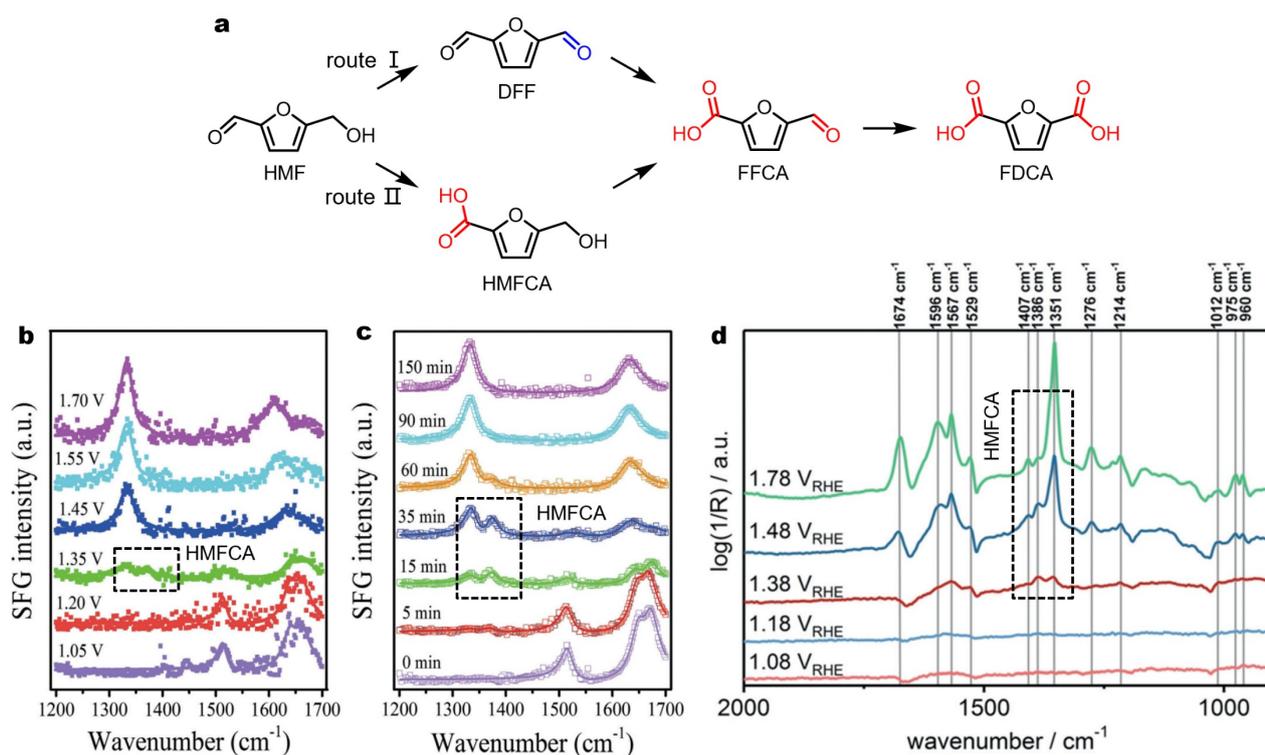
Figure 2. a) Two possible reaction routes of HMF oxidation. SFG spectra with ssp polarizations recorded at the $Ni_3N@C$ electrode/electrolyte interface b) after running the cell at different potentials for 90 min and c) by monitoring the reaction at different times at 1.45 V_{RHE}. The "ssp" indicates the polarization direction of the light source. The bands at about 1335 cm^{-1} and 1380 cm^{-1} indicate the formation of the HMFCA intermediate. Reproduced with permission.[40] Copyright 2019, Wiley-VCH. d) Operando ATR-FTIR spectra recorded at different applied potentials between 0.98 and 1.78 V_{RHE} after 20 min on a Ni_xB anode. The bands between 1335 cm^{-1} and 1400 cm^{-1} indicate that HMFCA is the intermediate. Reproduced with permission.[41] Copyright 2018, Wiley-VCH.

and HMFCA are then converted into 5-formyl-2-furancarboxylic acid (FFCA) and further to FDCA.[45] In 1997, Grabowski et al. reported the pioneering electrooxidation of HMF to FDCA on a nickel oxide/hydroxide anode.[46]

Since then, various electrocatalysts have been developed, such as, PdAu alloys,[47] Ni/Co/Fe-OOH,[48] defective CoO-CoSe$_2$,[49] CoP,[50] CuNi(OH)$_2$,[51] nanocrystalline Cu,[52] Ni NSs,[53] branched Ni NPs,[54] Ni$_x$B,[41] Ni$_2$P,[55] Ni$_3$S$_2$,[56] NiCo$_3$O$_4$ NWs,[57] mesostructured NiO,[58] NiFe-LDH,[59] NiCoFe-LDH,[60] Ni$_3$N@C,[40] MoO$_2$-FeP@C,[61] quinary (FeCrCoNiCu)$_3$O$_4$ NSs,[62] and Ir-Co$_3$O$_4$ (LDH = layered double hydroxide, NP = nanoparticle, NS = nanosheet, NW = nanowire).[63] In 1.0 M KOH, these materials revealed excellent electrocatalytic activity for the upgrading of HMF with high conversion ($\geq 98\%$), high selectivity ($\geq 99\%$), and a high FE ($\geq 95\%$) toward FDCA.[64] The active phase was generally recognized to be the in situ formed metal hydroxide/metal oxyhydroxide species. Using in situ sumfrequency generation (SFG) vibrational spectroscopy (Figure 2b,c), Wang and co-workers demonstrated that route II was the most likely way for the electrooxidation of HMF in a strong alkaline medium (e.g. pH higher than 13).[40] The same conclusion was also reached by utilizing operando electrochemistry coupled with attenuated total reflection infrared spectroscopy (EC-ATR-IR; Figure 2d)[41,65] and operando surface-enhanced Raman spectroscopy (SERS)[66–68] techniques. Furthermore, density functional theory (DFT) calculations were also used to simulate the reaction pathway.[69,70] However, the exact reaction mechanism/pathway still remains elusive, calling for more in situ/operando techniques and a detailed theoretical investigation (e.g. transition state, solvation effect). When coupled with the HER, FDCA and H$_2$ could be simultaneously produced on the anode and cathode, respectively.[71] Sun and co-workers integrated HMF conversion and H$_2$ evolution in 1.0 M KOH on bifunctional electrocatalysts, such as, CoP,[50] Ni$_2$P,[55] and Ni$_3$S$_2$,[56] thereby realizing the production of FDCA and H$_2$ with high FEs. Other bifunctional electrocatalysts, such as, CoNW/NF,[72] MoO$_2$-FeP@C,[61] NiSe@-NiO$_x$ NWs,[73] Cu$_x$S@NiCo-LDHs,[74] NF@Mo-Ni$_{0.85}$Se,[75] NiCo-LDH NiCo$_{NSs}$/Cu$_{NWs}$,[76] and Ni$_3$N@C[40] were also reported for the hybrid electrocatalysis. On the above representative electrocatalysts, the alcohol and aldehyde conversions typically follow the inner-sphere electrooxidation mechanism in alkaline media, where a strong interaction exists between the organic substrate and the electrode surface. The reactive oxygen species, adsorption of the substrate/intermediates, and reconstruction of the catalysts occur through the electrooxidation process.[77] Apart from inner-sphere electrooxidation, outer-sphere electrooxidation was also reported for alcohol/aldehyde conversion when using 2,2,6,6-tetramethylpiperidine-1-oxyl (TEMPO),[43] 4-acetamido-TEMPO (ACT),[78] polyoxometalates,[79] and metal ions[80] as redox mediators.

In 2021, Wang et al. successfully realized the low-potential electrooxidation of FUR and HMF at about 0.1 V$_{RHE}$ on a Cu catalyst.[81] In contrast to traditional aldehyde electrooxidation, where the H atom in the –CHO group is oxidized to H$_2$O at high potentials (> 1.0 V$_{RHE}$,

$3\,OH^- + R\text{–}CHO \rightleftharpoons 2\,H_2O + R\text{–}COO^- + 2\,e^-$), aldehyde oxidation at low potential combines the hydrogen atoms to generate H$_2$ gas ($2\,OH^- + R\text{–}CHO \rightleftharpoons 1/2\,H_2 + R\text{–}COO^- + H_2O + e^-$). When coupled with the HER, the assembled electrolyzer produced H$_2$ on both the cathode and the anode, with an apparent FE of about 200%. The energy input was about 0.35 kWh for 1 m^3 H$_2$ production, much lower than the 5 kWh for H$_2$ generation from conventional water electrolysis. In addition, 2-furoic acid or HMFCA was produced on the anode. This approch offers a promising avenue for hydrogen production with less electricity input. However, the catalytic performance of the low-potential electrooxidation of FUR and HMF is still insufficient, requiring further exploration of advanced catalysts.

2.3. Electrooxidation of Amines

The electrooxidation of amines can produce valuable imines, nitriles, amides, amine oxides, and azo compounds, which are widely applied in the syntheses of pharmaceuticals and agrochemicals.[82] In 2018, Zhang and co-workers coupled the electrooxidation of primary amines (–CH$_2$–NH$_2$) and the HER in a 1.0 M KOH solution (Figure 3a).[83] Different aromatic (3a–3d) and aliphatic (3e–3i) primary amines were electrooxidized into the corresponding nitriles (3a′–3i′) with excellent yields ($> 93\%$) and selectivity ($> 94\%$) on a NiSe nanorod array anode. Taking the conversion of benzylamine (BA, 3a) as an example, the electrooxidation of BA to benzyl nitrile (BN, 3a′) occurred at about 1.34 V$_{RHE}$, significantly lower than that of the OER (ca. 1.55 V$_{RHE}$). When employing NiSe as the anode for the conversion of BA and using CoP as the cathode for the HER, the as-assembled two-electrode electrolyzer achieved a
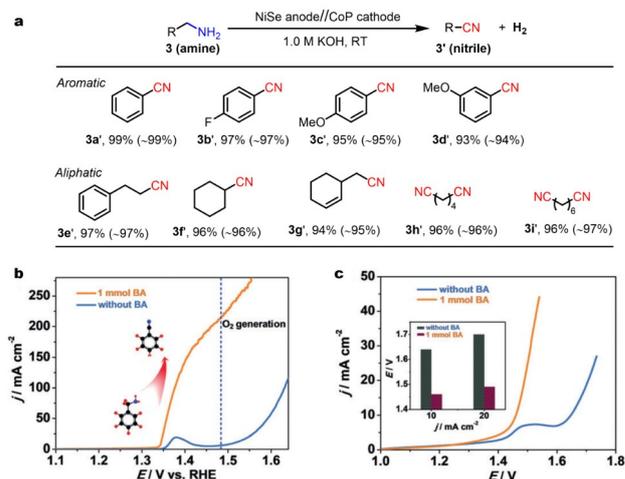
Figure 3. a) Coupling the electrooxidation of primary amines on a NiSe anode with the HER. b) LSV curves in 1.0 M KOH in the presence/absence of 1 mmol BA on the NiSe anode. c) LSV curves for the conversion of BA and the HER in a NiSe//CoP hybrid electrolyzer. The inset shows a comparison of the potentials for reaching current densities of 10 and 20 mA cm^{-2}. Reproduced with permission.[83] Copyright 2018, Wiley-VCH.

current density of $20\,\text{mA}\,\text{cm}^{-2}$ at only 1.59 V, much lower than the 1.70 V for the OWS. At 1.5 V, the FE for BN and H_2 was as high as 98 % and about 100 %, respectively. Recording the Raman spectra at different potentials uncovered that the in situ generated Ni^{II}/Ni^{III} sites on the NiSe acts as the redox-active species to facilitate the conversion of the primary amine to form nitriles. Later on, the Zhai research group reported the electrooxidation of propylamine on vacancy-rich $Ni(OH)_2$ atomic layers.[84] In a hybrid electrolyzer, propionitrile and H_2 were produced on the anode and cathode, respectively. Similar approaches were also reported by the groups of Huang, Yan, Mondal, and Xiong for amine upgrading and H_2 generation.[85–88]

2.4. Electrooxidation of Nitroalkanes

Conjugated nitroalkenes are important substrates in organic synthesis, because of the strong electron-withdrawing and coordinating ability of the nitro group.[89,90] In particular, conjugated nitroalkenes with an *E*-configuration (**4′**) act as the intermediates for the synthesis of important biologically active natural products and pharmaceuticals. Up to now, the main approaches for the synthesis of **4′** are nitration of the alkene by Henry condensation using organoselenides. However, such approaches often suffer from poor selectivity for **4′** and low yields for the reactions of nitroalkanes with ketones or aldehydes, as well as the harsh conditions with expensive reagents.[91] Recently, Zhang and co-workers realized the synthesis of **4′** by the electrooxidation of α-nitrotoluene (**4**) on NiSe nanorod arrays in an alkaline electrolyte.[92] A series of nitro compounds **4** with either electron-withdrawing or electron-donating functional groups on the aromatic ring can be converted into the related alkenes **4′** (**4a′–4j′**; Figure 4a) with high conversions (ca. 90 %) and selectivity (ca. 90 %) . Benefiting from the good HER activity of NiSe nanorod arrays, a hybrid electrolyzer using NiSe nanorod arrays as both the anode and cathode

was assembled to simultaneously produce **4′** and H_2. At 1.8 V, the FE for H_2 and the selectivity for **4a′** was as high as 100 % and 88 %, respectively (Figure 4b). In situ and ex situ experiments uncovered that the in situ formed NiOOH was the active component. At the same time, the adsorbed SeO_x^{2-} could promote the formation of **4′** by inhibiting the formation of the *Z*-isomer and other by-products (Figure 4c).

2.5. Semi-Dehydrogenation of Tetrahydroisoquinolines

Dihydroisoquinolines (DHIQs) exhibit various bioactivities towards tumor/fungal treatment, vasodilation, and nono-amine oxidase inhibition, thus suggesting potential utilization in disease treatment.[93] The catalytic dehydrogenation (oxidation) of 1,2,3,4-tetrahydroisoquinolines (THIOs) is an effective approach for producing DHIQs, but suffers from complete dehydrogenation during the formation of isoquinolines (IQs).[94] Furthermore, such dehydrogenations typically need noble-metal-based catalytic materials (e.g. Pd, Ir, or Ru) and often requires hazardous and toxic strong oxidants (e.g. $KMnO_4$, $NaIO_4$, $(KSO_3)_2NO$, and PhSSPh), thus limiting the safe and large-scale production of DHIQs.[95] In 2019, Zhang and co-workers reported the electrocatalytic semi-dehydrogenation (S-DHD) of THIQs (**5**) to synthesize DHIQs (**5′**) on a Ni_2P anode in alkaline solutions (Figure 5a).[96] In 1.0 M KOH, the THIQ electro-oxidation displayed faster kinetics than the OER. In a hybrid electrolyzer using Ni_2P as both the anode and cathode, the DHIQs and H_2 could be produced simultaneously with high activity and stability (Figure 5b,c). On the anode, the in situ formed Ni^{II}/Ni^{III} redox-active species are essential for the S-DHD of THIQs into DHIQs. The Ni_2P was the active component for the HER on the cathode. Similar results were also reported when using a Co_3O_4@NF anode and Pt cathode for THIQ upgrading and H_2 production.[97]

Figure 4. a) Coupling the selenite-promoted electrooxidation of α-nitro-toluenes to *E*-nitroethenes with the HER over a bifunctional NiSe nanorod arrays electrode. b) LSV curves for the conversion of α-nitrotoluene and the HER in a NiSe//NiSe hybride electrolyzer. c) Illustration of the reaction mechanism. Reproduced with permission.[92] Copyright 2021, Wiley-VCH.
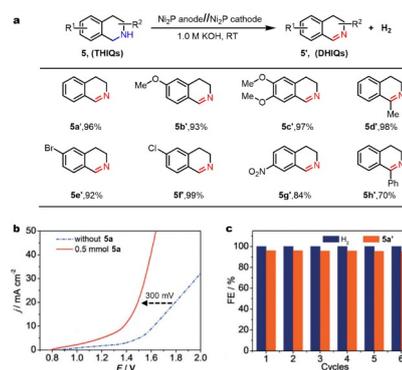
Figure 5. a) Coupling the electrooxidation of THIQs and the HER. The selectivity of the electrooxidation was not given. b) LSV curves over a Ni_2P/Ni_2P electrolyzer in 1.0 M KOH without and with 0.5 mmol **5a**. c) Cyclic FEs of a Ni_2P//Ni_2P electrolyzer for the production of **5a′** and H_2. Reproduced with permission.[96] Copyright 2019, Wiley-VCH.

2.6. Electrooxidation of Sulfides

Organic sulfoxides play prominent roles in medicinal chemistry, biological processes, and material science.[100] To date, the oxidation of sulfides is the main pathway for the synthesis of sulfoxides,[101] requiring strong oxidizing agents (e.g. iodine, H_2O_2, 3-chloroperbenzoic acid, or peroxy acids, oxone) and homogeneous catalysts (e.g. Fe- and Mn-containing materials) and bringing additional issues of toxicity, operationality, and the need to avoid the use of heavy metals from the standpoint of large-scale preparation. Recent studies demonstrated the successful electrooxidation of sulfides on Fe,[102] Ni[II] complexes,[103] graphite rods,[104] and CoFe-LDH[98] using water as the O source and MeCN as the solvent. On a CoFe-LDH/CC anode, different kinds of aryl, heteroaryl, and alkyl sulfides (**6a–6l**, left column of Figure 6a) could be selectively electrooxidized into the relevant sulfoxides (**6a′–6l′**) with high yields (85–96%) under ambient conditions. Importantly, such an approach was successfully expanded to the synthesis of complex pharmaceuticals with sulfoxide units, such as ricobendazole (**6m′**, 78%), omeprazole (**6n′**, 70%), sulindac (**6o′**, 63%), and the amino acid methionine (**6p′**, 89%), from the corresponding sulfides in excellent yields. Impressively, this method can be utilized in the large-scale synthesis of **6p′** (1.79 g) in high yield (86%), thus highlighting its potential use in pharmaceutically relevant sulfoxides. Synchronously, the H_2 was generated on the Pt cathode. Elementary studies imply that the in situ generated amorphous CoFe-oxyhydroxide serves as the active component for the selective electrooxidation of **6** to **6′** through a radical approach (Figure 6b). In 2021, Zhang and co-workers utilized Ni_2P hollow nanocubes as both the anode and cathode for the electrooxidation of sulfides to sulfoxides (**6a′**, **6b′**, **6i′**, and **6r′–6v′**, right column of Figure 6a) and H_2 production in a 1.0 M KOH solution.[99] They also unveiled that the in situ formed Ni[II]/Ni[III] sites were the active species and the oxidation followed a radical-mediated mechanism (Figure 6c).

2.7. Electrooxidation of Alkenes

Alkene oxidation is an effective approach for the synthesis of vicinal diols and epoxides, which are important intermediates in the fabrication of fine chemicals, food additives, perfumes, drug intermediates, and agrochemicals.[105] In 2020, the Sargent group coupled the electrooxidation of ethylene with H_2 production to realize the production of
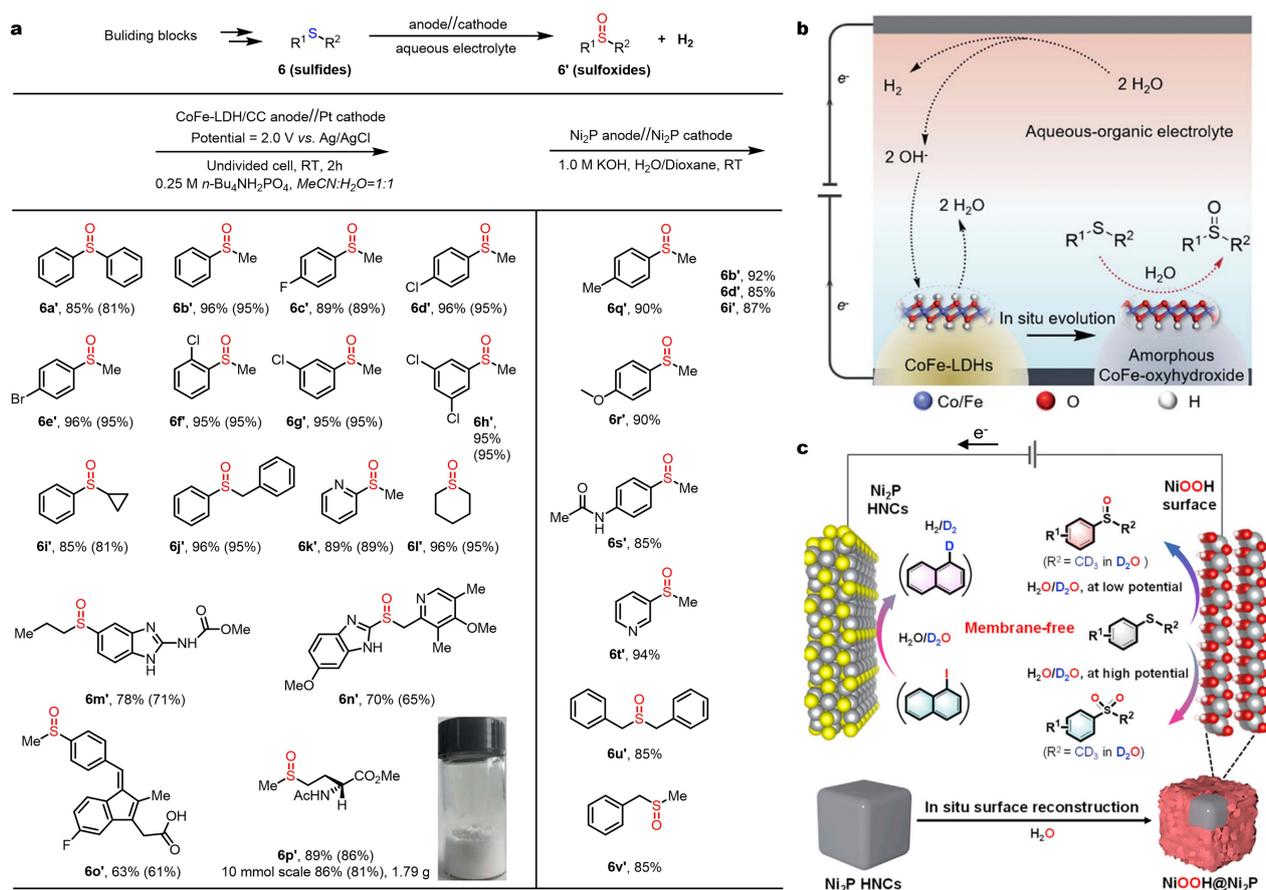
Figure 6. a) Coupling the electrooxidation of sulfides and the HER. b) Proposed reaction mechanism for the formation of sulfoxides and the HER in an aqueous organic electrolyte. Reproduced with permission.[98] Copyright 2021, Royal Society of Chemistry. c) Reaction mechanism for the selective electrooxidation of sulfides to sulfoxides and the HER on Ni_2P electrodes. Reproduced with permission.[99] Copyright 2021, Cell Press.

ethylene glycol on a gold-doped palladium nanostructured dendritic catalyst (PdAu-DNT) in aqueous 0.1 M NaClO$_4$ media (Figure 7a).[106] DFT calculations and experimental results demonstrated that Au doping could effectively regulate the OH bonding energy on Pd, thus promoting the formation of ethylene glycol. As a result, the best-performing PdAu-DNT with an Au doping of 3.2 at.% (3.2-PdAu-DNT) exhibited a FE of about 80% for the formation of ethylene glycol at a current density of about 5.7 mA cm^{-2}, which was much higher than that of Pd-DNT (ca. 60%; Figure 7b). Furthermore, the 3.2-PdAu-DNT revealed excellent stability for 100 hours at 1.1 V$_{Ag/AgCl}$. Simultaneously, valuable H$_2$ was produced on the Pt foil cathode. In 2019, Manthiram et al. demonstrated the successful integration of the electrocatalytic epoxidation of cyclooctene with the HER by using Mn$_3$O$_4$ as the anode material and Pt as the cathode material (Figure 7c).[107] Isotopic investigation and product analysis indicated the overall reaction consisted of the conversion of cyclooctene and water into cyclooctene oxide and hydrogen, respectively. The FE for the HER on the Pt cathode was as high as 94%. In contrast, the FE for the epoxidation of cyclooctene on an Mn$_3$O$_4$ anode was only about 30%, probably because of the uncontrolled overoxidation and OER at higher potentials. Later in 2020, the

Sargent group achieved the selective partial oxidation of ethylene for the formation of ethylene oxide in a 1.0 M KCl aqueous solution.[108] The key idea was to utilize Cl$^-$ as a redox mediator at the anode (Figure 7d). First, the Cl$^-$ was oxidized to Cl$_2$ at the Pt anode. Second, the Cl$_2$ disproportionated to form HOCl and HCl. Third, the HOCl reacted with ethylene to form ethylene chlorohydrin (HOCH$_2$CH$_2$Cl). After electrolysis, the pH value of the anolyte was acidic. On the cathode, the H$_2$ was generated and the catholyte became alkaline. After mixing the catholyte and anolyte output streams, ethylene oxide was generated from the HOCH$_2$CH$_2$Cl and OH$^-$. Furthermore, the HCl formed was also neutralized by OH$^-$. At 300–800 mA cm^{-2}, the FEs for the production of ethylene oxide were all >70%. This approach offers a smart way for the synthesis of epoxides by the oxidation of alkenes, while preventing overoxidation and the OER.

3. Conclusion and Perspectives

This Minireview summarizes the recent development of pairing the electrooxidation of organic compounds and hydrogen evolution in a hybrid water electrolyzer. The
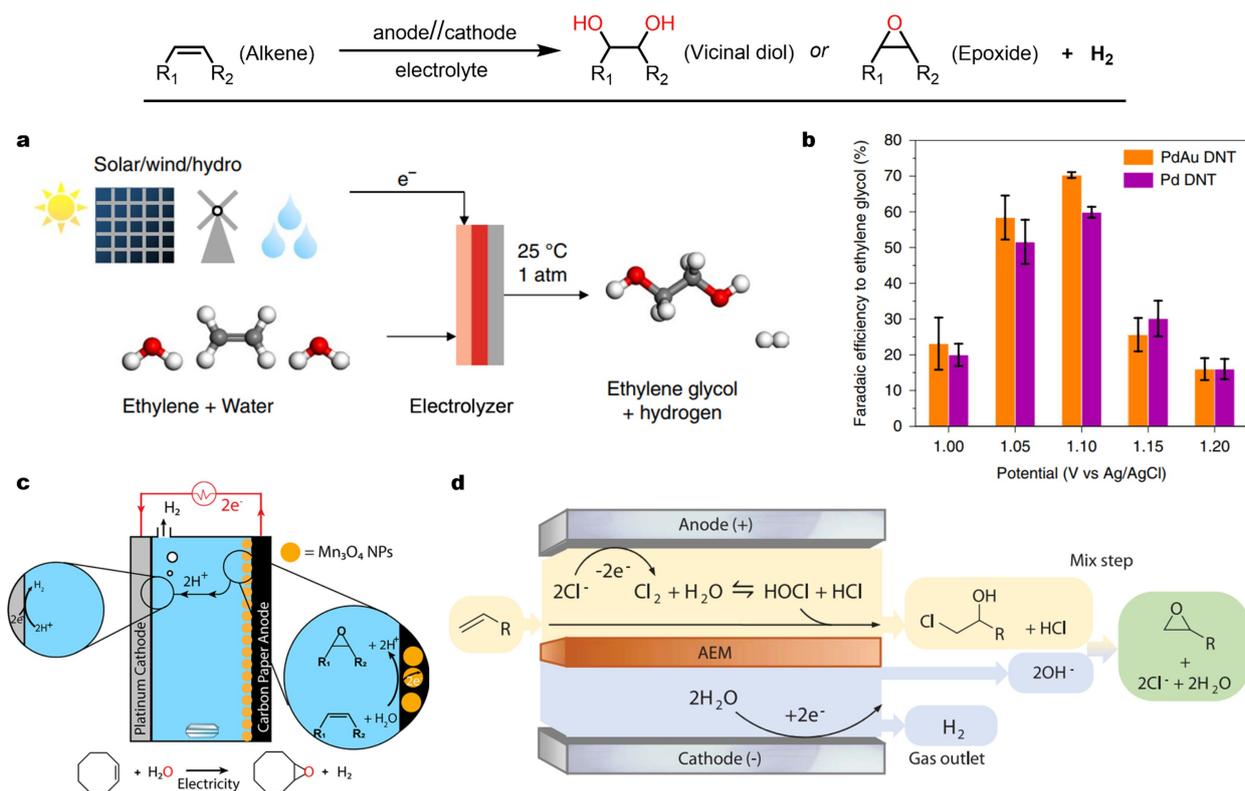
Figure 7. Coupling the electrooxidation of alkenes and the HER. a) Integrating the reaction of ethylene to ethylene glycol with the HER. b) FEs for the formation of ethylene glycol with PdAu DNT and Pd DNT at different potentials. Reproduced with permission.[106] Copyright 2020, Nature Publishing Group. c) Pairing the epoxidation of cyclooctene and the HER. Reproduced with permission.[107] Copyright 2019, American Chemical Society. d) Paired system for the electrochemical reaction of ethylene to ethylene oxide and the HER. Reproduced with permission.[108] Copyright 2020, American Association for the Advancement of Science.

typical electrooxidation reactions, including of alcohols, aldehydes, biomass, amines, nitro compounds, sulfides, and alkenes were examined. This fascinating synthetic strategy opens a sustainable approach for upgrading organic compounds on the anode. At the same time, renewable H_2 gas is produced more effectively on the cathode. Table 1 summa-

Table 1: Electrocatalytic performance of recently reported representative EOO electrocatalysts and EOO-HER systems.

Reaction type	Anode catalyst	Organic substrate	Concentration in electrolyte	Product	3-electrode system		2-electrode cell		Ref.
					E_{OER} at j_{10}[a] [V_{RHE}]	E_{EOO} at j_{10} [V_{RHE}]	$V_{OER-HER}$ at j_{10} [V]	$V_{EOO-HER}$ at j_{10} [V]	
alcohol oxidation	Co$_x$P@NiCo-LDH	methanol	0.5 M in 1.0 M KOH	formate	–	1.24	ca. 1.70	1.43	[20]
	Co(OH)$_2$@HOS	methanol	3.0 M in 1.0 M KOH	formate	1.571	1.385	1.631	1.497	[22]
	Co$_3$O$_4$ NSs	ethanol	1.0 M in 1.0 M KOH	ethyl acetate	1.50	1.445	–	–	[26]
	Rh nanosheets	2-propanol	1.0 M in 1.0 M KOH	acetone	1.61	0.233	ca. 1.8	0.4	[27]
	NC@CuCo$_2$N$_x$	benzyl alcohol	15 mM in 1.0 M KOH	benzaldehyde	1.46	1.25	1.62	1.56	[28]
	Mo–Ni alloy NP	benzyl alcohol	10 mM in 1.0 M KOH	benzoic acid	1.49	1.345	1.49	1.38	[29]
	PdAg	ethylene glycol	1 M in 0.5 M KOH	glycolic acid	1.55	0.57		1.02 at j_{20}	[31]
	MoO$_x$/Pt	glycerol	0.1 M in 1.0 M KOH	glycerate	–	–	1.6	0.7	[33]
	Co–Ni alloy	glucose	0.1 M in 1.0 M KOH	gluconic acid/gluconolactone	–	–	1.65	1.39	[35]
	Co$_2$(OH)$_3$Cl/FeOOH	cyclohexanol	2 mmol in 1.0 M KOH	cyclohexanone	–	–	1.56	1.46	[36]
	Ni$_3$S$_2$	furfuryl alcohol	10 mM in 1.0 M KOH	2-furoic acid	ca. 1.50 (onset)	ca. 1.35 (onset)	–	–	[56]
aldehyde oxidation	Ni$_2$P/Ni	FUR	30 mM in 1.0 M KOH	2-furoic acid	1.55 (onset)	1.34 (onset)	1.59	1.48	[39]
	PbO$_2$	FUR	10 mM in pH 1.0 H$_2$SO$_4$	maleic acid	1.85 (onset)	1.60 (onset)	–	–	[42]
	Ni$_2$P NPs	HMF	10 mM in 1.0 M KOH	FDCA	ca. 1.50 (onset)	ca. 1.35 (onset)	1.65	1.44	[55]
	CoNW	HMF	10 mM in 1.0 M KOH	FDCA	1.563	1.311	1.866	1.504 (0.1 M HMF)	[72]
	MoO$_2$–FeP@C	HMF	10 mM in 1.0 M KOH	FDCA	1.474	1.359	1.592	1.486	[61]
	Ni$_3$N@C	HMF	10 mM in 1.0 M KOH	FDCA	1.60 at j_{50}	1.38 at j_{50}	1.79 at j_{50}	1.55 at j_{50}	[40]
	(FeCrCoNiCu)$_3$O$_4$ NSs	HMF	50 mM in 1.0 M KOH	FDCA	1.50 (onset)	1.35 (onset)	–	–	[62]
amine oxidation	NiSe	benzylamine (**3a**)	1 mmol in 1.0 M KOH	benzyl nitrile (**3a′**)	1.48 (onset)	1.34 (onset)	1.70 at j_{20}	1.49 at j_{20}	[83]
	Ni–Ni$_3$N	benzylamine (**3a**)	2 mmol in 1.0 M KOH	benzyl nitrile (**3a′**)	1.60	1.35	ca. 1.55	1.4	[85]
	VP–Ni(OH)$_2$ NSs	propylamine	10 mmol 1.0 M KOH	propionitrile	ca. 1.53	1.36	1.74	1.48	[84]
nitroalkane oxidation	NiSe nanorods	α-nitrotoluene (**4a**)	0.4 mmol in 1.0 M KOH	*E*-nitroethene (**4a′**)	–	–	1.69	1.36	[92]
S-DHD of THIQ	Ni$_2$P	1,2,3,4-tetrahydroisoquinoline (**5a**)	0.5 mmol in 1.0 M KOH	3,4-dihydroisoquinoline (**5a′**)	ca. 1.48 (onset)	ca. 1.10 (onset)	ca. 1.62	ca. 1.35	[96]
	Co$_3$O$_4$ nanoribbon	**5a**	20 mM in 1.0 M KOH	**5a′**	ca. 1.48 (onset)	ca. 1.30 (onset)	1.620	1.446	[97]
sulfide oxidation	CoFe-LDH	diphenyl sulfide (**6a**)	0.25 M in MeCN/H$_2$O	diphenyl sulfoxide (**6a′**)	1.90 $V_{Ag/AgCl}$ at j_5	1.39 $V_{Ag/AgCl}$ at j_5	-	-	[98]

[a] j_{10}: current density at 10 mA cm^{-2}.

rizes representative examples of coupling the EOO and HER on various electrocatalysts. Clearly, this coupling process greatly lowers the cell voltage for water splitting and greatly improves the H_2 production. Despite the superior advantages of such a coupling approach and the enormous recent progress that has been made, the coupling technology is just at an early stage and the transformation efficiency is still unsatisfactory. Thus, the reasonable design of high-performance electrodes, insightful identification of active sites, and intelligent construction of the electrolyzer is highly necessary for future practical impartments in industry. Regarding the future direction relating to the integration of the EOO and HER, we provide our perspectives as follows:

1) Electrode materials are always prerequisite for promoting the electrooxidative transformation of organic compounds. Exploring effective electrode materials by active-site design and morphology engineering is essential for boosting the reaction kinetics and facilitating the reaction. Furthermore, a deep understanding of the reaction mechanism is indispensable for exploring more advanced catalysts. To achieve this goal, cutting-edge in situ methods are required to supplement existing techniques, such as in situ X-ray absorption fine structure (XAFS), in situ X-ray powder diffraction (XRD), in situ Raman spectroscopy, and in situ Fourier-transform infrared spectroscopy (FTIR) to identify the true active sites at the atomic level and to monitor the key intermediates. The in-depth identification of the active sites and understanding of the structure–property relationships can, thus, instruct the further smart design of effective materials. Furthermore, machine learning by DFT calculations can be another powerful technique for the discovery of electrocatalysts. The new mechanistic insights gained will then serve as feedback for knowledge-guided reactions and catalyst optimization. Moreover, the development of bifunctional materials based on earth-abundant elements for hybrid water electrolyzers is highly desirable for cost reduction and practical applications.

2) To date, most electrooxidation reactions have worked only in alkaline media (e,g. 1.0 M KOH; Table 1). However, the HER process is kinetically more sluggish in alkaline media than in acid media. Integration of the electrooxidation reaction with the HER in an acidic electrolyzer will be more energy-efficient. Hence, it is highly desirable to explore electrocatalysts for electrooxidation reactions with good activity, selectivity, and stability in acidic environments.

3) It is necessary to develop new electrooxidation reactions, such as, biomass upgrading, removal of industrial organic pollutants, and waste plastic reforming. In particular, the effective electrooxidation of organic pollutants offers a clean pathway for removing hazards and even for upgrading. The pairing of the pollutant electrooxidation and the HER will clearly provide a sustainable approach for the production of chemicals and the purification of water from industrial wastes.

4) Compared with the splitting of pure water, the splitting of seawater for H_2 production is more cost-effective without desalination/purification units.[109] However, the splitting of seawater is seriously limited by the chloride evolution reaction (ClER) occurring at the anode, which competes with the OER and generates unfavorable chlorine and/or hypochlorite that will corrode the catalysts, membranes, and other components over time. The EOO occurs at a lower potential than the OER and ClER.[110] Thus, coupling the EOO with HER could enable seawater electrolysis to proceed at a high current density without the interfering ClER, thereby making it more promising for the large-scale green production of hydrogen.

5) In terms of scale-up, feasibility investigations, including laboratory prototypes and pilot plants for industrial applicability, are essential for commercialization. This needs close cooperation between the chemists and engineers to optimize the catalytic performance by placing a particular emphasis on the catalyst development and electrolyzer design. The flow cell could be a good option, as it can supply enough substrate to the catalyst layer and promote mass transfer. Furthermore, the long-term operational stability of the catalyst, reaction activity and selectivity, and downstream separation, as well as purification issues need further consideration and improvement. The economics (e.g. energy cost) of any coupled process also requires careful consideration.

In summary, coupling the electrooxidation of organic compounds and hydrogen evolution can provide a sustainable and economic pathway for chemical upgrading and hydrogen production. It is expected that, through further electrode development and electrolyzer design, this appealing technology will be used in practical chemical manufacturing.

Acknowledgements

Conflict of Interest

The authors declare no conflict of interest.

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Minireviews

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Upgrading Organic Compounds through the Coupling of Electrooxidation with Hydrogen Evolution
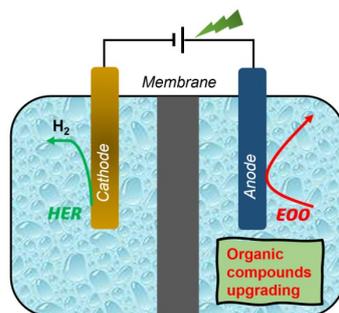
This Minireview summarizes the latest achievements and milestones in coupling the electrooxidation of organic compounds and the hydrogen evolution in a hybrid water electrolyzer. Emphasis is placed on exploiting the anode reaction and the design of the electrocatalyst. Prospects for the future development of this coupling technology and its potential implementation in practical organic synthesis and hydrogen production are also provided.