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Review

Electrocatalytic Production of a Liquid Organic Hydrogen Carrier with Anodic Valorization of the Process: Review and Outlook

Published as part of Energy & Fuels special issue "Novel Routes to Green Hydrogen Production in Europe".

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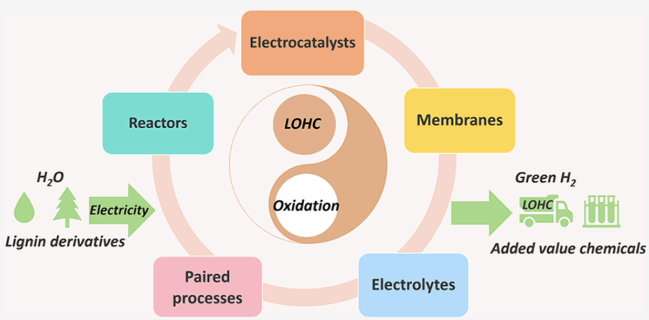
ABSTRACT: Green hydrogen plays a crucial role in decarbonization and the future of low-carbon society. Still, its transport/distribution and cost of production, mainly realized by electrolysis, are major hurdles. Liquid H_2 carriers reduce transport/distribution costs but add further expenses for their production. To address this challenge, we proposed a novel strategy for electrocatalytic production of a liquid organic hydrogen carrier with anodic valorization of the process. This review summarizes the state of the art and outlooks in this new concept. The electrocatalytic process is briefly introduced, and the main components are discussed. Subsequently, the electrocatalytic production of liquid organic hydrogen carriers and anodic oxidation from components to processes, together with the paired processes and reactors, are analyzed, highlighting challenges and prospects.



1. INTRODUCTION

Hydrogen (H_2) is a key component in the global strategy for decarbonization,[1] especially in the energy sector, where it serves as an energy carrier to facilitate the penetration of a higher share of intermittent renewable energy and the decarbonization of hard-to-abate industrial sectors. Meanwhile, H_2 is an important feedstock with already a worldwide production of nearly 100 Mtons, although made from fossil fuels (so-called gray H_2).[2,3] Green H_2, produced mainly by electrolysis, covers only about 1% of the world's production, even with increasing interest.

Being important in cross-sectorial coupling, linking power, gas, and other energy vectors or energy-intensive commodities and replacing them in their respective usages,[4] substituting gray with green H_2 and expanding the use of H_2 are current major worldwide objectives. However, the substitution is contrasted by two key issues: (i) the very intensive electrical energy demand (>50 kWh/kg of H_2) to produce green H_2[5] and (ii) the cost/energy for transporting/distributing as well as storing gaseous H_2.[6−8] Liquid H_2 carriers can greatly improve the latter aspects, with an impact also on the former, because these H_2 carriers allow the production of H_2 in remote areas where renewable electrical energy is available at low costs. Liquid organic hydrogen carriers (LOHCs)[9−11] are among the most intensively developed H_2 carriers. The hydrogenation-dehydrogenation of LOHC, typically organics containing multiple aromatic groups, is commonly realized by heterogeneous catalysis, with H_2 produced by electrolysis using renewable electrical energy. There is a rising interest in electrocatalytic processes to produce LOHC[12] to further decrease the carbon footprint. However, the typical anodic reaction is the oxygen evolution reaction (OER), which has main drawbacks: (i) a slugging kinetic requiring high overpotentials and thus decreasing energy efficiency and increasing costs and (ii) the production of O_2, which in most of the applications does not find onsite utilization.

Substituting OER with a reaction of oxidation leading to added-value chemicals could improve energy efficiency[4] and rate while at the same time lowering costs by selling the product.[13] In other words, realizing the electrocatalytic regeneration of LOHC in a device with the coupled valorization of the anodic reaction can (i) intensify the process and energy efficiency and (ii) reduce the costs, making the use

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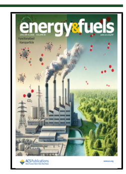

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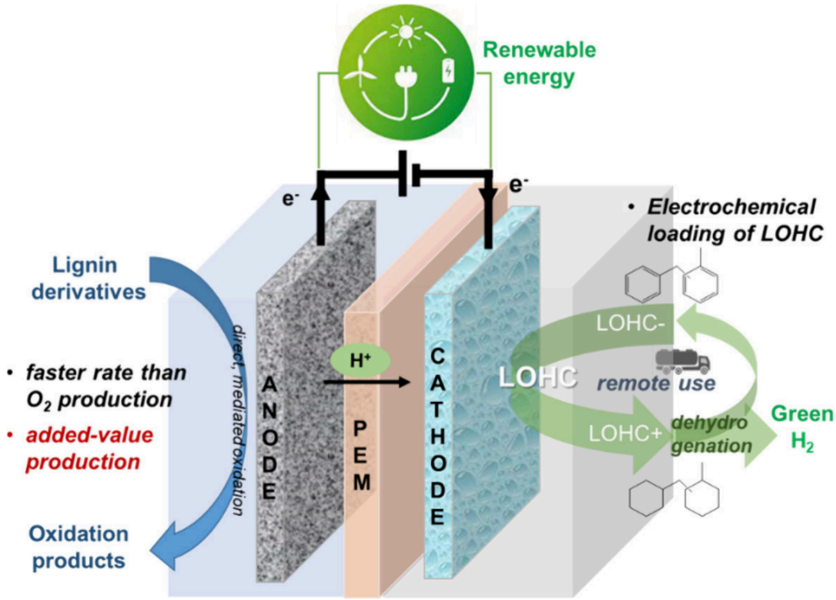

Figure 1. Framework on the electrocatalytic production of LOHC with anodic valorization.

of LOHC more competitive. In addition, it offers benefits of linking sections, such as biorefinery and H_2 economy, that lead to further synergies and potential benefits. The ongoing EU project EPOCH (grant 101070976) is exploring these aspects. The schematic illustration of the electrocatalytic device at the core of this project is presented in Figure 1.[14]

Figure 1 shows that the objectives of this project are to (i) integrate the step of electrocatalytic production of H_2 at the cathode side with the regeneration by hydrogenation of the LOHC carrier and (ii) valorize the anodic reaction by producing added-value chemicals. The benefits are the reduction in the cost and energy needs (by process intensification and reducing losses associated with OER), creating a value link between biorefineries and the green H_2 world that offers further potential synergies.

The performance of the proposed concept depends greatly upon the catalysts, membranes, and electrolytes. Even though the concept was newly proposed, its core of electrocatalytic conversion, together with the related components (catalysts, membranes, and electrolytes), has been widely studied.[15−17] Meanwhile, the proposed concept shows similarities with other processes, including electrocatalytic production of LOHC, anodic oxidation, and the combined processes (H_2 production with anodic valorization and anodic oxidation with H_2 co-production). Therefore, analyzing these aspects and providing insight into the similarities and differences as well as information for further performance comparison are essential. A brief introduction to state of the art based on the previously published reviews, listed in Table 1, is described below.

In summary, briefly, (a) LOHC is an active topic of discussion. Since 2020, 6 reviews have been published from the aspects of innovative LOHCs,[18] mechanism,[19] research progress,[20] and scientific limits and challenges.[21] To the best of our knowledge, only one review summarized the research on the electrocatalytic conversion of aromatic-based LOHCs.[12] (b) Electrocatalysis is a topic of large interest as a key technology toward low-carbon production,[24−26] while fewer studies deal with aspects more closely related to those presented in the scheme reported in Figure 1, such as advanced catalysts,[16] alloy-derived electrocatalysts,[27] earth-abundant amorphous-metal-based catalysts,[28] those based transition metal nitrides,[29] iron oxyhydroxide,[30] graphdiyne[31] as well as catalysts specifically for LOHCs.[22,23] In contrast, no specific reviews on electrocatalysts have been published that are linked directly to the process presented in Figure 1. (c) Membranes and electrolytes, in addition to electrocatalysts/electrode and device aspects mentioned above, are also important elements of electrocatalytic devices. For the membranes, the research work has been reviewed for proton-exchange membranes in electrolysis technology[17] and water electrolysis.[32] In contrast, the membrane research aspects directly related to coupling electrocatalytic regeneration of LOCH with anode valorization are not present in the literature, and, to the best of our knowledge, only one review is available, focusing specifically on electrolytes but in relation to aluminum electrolysis.[15] (d) In terms of the general concept associated with Figure 1, four reviews analyze (i) the combining of H_2 production and organic oxidation,[36] (ii) the coupling between the production of valuable chemicals at both anode and cathode,[33] (iii) paired electrolysis of biomass-derived compounds toward co-generation of value-added chemicals and fuels,[34] and (iv) the coupling of value-added anodic reactions with electrocatalytic CO_2 reduction.[35] In summary, very limited reviews are available to discuss the coupling process and related technology aspects of the process outlined in Figure 1.

Thus, the state-of-the-art field in terms of reviews is not exhaustive, and the brief analysis above remarks the need to review the research progress related to the electrocatalytic production of liquid organic hydrogen carriers with anodic valorization of the process, especially considering the importance of green hydrogen production and the novelty of the proposed concept and strategy. To discuss this field, we first briefly introduce the technology and the main components. Then, the electrocatalytic production of LOHC and the anodic oxidation are discussed, along with the paired processes and reactor type. The challenges and prospects in the various sections are discussed.

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Table 1. Related Reviews in Recent Years

article	topic	year
D'Ambra et al.[18]	reviewed LOHC and discussed the potential reactivities to design innovative LOHCs	2023
Valentini et al.[19]	summarized the mechanism of the hydrogen-transfer process of different LOHCs	2022
Rao et al.[20]	discussed the ideal LOHCs and reviewed the progress in developing LOHCs together with the catalytic approach	2020
Clematis et al.[21]	provided scientific limits and challenges from a system-level perspective for LOHC	2023
Katarína et al.[22]	summarized the novel catalysts for dibenzyltoluene as a potential LOHC	2021
Yang et al.[23]	summarized N-heterocycles as LOHC and their hydrogenation/dehydrogenation catalysts	2024
Gabriele et al.[24]	summarized the catalysis for an electrified chemical production	2023
Georgia et al.[25]	discussed the catalysis for e-chemistry: need and gaps for a future defossilized chemical production	2022
Siglinda et al.[26]	discussed the role of electrocatalysis in solar-driven chemistry	2019
Lebedeva et al.[12]	summarized the research on the electrocatalytic conversion of aromatic-based LOHCs	2023
Zeng et al.[16]	summarized the advanced catalysts for electrocatalytic hydrogeneration of organics in aqueous conditions	2023
Guo et al.[27]	reviewed alloy-derived electrocatalysts for 5-hydroxymethylfurfural toward 2,5-furandicarboxylic acid	2022
Chen et al.[28]	summarized the earth-abundant amorphous metal-based catalysts for the electrooxidation of small molecules	2023
Meng et al.[29]	reviewed the electrocatalytic applications of electrocatalysts based on transition metal nitrides	2022
Guo et al.[30]	reviewed the electrocatalytic applications of electrocatalysts based on iron oxyhydroxide	2023
Cui et al.[31]	reviewed the electrocatalytic applications of electrocatalysts based on graphdiyne	2020
Ayers et al.[17]	reviewed the proton-exchange membranes in electrolysis technology	2019
Feng et al.[32]	reviewed the proton-exchange membranes in water electrolysis	2017
Li et al.[33]	analyzed the coupling between the production of valuable chemicals at both anode and cathode	2021
Liu et al.[34]	reviewed the paired electrolysis of biomass-derived compounds toward co-generation of value-added chemicals and fuels	2021
Xu et al.[35]	reviewed the coupling value-added anodic reactions with electrocatalytic CO_2 reduction	2023
Chen et al.[36]	review of coupled electrochemical hydrogen production and organic oxidation for low energy consumption	2023

2. CONCISE INTRODUCTION TO THE ELECTROCATALYTIC TECHNOLOGY

Electrocatalytic processes represent complex multiphase chemical reactions that involve electron transfer steps at the electrode−solution interface. These reactions are influenced by a wide range of factors, including the temperature, pressure, solution medium, condition of the solid surface, and mass transfer conditions. Additionally, the influence of the double-layer structure at the electrode−solution interface, which affects the distribution of ions and potential near the electrodes, is a crucial factor in electrocatalytic processes. A defining characteristic of electrocatalysis is its involvement of multiple consecutive steps that produce chemically adsorbed intermediates on the electrode surface. These steps are essential for a variety of important electrode reactions, which include both the generation and degradation of molecules.

Electrocatalysis can be broadly categorized into two main functional areas: (i) formation of chemically adsorbed intermediates and (ii) chemical adsorption and transformation. In the formation of chemically adsorbed intermediates, ions or molecules engage in electron transfer steps on the electrode surface to form chemically adsorbed intermediates. These intermediates then convert into stable molecules through heterogeneous chemical reactions or chemical desorption processes, exemplified by the hydrogen evolution reaction (HER) and OER. For the chemical adsorption and transformation, reactants initially undergo chemical adsorption on the electrode surface via either dissociative or associative pathways. These adsorbed reactants then participate in subsequent electron transfers or engage in surface chemical reactions, such as formate electrooxidation.[37]

The main advantage of electrocatalysis is the ability to effectively modify the energy dynamics of the reaction system by adjusting the electronic field that forms between the electrode surface and the electrolyte solution at the interface. By controlling this field, electrocatalysts can lower activation energy barriers, stabilize reaction intermediates, and direct reaction pathways, thereby enhancing the efficiency and selectivity of electrochemical reactions. This modification is crucial for controlling the direction and rate of chemical reactions under the ambient conditions of temperature and pressure. Moreover, electrocatalysis can alter reaction pathways through interactions between the reactants and electrocatalysts, with changes in activation energy playing a key role in either accelerating or decelerating the reaction rates.[37]

As shown in Figure 1, the process of interest involves the electrocatalytic treatments of organic molecules, i.e., those for the electrocatalytic hydrogenation of LOHCs and the electrochemical oxidation of organics. The electrocatalytic developments in these reactions are briefly introduced below, together with the main components needed in the processes.

2.1. Reactions.

2.1.1. Electrocatalytic Hydrogenation (ECH). Electrochemical hydrogenation is carried out using two distinct mechanisms, each defined by specific pathways for electron and proton transfer.[38] The initial pathway involves direct electro-reduction (DER), where electrons are first transferred from the organic substrate to the working electrode surface, succeeded by a protonation phase in an aqueous solution, with water serving as the source of protons.[39] Another method is ECH, where protons are first adsorbed on the surface of the working electrode, followed by the adsorption of the organic material, and accompanied by electron transformation through the Volmer reaction process.[40] For the hydrogenation electrolysis in aqueous solutions, DER, HER, and ECH compete with each other, affecting the overall faradaic efficiency. Therefore, precise control of the reaction process is crucial to maximize the target reactions and enhance the efficiency and effectiveness of the electrolysis process.[40]

2.1.2. Electrocatalytic Oxidation. In the electrochemical oxidation processes, there are two main types: direct and indirect oxidations.[41] During direct anodic oxidation, the process primarily involves electron transfer, with molecules being directly oxidized by electrons after their adsorption onto the anode surface. Therefore, this process is largely governed by the transport of molecules and the electron transfer rate at the electrode/solution interface. Generally, the oxidation of molecules is theoretically possible at a potential that is less positive than that required for OER. However, this process frequently leads to electrode fouling due to the formation of polymer layers on the electrode surface, resulting in poor chemical decontamination efficiency and reducing the service life of the anode materials.[42] Indirect electrochemical oxidation occurs with the additional generation of intermediate oxidizing species during the reaction, known as physisorbed "active oxygen" (adsorbed hydroxyl radicals) or chemisorbed "active oxygen" (oxygen within the lattice of metal oxide anodes). These oxidizing species exhibit very high oxidative activity, which is particularly effective against organic compounds.[43] In fact, both direct and indirect oxidations typically coexist in practical electrochemical oxidation systems, and consequently, optimizing and controlling these two processes is especially crucial for effective utilization.

2.2. Main Device Components. To accomplish the electrocatalytic hydrogenation and oxidation reactions, electrodes/catalysts (anodes and cathodes), membranes, and electrolyte solutions are needed as the main components (Figure 1). They are briefly introduced below. Currently, the understanding of both electrochemical hydrogenation and oxidation processes is still unsatisfactory. The reaction kinetics for these types of reactions are still very slow. In the future, gaining a deeper understanding of these reactions, increasing the reaction rate, the efficiency of electrolytic cells, and the activity of catalysts, together with electrolytes and membranes, will be crucial.

2.2.1. Electrocatalysts for Cathode. Electrochemical catalysts play a critical role in determining the effectiveness of ECH.[16,44−46] The catalysts can generally be categorized into noble and non-noble metal types.[47,48] Noble metal catalysts, such as platinum,[49,50] palladium,[51,52] rhodium, and ruthenium,[53,54] are recognized for their remarkable catalytic properties and stability under various reaction conditions. Conversely, non-noble metal catalysts like nickel,[52,55] copper,[56,57] cobalt,[58] and iron[59] present a viable alternative due to their abundance, lower cost, and satisfactory catalytic performance. However, their amount is typically up to 2 orders of magnitude higher in weight compared to noble-metal-based catalysts to have comparable performances.

Nickel- and copper-based catalysts have remarkable hydrogenation activity,[60,61] especially when enhanced through alloy formation or nanostructuring, leading to improved performance in electrocatalytic applications. Cobalt catalysts are also promising,[62] particularly when used in alloyed forms, to enhance stability and activity. Iron-based catalysts,[63] noted for their environmentally favorable characteristics, contribute to the growing interest in sustainable catalytic systems. In addition to metal catalysts, metal oxides and hydroxides have gained increasing attention for their unique electronic and structural properties that facilitate efficient electrochemical reactions. These materials often demonstrate excellent catalytic activity and can be tailored through doping or composting with other materials to improve their performance in the ECH processes.

Carbon-based materials, such as graphene, carbon nanotubes (CNTs), and doped carbon, have shown promise as metal-free catalysts[64,65] in ECH due to their excellent conductivity, abundant active sites, and cost-effectiveness. Doping graphene with nitrogen or phosphorus enhances its hydrogen adsorption capacity and catalytic activity. CNTs, known for their mechanical strength, can be optimized by controlling their physical properties and combining them with functional materials. Additionally, emerging metal-free catalysts like boron−nitrogen co-doped carbon (BCN)[66] and phosphides[67] exhibit unique electronic structures that enhance their efficiency in hydrogenation reactions, making them viable for industrial applications.

2.2.2. Electrocatalysts for Anode. The development and design of electrocatalysts for the electrocatalytic oxidation of lignin-derived molecules primarily focus on the complete oxidation of these compounds, especially in wastewater treatment applications. Extensive research has explored various transition metals (such as platinum, nickel, and cobalt) as well as commonly used electrodes like PbO_2,[68,69] demonstrating significant advancements in this field. However, for the catalysts such as RuO_2-IrO_2[70] and SnO_2[71] showing excellent performance in electrooxidation, issues like catalyst deactivation and the formation of complex product mixtures that are difficult to separate are still prevalent. Moreover, there is a notable lack of systematic studies and established design criteria for tailoring catalysts to specific target molecules. In addition, a general concern is their cost of manufacture.

To develop new anode catalysts for effective electrochemical activity while achieving selective catalysis, thereby enhancing the efficiency of organic oxidation processes with cost-effective solutions, hydroxide-related catalysts, particularly layered double hydroxides (LDHs),[72] have demonstrated considerable potential in improving reaction selectivity, yield, and stability. To realize efficient electrooxidation catalysts, various optimization strategies targeting active sites have been investigated,[28,73] such as enhancing the electronic structure of active sites through heterojunction construction, vacancy engineering, and defect engineering. On the other hand, TiO_2[74,75] and boron-doped diamond (BDD)[76,77] have also exhibited good activity in phenol electrooxidation, with various modified materials continually emerging, including studies on the support materials used for TiO_2.

2.2.3. Membranes. In an electrolysis process, the role of the membrane is to isolate the anode and cathode as well as enable ions to travel through it. Because of the second function, they are named polymer electrolyte membranes.[78] They typically consist of hydrophobic long-chain backbone and hydrophilic ion exchange groups on the main or side chains. Cation-exchange membranes contain negatively charged species such as sulfonic acid groups ($-SO_3^-$), whereas anion-exchange membranes have positively charged species like ammonium ($-NH_3^+$) groups to enable selective transportation of the charged species.[79] Bipolar membranes, on the other hand, are made of cation and anion exchange layers that enable the electro-dissociation of water into protons (H^+) and hydroxide ions (OH^-) at the interface.[80] These relatively new membranes create an acidic and alkaline environment on the cathode and anode sides of the electrolyzer.[81]

2.2.4. Electrolyte Solutions. In the process of electrocatalytic production of LOHC and anodic oxidation valorization, the electrolyte plays a promoting role in effective ion transport and reactant solubilization. Therefore, selecting an appropriate electrolyte is crucial for enhancing the reaction efficiency, product selectivity, and yield.[82] First, the electrolyte needs to have a high solubility for the organic substrate to encounter the electrolyte and then undergo electrocatalytic conversion. An ideal electrolyte should also have high electrical conductivity to effectively shuttle charges between the electrodes, thereby facilitating the electrocatalytic reactions. In addition, the electrolyte needs to remain stable during the electrocatalytic process and not react with the reactants or products. It is also necessary to consider environmental friendliness and the recyclable use of electrolytes, as well as avoid the use of toxic substances.[83] In general, the electrolytes can be classified as inorganic electrolytes (such as H_2SO_4, HCl,

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Table 2. Comparison of LOHC Compounds, Including Toluene/Methylcyclohexane, Benzyltoluene (H0-BT/H12-BT), and Dibenzyltoluene (H0-DBT/H18-DBT)[a]

	MCH/TOL		H12-BT/H0-BT		H18-DBT/H0-DBT	
molecular formula	C_7H_{14}	C_7H_8	$C_{14}H_{26}$	$C_{14}H_{14}$	$C_{21}H_{38}$	$C_{21}H_{20}$
H_2 storage density at 20 °C (kg of H_2 m^{-3})	47.4	0	54.5	0	57.2	0
molecular weight (g mol^{-1})	98.189	92.141	194.357	182.261	290.54	272.384
isomeric peaks in GC	1	1	6	3	>20	>12
GHS labels	2, 7, 8, and 9	2, 7, and 8	7 and 8	7, 8, and 9	na	8 and 9
maximum diameter of the molecules (nm)	0.60	<0.60	1.15	<1.15	1.5	<1.5
phase at 290 °C and 3 bar_{abs}	vapor	vapor	liquid	liquid	liquid	liquid
dynamic viscosity at 20 °C (mPa s)	0.5	0.6	7	4	49	424
melting point at atm (°C)	−126	−95	from −80 to 70	−30	< −50	−34
boiling point at atm (°C)	101	111	264−272	277−290	≈371	≈392
density at 20 °C (kg m^{-3})	770	870	876	996	913	1044
$\Delta_r H^0$ at 25 °C per mole of H_2 (kJ mol^{-1})	+68.3	−68.3	+63.5	−63.5	+65.4	−65.4

[a]This table was reproduced with permission from ref 88. Copyright 2022 Royal Society of Chemistry.

NaOH, and KOH), organic electrolytes (acetonitrile and dimethylformamide), and novel electrolytes, including ionic liquids.[83]

3. ELECTROCATALYTIC REGENERATION OF LOHC BY HYDROGENATION

3.1. LOHC. Hydrogen is considered a green energy and fuel carrier, while in general, it is challenging to store and transport hydrogen itself. The LOHC concept ensures safe transport and long-term storage of these secondary energy sources. LOHC, mostly hydrocarbons, chemically stores hydrogen to be transported and stored safely at room temperature. It is mostly fuel-like and can be integrated into the existing fuel infrastructure with slight modifications without building a completely new one. In addition, LOHC does not pose a higher risk potential than known fuels.[11] Compared to other storage media, such as *n*-ethyl-carbazole, toluene, dibenzyl toluene, ammonia, and methanol, LOHCs can be used multiple times like aromatics (closed systems), instead of only once (MeOH, NH_3, etc.).[84]

In the past, aromatic systems had proven to be particularly promising, with the simplest representative being benzene/cyclohexane, followed by toluene/methylcyclohexane, benzyltoluene/perhydro-benzyltoluene and dibenzyltoluene/perhydro-dibenzyltoluene. Other multi-ring systems include decalin/naphthalene, biphenyl/bicyclohexyl, etc. A detailed overview of all possible LOHCs can be found in the review by Gébel et al.[84] The aromatic toluene, benzyltoluene, and dibenzyltoluene are the most studied, and their properties are listed in Table 2. In general, the hydrogen storage capacities of these LOHCs are 6−8 wt %, and the storage can be achieved at ambient temperature and pressure in highly stable forms. These LOHCs also possess high volumetric hydrogen storage density (>50 g_{H_2}/L) compared to the compressed hydrogen gas (20−30 g_{H_2}/L).[85,86]

For a desirable LOHC that can be used in a hydrogen circular economy, besides the high storage density, there are other important requirements, which are summarized below:[87]

- High volumetric storage density and excellent reversibility.
- High productivity (H_2 release capacity or H_2 storage capacity) with high selectivity in the hydrogenation and/or dehydrogenation of LOHC under technically reasonable conditions.
- High thermal and chemical stability as well as low loss during storage and transport.
- Good handling in LOHC logistics (a wide liquid range) and low viscosity of the hydrogen-rich and -poor LOHC forms (even at winter temperatures in the global north).
- High safety of LOHC logistics (low or non-flammability) and low to moderate toxicity.
- Commercial availability on a large scale and at low costs.
- Low effort for integrating the LOHC into the existing infrastructure.

The first three criteria mentioned above are often considered for the suitability of hydrocarbon-containing substances as LOHCs. In contrast, good manageability in logistics and commercial availability can be crucial for the successful market entry of the selected LOHCs.[87,89]

Three LOHCs meet all critical criteria. The first one is toluene, which can be produced in large quantities by petroleum refineries and is cost-effective. The Japanese company Chiyoda Corporation has rewarded this LOHC concept, and, in collaboration with other partners, it has demonstrated the feasibility of the first transport route via Brunei to Japan.[90] Dibenzyltoluene and benzyl-toluene are the other two, which are also commercially available. Both are known as a typical thermal oil (MARLOTHERM), and their production could be ramped up for LOHC uses. In addition, industrial development by the German company Hydrogenious LOHC Technologies pushes the commercialization of benzyl-toluene as the hydrogen carrier, and several projects have been implemented to demonstrate the feasibility of this LOHC technology.[87,90]

However, these three LOHCs possess some drawbacks. One concern is related to the stability of LOHCs after several cycles of hydrogenation/dehydrogenation due to unwanted side reactions.[91] Developing more selective catalysts and improving process implementation are currently being investigated, and attempts to reduce the use of expensive and rare catalysts containing precious metals are also being made.[92] Another concern is that LOHC is currently produced from the petroleum refining processes. It is worth mentioning that it is possible to produce the LOHCs mentioned above from renewable raw materials like (hemi)cellulose and lignin. Bio-based toluene is already commercially available (e.g., BioBTX B.V.), although still in small quantities, and it can be gradually introduced into the fossil-based LOHC system.[93−95]

3.2. Introduction to the Electrocatalytic Hydrogenation. Electrocatalytic hydrogenation (ECH) is an innovative process that uses electrical energy to drive the reduction of organic molecules (e.g., LOHCs), including biomolecules, in the presence of a catalyst. This method offers a promising alternative to traditional thermal catalytic hydrogenation by operating under milder conditions and enabling the utilization of "green hydrogen" generated by electrolysis.[96] This process is also valuable in converting biomass-derived compounds into fuels and chemicals, thereby contributing to sustainable energy solutions. By leveraging renewable electricity, ECH can potentially lower carbon emissions and improve energy efficiency, making it a critical technology in transitioning to a green economy.

Biomass-based molecules are a rich source of complex organic compounds that can be converted into high-value products through reactions such as hydrogenation or used as LOHC substrates. Traditionally, catalytic hydrogenation of such molecules requires high hydrogen pressures (80−200 bar) and elevated temperatures (250−450 °C),[97] and such harsh reaction conditions are energy-intensive and costly. ECH offers a promising alternative by utilizing electrical energy and green hydrogen under mild conditions, significantly reducing the severity of reaction parameters (Table 3, taking furfural hydrogenation as an example). ECH not only enhances the efficiency and selectivity of biomolecule conversion but also aligns with sustainable energy practices. By lowering the operational pressures and temperatures, ECH can potentially make the production of LOHCs more economically viable and environmentally friendly.

Table 3. Comparison of Electrocatalytic Hydrogenation and Thermocatalytic Hydrogenation of Furfural to Furfural Alcohol

factor	electrocatalytic hydrogenation[61,98,99]	thermocatalytic hydrogenation[100−103]
temperature	20−60 °C	120−180 °C
pressure	ambient	10−50 bar
energy source	electricity (potentially renewable)	high heat, usually fossil fuel based
hydrogen requirement	none (uses protons from electrolyte)	pure H_2 gas (at high pressure)
environmental impact	lower CO_2 emissions (if renewable powered)	higher CO_2 emissions (fossil fuel heat)
catalyst durability	high durability (Cu and Ni catalysts at mild conditions)	moderate (Pd and Pt can degrade at high temperatures)
safety	lower risks (ambient pressure, no H_2 gas)	higher risks (high pressure, H_2 gas handling)

3.3. Catalysts for ECH of Biomolecules. As mentioned in section 3.1, bio-based LOHCs are valuable directions. Here, we thus comment on recent results in the ECH of biomolecules beyond their use as LOHCs to provide a wider view of the topic.

3.3.1. Supported Nanoparticles Based on Noble Metals.

3.3.1.1. Platinum-Based Catalysts. Platinum-based catalysts are widely used in ECH due to their exceptional catalytic activity and stability. Platinum has excellent hydrogen adsorption and desorption capabilities, making it an efficient catalyst. In the ECH process, platinum catalysts can effectively facilitate the generation and transfer of hydrogen atoms, enabling the hydrogenation of organic molecules.

Although Pt electrodes exhibit excellent activity for producing H_{ad} (adsorbed hydrogen species) from water decomposition, their high selectivity for H_2 formation at low potentials limits their application in the ECH of aldehydes. Optimizing the binding energy between the metal catalyst and the reactants is necessary to enhance ECH efficiency. Lopez-Ruiz and colleagues,[104] based on the Sabatier principle, discovered that the reduction rate of the carbonyl group in aldehydes is related to the binding energy between the aldehyde and metal. Specifically, weak binding hinders the adsorption of reactants, while strong binding inhibits the desorption of products.[105]

ECH exhibits significant sensitivity to the structure of Pt. Bondue and colleagues[106] reported that the crystalline surface of the Pt catalyst influences the ECH reaction pathway of acetone. As shown in Figure 2, the hydrogenation of $*CH_3COCH_3$ to form $*CH_3HCOHCH_3$ is more favorable on Pt(110) and Pt(553) surfaces, leading to the production of 2-propanol. However, on the Pt(510) surface, the C−O bond cleavage to form $*CH_3CCH_3$ and OH is preferential to the hydrogenation of $*CH_3COCH_3$, resulting in the formation of propane. Additionally, acetone does not adsorb on the Pt(111) surface, leading to low ECH activity.

The surface reaction rate is proportional to the coverage of the reactants on the catalyst surface, which necessitates strong substrate adsorption by the catalyst. The application of platinum-group metals with high hydrogenation activity in phenol ECH has been studied. Song et al.[107] investigated the phenol ECH on Pt/C, Rh/C, and Pd/C, finding that Rh/C exhibited the highest hydrogenation rate, followed by Pt/C.

Currently, the high cost and limited supply of platinum restrict its large-scale application. Therefore, researchers are not only focused on developing efficient platinum-based catalysts but also exploring strategies to reduce platinum usage through alloying or nanostructuring.[108]

3.3.1.2. Palladium-Based Catalysts. Palladium-based catalysts exhibit excellent catalytic activity in ECH, particularly in selective hydrogenation reactions. The d-electron structure of palladium favors the adsorption of hydrogen molecules and promotes their dissociation, generating active hydrogen atoms. Palladium catalysts demonstrate high selectivity and activity in the hydrogenation of aromatic compounds and unsaturated organic molecules.

Lopez-Ruiz et al.[104] investigated the Pd catalysts that exhibit the highest turnover frequency (TOF) for the reduction of benzaldehyde and furfural, as they have the optimal interaction strength with these compounds (Figure 3).

Chen et al.[109] used Pd supported on carbon felt as an effective catalyst for the ECH of cinnamaldehyde (CAL), achieving a total faradaic efficiency (FE) of 87.54%. Villalba et al.[110] revealed that acetophenone and benzophenone could be converted into 1-phenylethanol, ethylbenzene, diphenylmethanol, and diphenylmethane through ECH on the Pd electrode.

Similar to platinum-based catalysts, the cost and resource scarcity of palladium-based catalysts also limit their application. However, it is possible to reduce costs while maintaining catalytic activity by alloying palladium with other metals, such as silver or copper. Peng et al.[111] synthesized bimetallic $Ag_{32}Pd_{68}$ nanoparticles, achieving a removal rate of approximately 88% for 2,4-DCP. The optimal incorporation of Ag not only enhanced the adsorption of H* atoms on the catalyst surface but also facilitated the desorption of the formed phenol. Similarly, Chen et al.[112] designed bimetallic Pd−Au

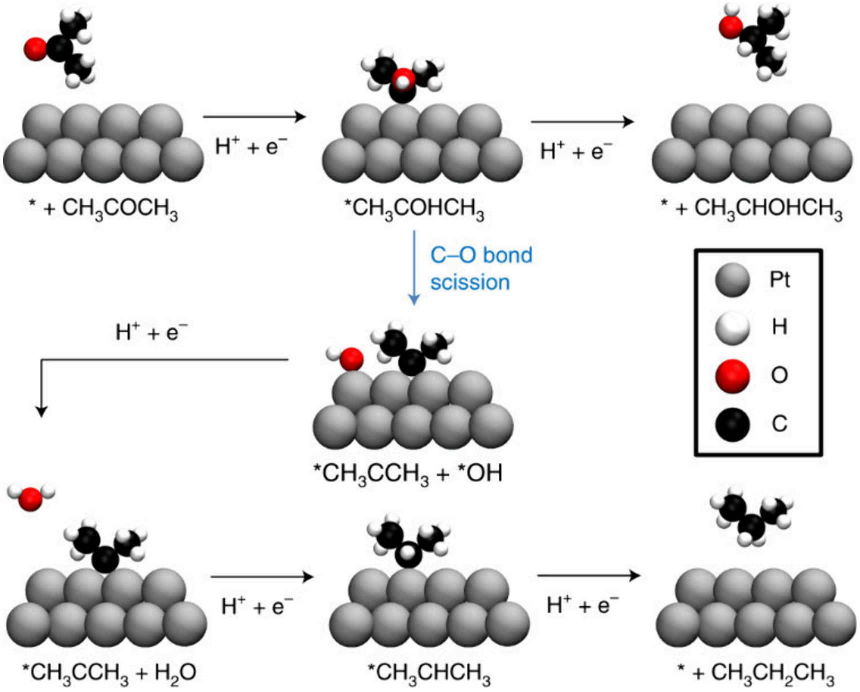

Figure 2. Reaction pathway of acetone. This figure was reproduced with permission from ref 106. Copyright 2019 Springer Nature.

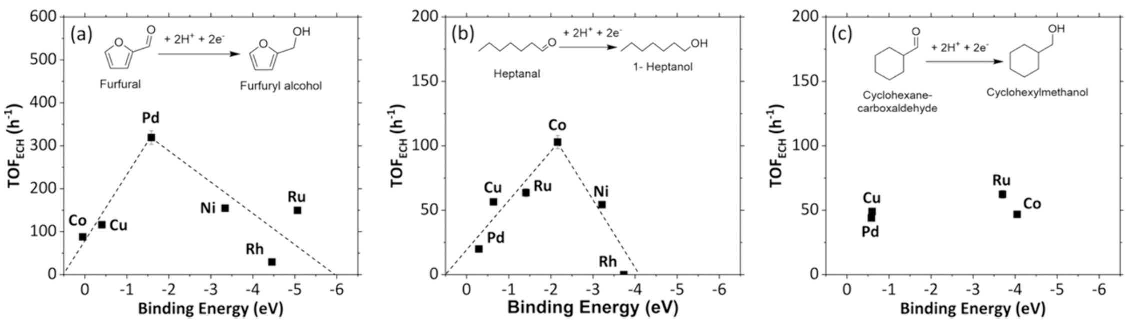

Figure 3. ECH of aldehydes. This figure was reproduced with permission from ref 104. Copyright 2019 American Chemical Society.

alloy nanoparticles as electrocatalysts for the electrochemical hydrodechlorination (EHDC) of 4-chlorophenol, achieving an EHDC efficiency of up to 98.35%. Zhou et al.[113] fabricated $CuPd_{0.021}$ bimetallic electrocatalysts for ECH of furfural to 2-methylfuran with a high FE of 75%.

3.3.1.3. Other Noble Metals (e.g., Rh and Ru). In addition to platinum and palladium, noble metals such as ruthenium (Ru) and rhodium (Rh) have also been applied in ECH. Ruthenium-based catalysts have attracted attention for their high catalytic activity under mild conditions, particularly demonstrating good selectivity in hydrogenation reactions in aqueous solutions.

Abdel-Mageed et al.[114] found that the Ru catalysts exhibit poor selectivity for CO methanation in CO_2-rich reformate gas with low CO content. However, when a high amount of H_2O is present in the gas feed, the selectivity of Ru catalysts significantly increases, reaching up to 100%.[114] Ruthenium also has good sulfur tolerance, which gives it a significant advantage in hydrogenation reactions involving sulfur-containing compounds. Wang et al.[115] found that sulfur vacancies on the surface of Ru clusters bind with thiophene and, in a quasi-equilibrium step, activate H_2 and H_2S, forming intermediates that participate in kinetically relevant hydrogenation and H-assisted C–S bond cleavage reactions. The turnover rates for desulfurization and hydrogenation increase with larger cluster sizes because sulfur atoms bind more weakly to larger Ru metal clusters, resulting in a greater number of sulfur vacancies during steady-state catalysis.

Rhodium catalysts are renowned for their high selectivity in the hydrogenation of nitrogen-containing heterocycles and alkenes in ECH reactions, making them valuable for applications in fine chemicals and pharmaceutical synthesis.

Overall, despite the excellent performance and selectivity of noble metal catalysts in ECH, their high cost and scarcity have driven researchers to continuously explore new materials and technologies to reduce reliance on these precious metals and enable broader applications.

3.3.2. Supported Nanoparticles Based on Non-noble Metals. 3.3.2.1. Nickel-Based Catalysts. Nickel-based catalysts have garnered significant attention in ECH due to their cost-effectiveness, abundance, and excellent catalytic activity, especially in hydrogen evolution reactions (HER). Nickel's ability to efficiently adsorb hydrogen atoms and facilitate electron transfer makes it a promising alternative to noble metal catalysts. The d-electron configuration of nickel allows

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for effective hydrogen adsorption and activation, which is crucial in the ECH processes.

Recent research has focused on enhancing the performance of nickel catalysts through alloying and nanostructuring. Nickel alloys, such as Ni−Mo, Ni−Fe, and Ni−Co, have demonstrated superior catalytic activities due to synergistic effects between nickel and the alloying metals.[116,117] For instance, Ni−Mo alloys show enhanced hydrogen evolution activity due to the modification of the electronic structure and the creation of additional active sites. Similarly, Ni−Fe and Ni−Co alloys improve the catalytic efficiency by altering the binding energy of hydrogen on the catalyst surface, thereby optimizing the reaction kinetics.

Nanostructuring nickel-based catalysts, including the creation of nanoparticles, nanowires, and nanosheets, significantly increases the surface area and the density of active sites. This morphological control not only enhances the catalyst's intrinsic activity but also improves its stability under operational conditions. Chen et al.[118] designed Ni nanosheets exhibiting excellent catalytic performance due to their high surface area and favorable electronic properties. Additionally, core−shell structures, where nickel is coated with another material (e.g., carbon or metal oxides), have been developed to improve both the activity and durability of the catalyst.[119]

Despite these advancements, nickel-based catalysts face challenges such as surface oxidation, which can lead to decreased catalytic activity over time. Strategies to mitigate this include surface passivation, the use of protective layers, and the development of nickel-based composites that maintain high activity while preventing oxidation. Furthermore, the selectivity of nickel catalysts in complex organic transformations remains a critical area of research, with ongoing efforts to tailor the electronic and geometric properties of these catalysts to achieve high selectivity.

3.3.2.2. Cobalt-Based Catalysts. Cobalt-based catalysts are another class of non-noble metal catalysts that have shown promise in ECH due to their robust catalytic activity and relatively low cost. Cobalt's ability to interact strongly with hydrogen allows it to effectively catalyze the hydrogenation reactions, making it a suitable candidate for replacing noble metals in various applications.

Cobalt catalysts are often employed in the form of alloys (e.g., Co−P, Co−S, and Co−Ni) or as part of composite materials to enhance their catalytic properties.[120,121] Co−P catalysts have been widely studied for their ability to efficiently catalyze hydrogen evolution, with phosphorus playing a crucial role in modifying the electronic structure of cobalt to improve its activity. Han et al.[122] prepared Co−S catalysts with excellent conductivity and catalytic activity, particularly in the acidic and neutral media. These materials not only exhibit high catalytic efficiency but also show good stability under operating conditions, making them viable for long-term use in ECH.

Nanostructured cobalt catalysts, including nanoparticles, nanowires, and nanosheets, have been developed to maximize surface area and active site density, thereby enhancing catalytic performance. Nanoparticles have demonstrated significant promise in ECH due to their high surface area and the presence of multiple oxidation states that facilitate various catalytic pathways.[123]

One of the significant advantages of cobalt-based catalysts is their versatility in catalyzing a broad range of hydrogenation reactions, including those involving complex organic molecules. However, cobalt catalysts are not without challenges. Issues such as catalyst poisoning, deactivation over time, and the formation of inactive phases under specific reaction conditions need to be addressed. Ongoing research focuses on developing more stable cobalt-based catalysts through surface modification, alloying, and the use of stabilizing agents that can prevent catalyst deactivation.

3.3.2.3. Iron-Based Catalysts. Iron-based catalysts have emerged as an attractive alternative in ECH due to their abundance, low cost, and environmentally benign nature. As one of the most abundant transition metals, iron presents a sustainable option for large-scale catalytic processes. Iron-based catalysts such as Fe−N−C, Fe_3O_4, and FeS_2 have shown notable activity and selectivity in hydrogenation reactions.[124−126]

The catalytic performance of iron-based materials is often enhanced through doping or surface modification. Li et al.[126] revealed that nitrogen-doped iron catalysts (Fe−N−C) have demonstrated exceptional HER activity, attributed to the introduction of active sites that facilitate hydrogen adsorption and activation. These catalysts have shown stability across a range of pH conditions, making them versatile for various ECH applications.

Moreover, the combination of iron with other metals, such as cobalt or nickel, has been explored to create bimetallic catalysts with improved performance. Fe−Ni catalysts exhibit enhanced catalytic activity due to synergistic effects that optimize electronic properties and promote efficient hydrogenation pathways. Additionally, iron-based catalysts have been incorporated into composite materials with carbon or metal oxides[127,128] to enhance their stability and activity further.

3.3.3. Metal Oxides and Hydroxides. Metal oxides and hydroxides have gained significant attention as electrocatalysts for hydrogenation reactions due to their unique structural and electronic properties. These materials are characterized by their ability to undergo reversible redox reactions, making them highly effective in catalyzing electrochemical processes. Metal oxides such as titanium dioxide (TiO_2), nickel oxide (NiO), and cobalt oxide (Co_3O_4) are commonly used in ECH due to their stability, abundance, and ability to promote HER.[129−131] Nevertheless, a general aspect often underestimated is that these materials are poorly conductive, while this is a requirement for electrocatalysis. Thus, improving conductivity by either introducing elements facilitating electron transport (for example, carbon nanofibers) or modifying the material to improve electron conductivity (by doping, for example) is critical. In addition, measuring the electrocatalytically active surface area is fundamental, but it is often not made.

TiO_2 is a widely studied metal oxide catalyst due to its excellent chemical stability. It is often used in conjunction with other metals or dopants to enhance its catalytic activity. Zhang and co-workers[132] synthesized TiO_2 doped with nitrogen or carbon to improve conductivity and HER activity. Similarly, NiO and Co_3O_4 are known for their high catalytic efficiency in HER, particularly when combined with conductive materials like graphene or carbon nanotubes, which enhance their electron transfer capabilities and overall performance.[132,133]

Metal hydroxides, such as nickel hydroxide [$Ni(OH)_2$] and cobalt hydroxide [$Co(OH)_2$], also play a critical role in ECH.[134] These hydroxides exhibit layered structures that facilitate the intercalation and deintercalation of protons, a key process in HER. The structural flexibility of metal hydroxides

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allows for the incorporation of various dopants, which can tailor the catalytic activity and stability. Hunter[135] reported the addition of iron to nickel hydroxide to form NiFe-LDH (layered double hydroxide), resulting in a significantly enhanced catalytic performance. The iron addition improves the electron transfer kinetics.

Metal oxides and hydroxides possess multiple features relevant to the ECH mechanism and catalytic behavior, such as the presence of active sites (i) for hydrogen adsorption, (ii) to promote proton-coupled electron transfer (PCET), and (iii) to stabilize the reaction intermediates or adsorb the organic reactants preferentially. The surface chemistry of these materials is crucial for their catalytic performance, as it determines the binding energy of hydrogen and the reaction pathways for hydrogenation.

In metal oxides, the catalytic activity is often associated with the presence of oxygen vacancies or defects that act as active sites for hydrogen adsorption.[136,137] These defects can enhance the binding of hydrogen molecules, making them more reactive and promoting their conversion into atomic hydrogen, which can then participate in the hydrogenation of organic molecules. Additionally, the electronic structure of metal oxides can be tuned through doping or the creation of heterojunctions with other materials, further optimizing their catalytic performance in ECH.

Metal hydroxides, on the other hand, are known for their ability to undergo redox transitions between different oxidation states (e.g., Ni^{2+}/Ni^{3+} and Co^{2+}/Co^{3+}).[133,134] This redox flexibility enables them to mediate electron transfer processes during hydrogenation reactions effectively. Moreover, the layered structure of hydroxides allows for efficient proton diffusion, which is essential for maintaining high reaction rates in ECH. The ability to control the oxidation state of metal centers in hydroxides provides an additional level for tuning catalytic activity and selectivity. Overall, metal oxides and hydroxides offer a versatile platform for the design of efficient and stable electrocatalysts for hydrogenation reactions. Their ability to undergo reversible redox transitions, coupled with their structural tunability, makes them attractive candidates for further development in sustainable energy applications.

3.3.4. Metal-Free Catalysts. 3.3.4.1. Carbon-Based Materials. Carbon-based materials have shown great potential as metal-free catalysts in ECH.[138−140] Materials such as graphene, carbon nanotubes (CNTs), and doped carbon materials (e.g., nitrogen-doped carbon) are of particular interest due to their excellent conductivity, abundant surface active sites, and tunable structures. In comparison to traditional metal catalysts, a significant advantage of carbon-based catalysts is their cost-effectiveness and the abundant availability of raw materials, making them more economically viable for large-scale industrial applications.

Graphene, with its unique two-dimensional structure and excellent conductivity, has been extensively studied as a foundational material for electrocatalysts. The catalytic performance of graphene can be significantly enhanced by doping with elements such as nitrogen, sulfur, or phosphorus. These dopants modify the electronic structure of the carbon material, enhancing its hydrogen adsorption capacity and, in turn, improving its activity in hydrogenation reactions.[141,142] CNTs, known for their unique structure, mechanical strength, and conductivity, are also widely used in electrocatalysis. The catalytic performance of CNTs can be further optimized by controlling their diameter, wall thickness, and surface defects.[142] Additionally, the catalytic activity and stability of CNTs can be effectively enhanced by combining them with other functional materials, such as metal oxides or other inorganic nanoparticles.

3.3.4.2. Emerging Metal-Free Catalysts. In addition to carbon-based materials, several emerging metal-free catalysts have garnered attention recently.[143,144] These include carbides, boron−nitrogen co-doped carbon (BCN) materials, and phosphides. These novel materials exhibit unique electronic structures and surface chemistry, making them promising candidates for application in ECH.

BCN materials create novel active sites by incorporating boron and nitrogen atoms into the carbon matrix. These active sites have high hydrogen adsorption capacity and low reaction barriers, allowing BCN materials to exhibit high catalytic efficiency in hydrogenation reactions.[145,146] Additionally, the preparation process of these materials is relatively simple and environmentally friendly, further enhancing their feasibility for industrial applications.

Phosphides are another promising category of metal-free catalysts, particularly in electrocatalytic water splitting and hydrogenation reactions. Zhang et al. reported carbon phosphorus (PC) materials, and with their unique layered structure and electronic properties, they can effectively catalyze hydrogenation reactions at lower potentials.[147] Phosphide materials also offer good chemical stability and durability, maintaining high catalytic activity over extended times.

3.4. Membrane. The specific paired electrolysis of interest (Figure 1) requires proton transfer from the anodic to the cathodic part. We thus limit the discussion here to proton-exchange membranes (PEMs).

3.4.1. Classes of PEM. 3.4.1.1. Perfluorosulfonic Acid (PFSA) Membranes. PFSA membranes contain a PTFE backbone for enhanced thermal and chemical stability and hydrophilic perfluoro vinyl ether side chains that contain $-SO_3^-$ groups. These membranes are known for their ability to conduct protons very effectively. However, when operating under low humidity or at elevated temperatures, the proton conductivity and stability can be significantly compromised. Nafion, which is considered the most recognized PEM material, is highly affected under these conditions.[148] Aquivion, with a shorter side chain, provides better stability under relatively higher temperatures.[149]

3.4.1.2. Sulfonated Aromatic Polymer (SAP)-Based Membranes. These membranes are typically made from hydrocarbon polymers, such as polyether ether ketone (PEEK), polyether sulfone (PES), polysulfone (PSU), polyphenyl sulfone (PPSU), and poly(2,6-dimethyl-1,4-phenylene oxide) (PPO).[78] Sulfonic acid groups can be introduced by treating them with a sulfonating agent (H_2SO_4). Due to better chemical and thermal stability and easy preparation, they appear as a good alternative to Nafion. However, they generally exhibit lower proton conductivity due to less developed interconnected hydrophilic channels.[150] SAPs are often available as raw polymers and can be sulfonated after purchase.

3.4.1.3. Polybenzimidazole (PBI)-Based Membranes. Partially or fully aromatic PBI polymers are utilized for PEM due to their high mechanical and thermal stability. The proton conductivity of these membranes is provided by the incorporation of phosphoric acid groups into the polymer structure.[151] Unlike Nafion, PBI-based membranes can operate at higher temperatures and conduct protons without the existence of water.

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3.4.1.4. Composite Membranes. Hydrocarbon-based membranes require a high amount of $-SO_3^{2-}$ groups to achieve higher proton conductivities than Nafion. Given that the sulfonation procedure results in excess swelling of the membranes, the stability of the membrane will decay. Because of these reasons, organic−inorganic composite materials are studied, aiming to combine organic properties (processability and electrical characteristics) with inorganic properties (thermal and chemical stability) (Table 4).[152]

Table 4. Commercially Available Proton-Exchange Membranes

membrane	manufacturer	type
Nafion	Chemours	PFSA-based
Aquivion	Syensqo	PFSA-based
Celtec[153]	BASF	sulfonated PBI
Pemion[154]	Ionomr Innovations	sulfonated hydrocarbon
Gore PEM[155]	W.L. Gore & Associates	na

3.4.2. Recent Research. Aquivion membrane with a short side chain (SSC) was compared with Nafion in the work of Nagasawa et al.[156] It was concluded that the structure and equivalent weight (EW) of the PEM significantly impact toluene permeability. Aquivion with a short side chain has an increased concentration of sulfonic acid groups. These ionic groups attract and bind water molecules, forming hydration shells around these ionic sites. This fact reduces the availability of water molecules to solvate nonpolar molecules such as toluene. As a result, toluene becomes less soluble in the water-rich regions of the membrane, and its permeation is suppressed. However, Nafion, with a long side chain (LSC) structure and high EW, shows higher electrochemical performance. This fact was attributed to the better transport to the reaction sites (three-phase boundary), enhancing the reaction kinetics. LSC membranes are likely better in the short term operations, whereas SSC membranes would perform better in the long term.

3.5. Electrolytes. The choice of electrolyte for electrocatalytic hydrogenation is closely related to the specific organic substrate, reaction conditions, and target product properties.[157] The common organic substrates used for electrocatalytic production of LOHC mainly include unsaturated aromatic hydrocarbons, heterocyclic compounds, ketones or aldehydes, alcohol compounds, etc.[158] Lignin model compounds (such as phenol, benzene, and guaiacol, etc.) are the desirable candidates for hydrogen storage due to their unique structure. They can be converted and upgraded to hydrogen-rich and stable products after ECH, such as cyclohexanol, cyclohexane, and cyclohexanone.

3.5.1. Aqueous Electrolyte. In the electrocatalytic hydrogenation reaction, the protons are transferred to the cathode and reduced to adsorbed hydrogen (H_{ad}). The H_{ad} subsequently migrates to the reaction interface to hydrogenate the unsaturated substrate. Electrocatalytic hydrogenation is mainly carried out in acidic solutions, such as H_2SO_4,[44,159−162] HCl,[54] $HClO_4$,[163,164] etc. Song et al.[107] conducted a series of studies on the ECH of phenol in a H-cell using three different electrolytes, among which CH_3COOH had the highest activity, followed by H_3PO_4. Instead, H_2SO_4 showed the lowest phenol conversion rate.

The pH affects the selectivity and yield of products. In the study of Xin et al.[165] levulinic acid (LA) was reduced to valeric acid (VA) or γ-valerolactone (GVL) by ECH in a flow cell. They observed a 95% selectivity for VA in an acidic electrolyte (0.5 M H_2SO_4 solution, pH 0), and a 100% selectivity for GVL in a neutral electrolyte (KH_2PO_4/K_2HPO_4 buffer solution, pH 7.5). Nilges et al.[166] investigated 5-hydroxymethylfurfural (HMF), which was completely reduced to 2,5-dimethylfuran (DMF) in a mixture of 0.5 M H_2SO_4 with ethanol (1:1, v/v). HMF preferentially generated furfuryl alcohol (FA) in the phosphate buffer solution (pH 7). Tao et al.[167] observed that the pH value regulated the selectivity. Specifically, when using Pt/C as the catalyst, the highest conversion of phenol in CH_3COOH was observed at pH 5 compared to pH 3 and 10. In contrast, when using Rh/C as the catalyst, the conversion of phenol increased with increasing pH.

In addition, a variety of buffer solutions are used in ECH, and they usually have good electrical conductivity, such as acetate buffer solution,[48,168,169] sulfate buffer solution,[170] phosphate buffer solution,[165] and borate buffer solution.[171,172] The buffer solution can maintain the pH stability and provide a relatively stable chemical environment for the electrocatalytic reaction, which in turn improves the product selectivity. Roylance et al.[173] converted HMF to 2,5-hexanedione (HD) by ECR in the 0.2 M sulfate buffer solution (pH 2). They found that the local pH at the working electrode increases rapidly due to the proton consumption during the HMF reduction in an unbuffered, weakly acidic solution. The pH change alters the yield, selectivity, and product type.

The kind of anode electrolyte (anolyte) to combine with cathode electrolyte (catholyte) is also critical and has a significant impact on the reaction results. Wijaya et al.[174] investigated the different combinations of "catholyte−anolyte" on the efficiency of ECH. The result showed that the conversion rate of guaiacol decreased in the following order: acid−acid (38%) > neutral−acid (36%) > acid−alkaline (16%) > alkaline−acid (0%), i.e., acid−acid pair is the most efficient combinations for the reaction. It was also found that the neutral−acid pair produced the highest FE, suggesting that most of the protons required for ECH come from the anode side.

3.5.2. Organic Solvents as Co-solvents. Some organic substrates are difficult to dissolve in acidic aqueous solutions. Therefore, organic solvents can be added to the electrolyte solution as co-solvents to increase the solubility of substrates. Organic solvents are classified into three categories:

- Polar protonic solvents, such as methanol, ethanol, and isopropanol, act as either hydrogen bond donors or acceptors.[167]
- Polar non-protonic solvents: acetonitrile (MeCN), dimethylformamide (DMF),[175] dimethyl sulfoxide (DMSO), ethyl acetate, tetrahydrofuran (THF), 2-methyltetrahydrofuran (2-Me-THF), and ketone.
- Nonpolar solvents, such as hexane, benzene, and toluene.

For ECH involving aromatic compounds, the protonated organic solvents are a preferable option. Mulero et al.[176] studied the ECH of benzophenone in ethanol/water (90:10, v/v) plus 0.1 M H_2SO_4 solution in a polymer electrolyte membrane electrochemical reactor (PEMER). At low current densities, the conversion of benzophenone was up to 30%, with a selectivity of dibenzyl alcohol >90%.

Although organic solvents can increase the solubility of reactants, their presence also decreases the conductivity. The

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use of alcohols as co-solvents may lead to a decrease in the ECH rate and FE. Lopez-Ruiz et al.[177] added methanol, ethanol, or isopropanol to the electrolyte to explore the effects of alcohol on the rates of benzaldehyde ECH. The FE and reaction rate decreased with increasing alcohol concentration. The influence of alcohol type became gradually significant as the length of the alcohol chain increased.

In addition, some organic solvents tend to adsorb competitively onto the active sites of electrodes (catalysts), thereby weakening their overall activity. Alternative solvents were thus proposed and developed. Wijaya et al.[178] identified methanesulfonic acid (MSA) as a promising green alternative to conventional organic solvents, which possess ionic conductivity comparable to that of inorganic acids, as well as low toxicity and corrosivity. They used this solvent to perform the ECH of guaiacol using Pt/C catalyst powder in a stirred slurry electrocatalytic reactor. They obtained products, including cyclohexanol (45−53%) and 2-methoxycyclohexanol (20−26%), thus confirming the feasibility of MSA.

3.5.3. Ionic Liquids. Recently, ionic liquids (ILs) have emerged as a promising class of green organic solvents that have the potential to replace conventional electrolytes due to their unique properties. ILs are salts with a melting point below 100 °C. Typically, ILs consist of organic cations (e.g., imidazolium, pyridinium, pyrrolidinium, phosphonium, and ammonium) and inorganic or organic anions (e.g., halogens, BF_4^-, Tf_2N^-, PF_6^-, etc.). ILs typically not only exhibit high conductivity but also high solubility for unsaturated compounds, such as polycyclic aromatic hydrocarbons and aromatic compounds. ILs have a wide electrochemical stabilization window, which enables them to operate stably over a wide range of potentials.[179] In addition, ILs have modifiable anionic and cationic structures. Using ILs as the electrolyte in the electrocatalytic production of LOHC offers a promising way to achieve a sustainable and efficient energy conversion process.[180] However, generally, the viscosity of ILs is relatively high, and water or organic solvents are added as co-solvents.

Andrey et al.[181] used 1-butyl-3-methylimidazolium hexafluorophosphate ([BMIM][PF_6]) ILs/water (80:20, v/v) as the electrolyte solution in a flow-cell to study the ECH of aromatic compounds (naphthalene, quinoline, and carbazole). Their study successfully obtained the desired products under mild conditions, validating the potential of ILs as effective electrolytes. Chu et al.[182] reported the ECH of furfural (FF) in a H-cell, where 1-ethyl-3-methylimidazolium tetrafluoroborate ([EMIM][BF_4]) plus water (H_2O) was used as the cathode electrolyte. The FF was converted to FA with a total conversion efficiency of 61.7%. Wu et al.[183] investigated the effect of ILs on the ECH of LA to GVL in a typical H-cell. The comparison of the FE and current density indicates that [BMIM][BF_4] had the best performance among the studied ILs ([EMIM][BF_4], [BMIM][BF_4], [HMIM][BF_4], [OMIM][BF_4], [TBA][BF_4] and [TBP][BF_4]). Consequently, they used [BMIM][BF_4]−MeCN−H_2O as the electrolyte solution to perform the ECH of LA, GVL was found as the only product, and [BMIM][BF_4] (1.8 wt %)−MeCN−H_2O (1.8 wt %) was identified as the optimal electrolyte solution.

ILs with specific structures and functions can be further designed and synthesized by changing the combination of anions and cations as well as their functionalization to improve the efficiency of ECH of LOHC. According to the survey, proton ionic liquids (PILs) are preferred, and hydrophilic ILs would be better, while more work needs to be conducted further.[12]

4. ANODIC OXIDATION

Biomass and biomass-derived mainly consist of cellulose, hemicellulose, and lignin, which are abundant resources for synthesizing high-value chemicals by electrocatalytic oxidation. The value-added processing biomass consists of two key stages: the initial depolymerization into its constituent monomers and the upgrading of the monomers by electrocatalytic reduction or oxidation into a variety of value-added fuels and chemicals.[184−186]

In recent years, research on the electrocatalytic oxidation of biomass-derived key platform chemicals, such as HMF, FF,[187,188] and glycerol[189−192] has attracted widespread attention and made significant progress. As lignin is the richest source of aromatic compounds on Earth and is a key feedstock for the production of high-value-added products, recently, the electrocatalytic oxidation of lignin and its model compounds has also been greatly developed.[192−198]

4.1. Substrates and Products. Coupling the electrocatalytic cathodic regeneration of LOHCs with an anodic oxidation process to valorize lignin derivatives producing high-value chemicals is a promising strategy to (i) improve process economics, (ii) link H_2 and biorefinery economies, and (iii) improve environmental sustainability. The oxidation reaction at the anode serves as a pivotal component of the entire electrocatalytic system, facilitating the provision of electrons and protons necessary for the ECH of precursors into LOHCs. Conventionally, OER is coupled with the cathodic reaction.[25,199] However, this approach demands a substantial overpotential to drive the reaction, has slow kinetics, and the oxygen produced may often need to find application. Hence, the substitution of OER with thermodynamically favorable organic oxidation reactions has generated significant interest. While often the total oxidation of waste is explored,[41,200,201] the selective oxidation path has undoubtedly greater interest, although more challenging.

Most of the literature data is focused on the electrocatalytic oxidation of small alcohols and cellulose-derived products, such as furans. Many organic molecules, such as methanol, ethanol, formic acid, and urea, have been widely used in electrocatalytic oxidation to replace OER. In contrast, the research concerning the electrocatalytic oxidation of lignin-derived molecules has predominantly centered on the complete oxidation (or degradation) of these compounds, driven by wastewater treatment application,[202,203] and the discussions on the electro-oxidation of lignin-derived molecules to value-added chemicals are still very limited. Also, depolymerization of lignin molecules generally generates various monomers, dimers, and macromolecules, with monomers and dimers being predominant, and the chemical properties of these molecules also depend upon the method used for lignin depolymerization.[204,205]

Assessing whether lignin-derived molecules are suitable for electrochemical oxidation involves evaluating their thermodynamic feasibility, solubility in aqueous solutions, and the value of the products generated. For aromatic molecules such as guaiacol, vanillin, toluene, *p*-xylene, *m*-xylene, *o*-xylene, and anisole, their standard electrode potentials are mostly below 1 V versus reversible hydrogen electrode (RHE), which is lower than 1.23 V versus RHE required for OER.[206,207] Therefore, from an energy standpoint, these molecules are not suitable

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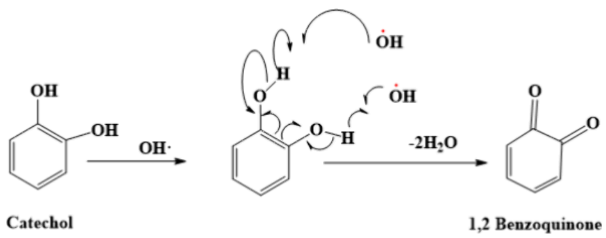
due to their high energy demand. In terms of solubility, lignin-derived aromatic molecules such as catechol, resorcinol, and *p*-cresol demonstrate better solubility.[208−211] The solubility of all lignin-derived molecules depends upon the salt or buffer used for dissolution and increases with temperature, varying depending upon the specific pH level. The major oxidation products of these aromatic molecules have also been identified, along with their potential industrial applications, depending upon the selectivity of the method used. This indication offers insights into the potential commercial value of the products derived from the electrochemical oxidation of lignin. Below, these aspects are evidenced by taking four molecules as examples:

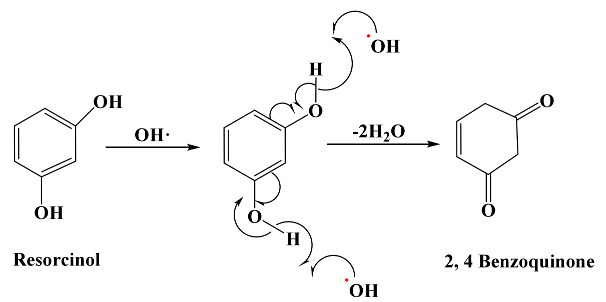
4.1.1. Catechol.[209] This process is a $2H^+/2e^-$ oxidation with an oxidation potential of 0.2 V, producing a substance that is used as a fungicide, a reagent in photography, and the production of dyes, with a solubility of 430 g/L (Scheme 1).

Scheme 1. Oxidation of Catechol to 1,2-Benzoquinone



4.1.2. Resorcinol.[210] 2,4-Benzoquinone, with a solubility of 1100 g/L and an oxidation potential of 0.6 V, is used as a chemical intermediate, a polymerization inhibitor, an oxidizing agent, a photographic chemical, a tanning agent, and in the cosmetic industry (Scheme 2).

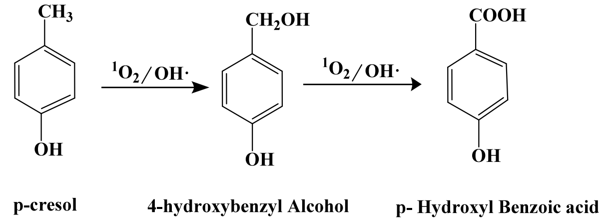
Scheme 2. Oxidation of Resorcinol to 2,4-Benzoquinone



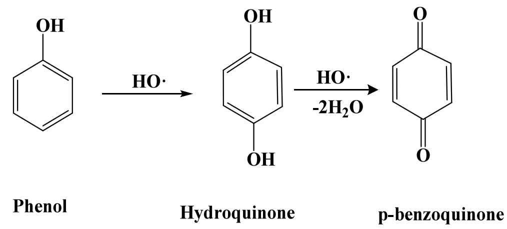
4.1.3. p-Cresol.[211] Parabens (*p*-hydroxybenzoic acid), with a solubility of 240 g/L and oxidation potential of 1.038 V, are an important class of preservatives extensively used in the cosmetic and pharmaceutical industries for preparing shampoos, commercial moisturizers, shaving gels, personal lubricants, topical/parenteral pharmaceuticals, spray tanning solutions, and toothpaste (Scheme 3).

4.1.4. Phenol.[208] Phenol oxidation produces hydroquinone and *p*-benzoquinone, with product selectivity controlled by the electrooxidation parameters (Scheme 4). Hydroquinone, with a solubility of 83 g/L and an oxidation potential of 0.65 V, is clinically used to treat dyschromia, including melasma, chloasma, solar lentigines, freckles, and post-inflammatory hyperpigmentation. *p*-Benzoquinone is utilized in the dye, textile, chemical, tanning, and cosmetic industries.

Scheme 3. Oxidation of *p*-Cresol to 4-Hydroxybenzyl Alcohol and *p*-Hydroxyl Benzoic Acid



Scheme 4. Oxidation of *p*-Cresol to 4-Hydroxybenzyl Alcohol and *p*-Hydroxyl Benzoic Acid



4.2. Brief Introduction of Electrocatalytic Oxidation.

The electrocatalytic oxidation (ECO) of organic compounds can proceed through two primary pathways: (i) direct oxidation at the interface between the electrode and electrolyte or (ii) indirect oxidation involving both heterogeneous electron transfer reactions and homogeneous redox reactions.

Direct oxidation occurs through the electron transfer between the organic substrates and the anode, usually at low anodic potentials. During electrolysis in an acidic or alkaline solution, H_2O (or OH^-) undergoes discharge at the anode, leading to the generation of adsorbed hydroxyl radicals on the surface of the anode, as reported by the following equations (eqs 1 and 2):[205,212]

$$MO_x + H_2O \rightarrow MO_x(^\bullet OH) + H^+ + e^- \quad (1)$$

$$MO_x + OH^- \rightarrow MO_x(^\bullet OH) + e^- \quad (2)$$

The oxidation of organic species adsorbed on an electrocatalytic surface proceeds through interactions with a so-called higher metal oxide and adsorbed hydroxyl radicals (eqs 3−5).

$$MO_x(^\bullet OH) \rightarrow MO_{x+1} + H^+ + e^- \quad (3)$$

$$MO_{x+1} + R \rightarrow RO + MO_x + e^- \quad (4)$$

$$MO_x(^\bullet OH) + R \rightarrow MO_x + CO_2 + H_2O + H^+ + e^- \quad (5)$$

As already mentioned ECO of organic compounds include multiple mechanisms, each with distinctive pathways, intermediates, and reaction conditions, which can be optimized for various applications. Examples of ECO applications illustrate how diverse mechanistic pathways can selectively target specific organic pollutants or achieve higher efficiencies toward different products in specific reaction environments. Direct oxidation is frequently employed for the degradation of organic contaminants in water treatment, primarily due to the high reactivity of hydroxyl radicals ($^\bullet OH$) generated at the anode surface. In this case, the organic pollutants such for example phenols and dyes adsorbed on the anode surface undergo oxidation via electron transfer directly with the anode or through interactions with $^\bullet OH$.[213] An example of this type of

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mechanism has been found through the use of boron-doped diamond (BDD) electrodes highly effective anodes for generating hydroxyl radicals, which enable the direct oxidation of phenolic compounds in wastewater treatments.[214] Hydroxyl radicals ($^{\bullet}$OH) generated at the anode surface break down contaminants effectively. These radicals are produced by the oxidation of water molecules in acidic or neutral conditions, or from hydroxide ions when the pH is 10 or higher.[215] In fact, for a metal oxide (MO) anode with a high oxygen overvoltage, the initial oxidation of water leads to the formation of a physisorbed hydroxyl radical through eq 1. This intermediate can then undergo further oxidation to form a chemically adsorbed "superoxide" species (eq 3). However, the predominance of reaction 3 to the detriment of reaction 1 on the anode surface means that anodes are classified as active and inactive, respectively. The use of anodes based on RuO_2, IrO_2 and Pt lead to a large amount of (MO_{x+1}), this species then oxidizes aromatic organic compounds, converting them primarily into carboxylic acids, though with relatively low levels of complete mineralization.[216] Conversely, in non-active metal oxide anodes such as SnO_2 and PbO_2, $MO_x(^{\bullet}OH)$ is primarily generated. Once generated this physisorbed radical interacts more efficiently with a wide range of aromatic compounds, resulting in their complete mineralization or breakdown. One of the most effective non-active anode is the boron-doped diamond and its use lead as only reaction 1.[217] Meanwhile, dioxygen is concurrently generated via water oxidation or OER (eqs 6 and 7).[205] This process diverts some of the oxidizing currents away from the desired substrate transformations, affecting the FE of the reaction.

$$MO_x(^{\bullet}OH) + MO_x(^{\bullet}OH) \rightarrow O_2 + 2MO_x + 2e^- + 2H^+ \quad (6)$$

$$MO_{x+1} + MO_{x+1} \rightarrow O_2 + 2MO_x + 2e^- \quad (7)$$

Indirect oxidation reactions commonly use an electrolyte medium, with an electrocatalyst or mediator facilitating electron transfer between the electrode and substrates.[218] This process involves both heterogeneous electron transfer and homogeneous redox reactions, where a mediator interacts with the substrate and is subsequently regenerated at the electrode surface. Mediators must be stable in both oxidized and reduced forms to prevent decomposition. Two main types of mediator systems, laccase and electrolytic mediator systems, are proposed as environmentally friendly methods for organic electro-oxidation.[219] The efficiency and selectivity of these systems significantly depend upon the chosen mediator, with studies exploring a variety of mediators like nitrobenzene, transition metal complexes, and iodide ions. However, further research is required to fully understand the optimal selection of mediators and their effect on various substructures of substrates.

In laccase-mediated systems (LMS), the enzyme laccase catalyzes oxidation with the help of mediators, extending the enzyme's capability to oxidize substrates that would otherwise be unreactive.[220] Notable mediators such as 2,2′-azine-bis(3-ethylbenzothiazoline-6-sulfonic acid (ABTS), 1-hydroxybenzotriazole (HBT),[205] 2,2,6,6-tetramethyl-1-piperidinyloxyl (TEMPO), and *N*-hydroxyphthalimide (NHPI)[221] facilitate the oxidation of organic components, improving reaction efficiency and selectivity for potential industrial applications. LMS mediators are classified by mechanism-hydrogen atom transfer, ionic, and electron transfer, influencing the oxidation pathways and products formed in lignin processing. For example, NHPI has demonstrated high effectiveness for the electrochemical oxidation of lignin, selectively targeting β-O-4 linkages and other structures under mild conditions.[222]

Electrolytic mediator systems (EMS) differ using an anode to facilitate electron transfer, allowing for oxidation under broader pH and temperature conditions.[223] Similar mediators, like NHPI and HBT, can be employed in EMS, yielding different oxidation outcomes compared to LMS.[205] For instance, for lignin electro-oxidation, EMS with HBT produces a mixture of C−carbonyl and Cα−Cβ cleavage products, whereas LMS yields only C−carbonyl products. While EMS offers greater versatility and broader conditions for lignin valorization, further investigation is needed to refine these systems for consistent selectivity and efficiency.[224]

However, another mechanism, although less studied, in which electrocatalysts can also induce the formation of other oxidizing and more selective species on the electrode surface, such as peroxo and hydroperoxo species, superoxo, dioxygen radicals, singlet oxygen, etc., can occur. The generation of these oxidizing species and the design of electrodes for their selective production are still under exploration, unlike hydroxyl radical species, which have been extensively studied in the oxidative degradation of organics in wastewater treatments.[225−228]

The *in situ* generation of H_2O_2 represents an appealing strategy due to its selective oxidizing properties. H_2O_2 can further interact with isolated Ti ions on the electrode surface or within a solid catalyst (such as Ti silicate-TS-1[229,230]) at the liquid interface with the electrode, leading to the formation of peroxo species. Additionally, the oxidation of H_2O_2 can facilitate the production of superoxide ions ($O_2^{\bullet -}$), which readily react in the presence of protic solvents, leading to the formation of O_2 and hydroperoxide anion ($HO_2^{\bullet -}$).[231]

Numerous systems for the electrocatalytic oxidation of small organic molecules have been documented in the literature, offering insights into how various organic compounds undergo electrochemical oxidation through distinct reaction mechanisms across different pH environments. This understanding provide insights into catalyst selection and applications in renewable energy and chemical synthesis. Feng et al. reported a review in recent advances in Ni-based catalysts for the electrochemical oxidation of ethanol (EOR). The EOR can in fact, represent a promising alternative to the anodic OER due to a lower overpotential, in comparison to the anodic OER. Ethanol can partial oxidized to acetate in an alkali environment with an equilibrium potential of 0.11 V versus RHE[232] considerably lower than the 1.23 V versus RHE required for the oxygen evolution reaction (OER). The high electrical conductivity of Nickel plays an essential role in boosting the efficiency of EOR, together with the metal's capacity for multiple oxidation states, especially the +3 oxidation state as nickel oxyhydroxide (NiOOH), exhibits significant electroactivity throughout the EOR process, further enchancing the reaction's effectiveness.[233] The nature of the electrolyte also plays an important role when Ni-based materials are employed for EOR. Usually alkaline conditions are used to avoid corrosion phenomena that instead occur under oxidative potentials in acidic electrolytes.[234] The addition of noble metals helps prevent corrosion and makes it possible to use nickel-based materials for ethanol oxidation reactions (EOR) in acidic environments.[235]

Lai et al.[236] have explored the EOR on platinum and gold electrodes, employing both electrochemical and spectroscopic

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methods across electrolytes with varying pH and compositions, largely influenced by buffering anions. The study found that reaction activity increases significantly when the electrolyte pH is above 10. Moreover, the results suggest that reaction selectivity is highly influenced by the type of electrolyte used and, to a lesser degree, by the pH value. The observations of this research supported the proposal of a potential overall mechanism for the EOR. Specifically, breaking the carbon−carbon bonds a key step for full oxidation was observed only on platinum when strongly adsorbing anions were not present.

The electroxidation of methanol (MOR) is another important process thanks to the release of energy. In fact, methanol, known for its high hydrogen content, has gained significant attention as a fuel in energy storage and conversion technologies.[237] This reaction serves as a crucial half-reaction in hydrogen production via methanol reforming and in the operation of direct methanol fuel cells (DMFCs).[238,239] Moreover, the methanol oxidation reaction (MOR) is also important for converting methanol into valuable products like formate.[240,241] The nature of the electrolyte plays an important role in MOR, acid environments induce an easier oxidation of methanol but the process depends a lot upon the presence of catalysts based on noble metals, given the low stability of catalysts based on non-noble metals that are easily dissolved. However, the use of alkaline environments favors the polarization at low anodic overpotential and the deprotonation of methanol.[242,243] Tripković et al.[244] report a study regarding the kinetics of MOR using Pt and Pt/Ru catalysts in two different electrolytes (0.5 M H_2SO_4 and 0.1 NaOH) and at two different temperatures (295 and 333 K). The results obtained highlighted that the activity of Pt and Pt/Ru catalysts for methanol oxidation depends significantly upon the electrolyte pH and temperature. Alkaline solutions, favors the reaction kinetics resulting much faster than in acidic conditions. This pH-dependent effect is thought to result from competitive adsorption between oxygenated species and anions from the electrolyte. Furthermore, both Pt and Pt_2Ru_3 catalysts display enhanced activity at elevated temperatures, with an increase of about 5 times in activity at 333 K compared to 295 K. However, only minor differences in activity are observed between pure Pt and Pt alloys with high Ru content. This was attributed, probably to the slower methanol dehydrogenation on Ru-rich surfaces, combined with an insufficient number of Pt active sites necessary for the efficient dissociative chemisorption of methanol.

The electrochemistry aimed at selectively oxidizing bio-based molecules is still in its early stages, although some interesting findings have been yielded.[245−249]

4.3. Electrocatalysts.

4.3.1. Lignin and Lignin-Derived Molecules. The research concerning the development and design of electrocatalysts for the ECO of lignin-derived molecules has predominantly centered on the complete oxidation of these compounds in wastewater. Electrochemical degradation of lignin to low molecular phenolic compounds was studied on various transition metals (Pt, Ni, Co, Ni, Co, etc.) in aqueous alkaline media,[193,250] PbO_2 (a widely used anode),[197] and other electrodes based on Ir which may be too expensive for an effective use.[251] Parpot et al.[252] discussed various examples of direct electro-oxidation of lignin for vanillin production, including (i) PbO_2 anode (giving up to 64% yield of vanillin, the best performances), and (ii) Ni anode and dimensionally stable anodes (DSAs), e.g., electrochemically active metal oxides deposited on an inert but metallic substrate (typically titanium, Ti). Other authors also studied this reaction using Pb/PbO_2 anodes.[197,198,253] NiSn20% alloy anodes[254] and $Ti/RuO_2{-}IrO_2$ anodes[251] were also investigated. The main common issues are the deactivation and obtaining a complex mixture that is difficult to separate. Electron-transfer mediators of nitroaromatic oxidants improve the reaction rate of the cleavage of β-O-4 linkages. However, selectivity and yields are generally poor.

Significant advancements have been achieved in the direct electro-oxidation of lignin-derived molecules. For instance, the electrooxidation of guaiacol on a PbO_2/Nb electrode at 70 °C resulted in over 90% conversion in less than 1 h, albeit yielding various products, including catechol, methoxyhydroquinone, 3-methoxycatechol, formic acid, oxalic acid, maleic acid, and insoluble polymers.[255] Polymerization of these products represents a common drawback in ECO. Interestingly, Zhou et al.[256] recently introduced a Mn-doped cobalt oxyhydroxide catalyst that operates via a base-catalyzed mechanism for converting lignin derivatives into carboxylates. Remarkably high yields (80−99%) and operational stability (200 h) were reported. Furthermore, the conversion of guaiacol on Ti/Sb-SnO_2 and Ti/Pb_3O_4 anodes results in the formation of maleic acid as an intermediate, although complete degradation remains the predominant pathway.[201]

In the applications above, the primary objective is to generate hydroxyl radicals on the anode surface efficiently. These radicals serve as potent oxidizing agents, facilitating the complete conversion of organics into CO_2. Conversely, for selective oxidation, the focus shifts toward the generation of specific oxygen species capable of selectively oxidizing organic molecules under conditions of ECO. However, there remains a notable absence of systematic studies and established design criteria for developing catalysts tailored to the specific target molecules.

Even though the active species for heterogeneous selective oxidation catalysts are well understood,[257] these catalysts typically operate within distinct temperature ranges and often are not conductive. Consequently, there is a high need for the development of novel anodes tailored specifically for the selective electro-oxidation of organic molecules. Designed anodes must bridge the gap between the requirements for effective electrochemical activity and the demands for selective catalysis, enhancing efficiency and selectivity in organic molecule oxidation processes.

Tang et al.[249] recently conducted a comprehensive review of various strategies, including photo-, electro-, and photo-electrocatalytic methods, employed for the selective oxidation of alcohols. While such reactions are significantly promising, several challenges persist, particularly in the field of lignin-derived molecules, often without clear elucidation. The selective oxidation of alcohol leads to the formation of the corresponding aldehyde as a primary byproduct. The presence of aldehyde, even in trace amounts, can trigger autocatalytic or organocatalytic oxidation processes.[258,259] This behavior is enhanced in the presence of an anode, potentially leading to non-ideal electrocatalytic behavior.[260] Consequently, achieving true electrocatalytic behavior becomes elusive, significantly limiting the scalability and reproducibility of results.

Moreover, in these contexts, the formation of polymeric species, such as humins, occurs, which are hard to detect (often not analyzed) and can also deactivate the electrocatalyst by fouling. While studies conducted under highly diluted conditions may mitigate some of these challenges, they become

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increasingly pronounced when tests are performed using concentrated solutions for practical applications. Therefore, addressing these intrinsic issues is of crucial importance from a practical point of view. This necessitates a concerted effort toward developing appropriate methodologies and mitigating the negative effects of byproducts and polymeric species on electrocatalytic performance.

Li et al. recently explored anodic oxidation reactions aimed at valorizing the cathodic production of H_2.[33] While they extensively discussed alcohol oxidation reactions, particularly focusing on simple alcohols like methanol, ethanol, and isopropanol, as well as polyalcohols such as glycerol and 1,2-propanediol, they do not mention the issues above, often hidden in the literature. Furthermore, the extension of findings from studies on these simpler alcohols to more complex molecules derived from lignin is not straight. Several notable studies exemplify the conversion of various alcohols to valuable products: the conversion of (i) methanol to formate with very high FE over CoxP@NiCo-LDH/NF electrocatalyst,[261] (ii) ethanol to acetate on Pd-based electrocatalysts[262,263] or to ethyl acetate on Co_3O_4 nanosheets,[264] (iii) Rh nanosheets for isopropanol to acetone,[265] (iv) 1,2-propanediol oxidation to corresponding lactate on Pt/C, or pyruvate on Au/C,[266] and (v) Bi-doped Pt electrocatalysts for glycerol oxidation to glyceraldehyde and other products.[267]

These and other studies show the absence of clear emerging anodic electrocatalysts for the selective conversion of this even-restricted class of organics. In parallel, there are no valid design criteria for selecting anodic electrocatalysts and their mechanistic aspects, including the nature of the active surface oxygen species, to develop selective electro-oxidation catalysts.

4.3.2. Glucose and Furanic Compounds. The electro-oxidation of glucose and furanic compounds stands as another interesting area within the ECO research. Various electrocatalysts have been investigated for glucose oxidation, including Au−Pd- and Ag−Au-based catalysts,[268,269] as well as Fe_2P-based electrocatalysts as studied by Du et al.[270] While the primary target in glucose electro-oxidation is gluconic acid, the formation of secondary compounds such as gluconate, glucaric acid, and gluconolactone is also observed. Notably, bifunctional Co−Ni alloy electrocatalysts have demonstrated efficacy in this domain.[271] In parallel, furanic compounds, notably derived from biomass, have garnered significant attention, encompassing molecules such as furfural and 5-hydroxymethylfurfural.[272] These compounds, integral to the furan platform, have been studied extensively, particularly concerning tandem or paired anodic reactions aimed at valorizing biomass-derived molecules originating from cellulose.[34,273,274] Various anodes have been explored in these investigations, including bifunctional Ni_2P/Ni/NF,[275] Ni_3S_2/NF,[276] and Ni_2P nanoparticles on nickel foam.[277]

4.4. Membranes.

This section discusses aspects related to membranes only with reference to those relevant to coupling with the ECO anodic part.

4.4.1. PEM Electrolysis for Value-Added Oxidation Products. PEM electrolyzers are employed for hydrogen production from organic compound oxidation.[278] This technology offers various advantages to the principles of green chemistry.[279]

Caravaca et al.[280] first reported the direct lignin electrolysis on the PEM electrolyzer. Alkaline lignin solution with 10 g/L lignin and 1 M NaOH was continuously supplied to the anode, and anion-exchange membrane Fumapem FAA-3-50 was utilized. Hydrogen was produced at around 0.45 V, lower than the conventional water electrolysis. Khalid et al.[281] prepared a three-dimensional (3D)-printed electrolysis cell that operates at room temperature. Aemion anion-exchange membrane was sandwiched between the commercial nickel foams (for both anode and cathode). 1.38 mL/min hydrogen production rate was achieved, which was 2.7 times higher than the water electrolysis at the chronoamperometry test.

Du et al.[282] used Nafion 115 for lignin depolymerization. Polyoxometalate (POM) or $FeCl_3$ served as charge transfer and also cleaved the complex lignin structure under mild reaction conditions. In a recent work of Umer et al., glucose, starch, lignin, and glucose were used in the H-type PEM cells equipped with Nafion 117. $FeCl_3$ (Lewis acid) was used to aid in the depolymerization and oxidation of biomass components during the hydrogen production.

4.5. Electrolytes.

This section also discusses aspects only related to ECO from three aspects.

4.5.1. Aqueous Electrolyte. In general, biomass and its derivatives are insoluble in weakly acidic and weakly alkaline solutions, and strong alkaline solutions (such as NaOH and KOH) facilitate their dissolution. For this reason, they are widely used in electrocatalytic oxidation reactions.[193,195−198] Wang et al.[283] investigated the electrocatalytic oxidation of aspen lignin in 1 M NaOH solution. After 8 h of reaction, lignin was converted into valuable products such as 4-methylbenzyl ether, vanillin, and syringaldehyde. Chakthranton et al.[284] pointed out that alkaline electrolytes are the most commonly used medium for the oxidation of furan compounds.

ECO is highly dependent upon the pH of the electrolyte, which is critical for the solubility of the reactants and final products. In the ECO of HMF to 2,5-furandicarboxylic acid (FDCA), one of the top ten value-added chemicals, due to the extremely low solubility of FDCA in water, an alkaline environment (0.1 M KOH solution) is required to convert carboxyl groups into water-soluble carboxylate ions, preventing the product from crystallizing on the electrode and causing permanent deactivation. Chakthranton et al.[284] found that 0.33 M KOH is the optimal electrolyte concentration, which can completely dissolve the product and prevent it from crystallizing on the electrode.

The pH value of the electrolyte solutions largely determines the activity and product selectivity of ECO.[285,286] Hauke et al.[287] studied the ECO of HMF. They found that by changing the electrolyte solution from 0.1 M KOH (pH 13) to 1 M KOH (pH 14), the time for completing the electrocatalytic conversion of HMF to FDCA was greatly reduced. Suzuki et al.[288] investigated the glycerol oxidation activity in the NaOH solution at different pH values and found that the catalytic activity increased with increasing the pH value. Liu et al.[245] studied the effect of pH on the selectivity of glycerol oxidation, and they found that glycerol tended to convert into formate and dihydroxyacetone (DHA) in the electrolytes with low pH (pH 9). In contrast, it tended to form formate and glyceraldehyde (GLAD) at high pH (pH 13). Zhou et al.[256] performed selectively upgrading lignin-derived secondary alcohols or ketones to carboxylates in an alkaline electrolyte solution using MnCoOOH/NF as the catalyst. In a nearly neutral electrolyte (pH 8.3), 1-phenylethanol was quantitatively converted to acetophenone. As the pH value increases (pH 13.9), high concentrations of hydroxide ions promote the

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cleavage of the C−C bond, leading to a significant increase in the conversion rate and selectivity of benzoate esters.

Although low-cost alkaline solutions are desirable solvents for electrocatalytic oxidation, high concentrations of alkaline solutions may lead to electrode corrosion, and some metal catalysts cannot maintain long-term stability. In the study by Cai et al.,[197] the Pb/PbO_2 electrode showed the highest efficiency in electrocatalytic depolymerization of lignin in the 1 M NaOH solution. When the NaOH concentration exceeds 1 M, the oxide layer on the surface of Pb/PbO_2 will be destroyed. Moreover, the condensation of the produced lignin intermediates will aggravate when the alkali concentration increases to a certain value, which is not conducive to obtaining the target product. The study by Zirbes[250] also observed that the maximum yield of vanillin by electrochemical depolymerization of lignin was achieved using 3 M NaOH, and concentrations up to 5 M resulted in a decrease in yield.

Kubota et al.[187] reported for the first time the ECO of HMF to FDCA using MnOx as a catalyst in a strongly acidic solution (H_2SO_4, pH 1). FDCA can spontaneously precipitate without the need to change the pH of the solution components or use other solutions to separate the product, providing references for the production of FDCA in acid media. In the study by Kubota et al.,[289] a new electrochemical oxidation method was proposed to convert FF to maleic acid (MA) with a yield of 65.1% using PbO_2 in the same acidic solution, with 2-furanol as the reaction intermediate.

4.5.2. Organic Solvents. Organic solvents can increase the solubility of substrates, and the addition of organic solvents to the electrolyte solution facilitates electrocatalytic oxidation. Hasan et al.[290] reported that the treatment of lignin by combining electro-oxidation and electro-reduction using THF−H_2SO_4 as an electrolyte can selectively break the β-O-4 bond of lignin, which can improve the selectivity of the aromatic products. Ma et al.[291] investigated the electrocatalytic oxidation of lignin model compounds in the *tert*-butylhydroxides solution (*t*-BuOOH in 70% water). The β-O-4 bonds were efficiently cleaved, and the aromatic aldehydes and phenols were obtained with high selectivity yields.

4.5.3. Ionic Liquids. Many studies have shown that ILs, as designable solvents, have good solubility for biomolecules, and electrocatalytic oxidation using ILs as reaction media has been developed.[292] Reichert et al.[293] studied triethylamine methanesulfonate ($[HNEt_3][MeSO_3]$) for the electro-oxidation cleavage of lignin to obtain aromatic products. As a proton ionic liquid (PIL), $[HNEt_3][MeSO_3]$ has good solubility for lignin and dissociable protons to provide proton donor and acceptor sites, as well as high ionic conductivity, leading to relatively low overpotential, superior solubility, and electrochemical stability compared to aqueous-phase electrolytes. Liu et al.[294] used the PIL $[BSO_3Hmim][OTf]$ with H_2O as the electrolyte to electrocatalytically oxidize four phenolic lignin model compounds to quinone. They also studied the effect of different ratios of IL to H_2O on the electrolysis reaction, and it showed the highest catalytic activity when the ratio of IL to water was 2:1. In comparison to pure IL, the IL−H_2O system is more conducive to the electrocatalytic degradation of the substrates. Later,[295] the IL was mixed with MeCN (2:1, v/v) to perform the electrocatalytic depolymerization of lignin in a H-cell. The substrate was completely converted into monomers, such as phenols (80−99%) and acetophenone (75−96%). They also investigated the performance of 5 ILs ($[py_{13}][NTf_2]$, ($[N_{1113}][NTf_2]$, $[py_{14}][OTf]$, $[EMIM][BF_4]$, and [EMIM][OTf]), in which $[EMIM][BF_4]$ and [EMIM]-[OTf] showed the highest conversion and yield rate, while $[py_{14}][OTf]$ had the lowest conversion rate.

Zhu et al.[296] reported that methyl-substituted aromatic compounds enable electrooxidation to the corresponding aldehydes in the aqueous imidazole ILs solutions ($[BMIM][BF_4]$, $[BMIM][HSO_4]$, $[BMIM][O_3SCF_3]$, $[BMIM][O_3SC_6H_4CH_3]$, $[BMIM][OOCCH_3]$, and $[EMIM][BF_4]$). The electrooxidation process was sensitive to the electrolyte pH value, and the selectivity for aldehydes is 87−92% when the pH of the electrolyte is between about 2−6 with $[EMIM][BF_4]$. The aldehydes were further oxidized to the corresponding carboxylic acids in the most acidic IL ($[BMIM][HSO_4]$, pH 0.6), and the process led preferentially to form *p*-methoxybenzyl alcohol in a slightly alkaline IL ($[BMIM][OOCCH_3]$, pH 8.53). Moreover, ILs showed excellent electrochemical stability and can be recovered at least 35 times.

Recently, deep eutectic solvents (DESs) have also received increasing attention in the field of biomass oxidation to value-added products.[297] DES contains both hydrogen bond donors (HBDs) and hydrogen bond acceptors (HBAs), and the excellent solubility of DES is attributed to their ability to form hydrogen bonds that can give and receive protons and electrons.[298] DES exhibits similar characteristics to traditional ILs, while the preparation process is simple, and it is cost-effective and biodegradable.[292] Davide et al.[299] prepared DESs of urea/choline chloride (urea−ChCl) and ethylene glycol/choline chloride (EtGly−ChCl) to dissolve and electrochemically oxidize lignin. In comparison to urea−ChCl and 1 M NaOH, EtGly−ChCl showed the highest solubility for lignin. When lignin was electrocatalytically depolymerized using EtGly−ChCl−H_2O (10% H_2O) as electrolyte, depolymerization products, such as guaiacol, vanillin, acetyl vanillinone, and eugenol, were obtained, and guaiacol and vanillin were the two most abundant compounds, with relative yields of 30−38% for guaiacol and 34−37% for vanillin.

5. PROCESSES AND REACTORS

5.1. Paired/Coupled Processes. Even though the initial studies on paired/coupled electrocatalytic processes focused mainly (for the anodic part) on the removal of organic contaminants in wastewater, recently, attention was given especially to the valorization of organic compounds,[300−302] being a more valuable area. However, at the same time, it also creates more challenges in the design of the electrochemical reactors capable of increasing mass transfer and energy efficiency while optimizing at the same time the coupled electrocatalytic systems.

Paired electrolysis is a highly effective method for improving the generation of valuable chemicals at both the anode and cathode. In these systems, valuable products are generated at both electrodes using H^+ and HO^- as electron carriers, thus avoiding the necessity for additional supporting ions or redox couples. The majority of research on paired electrolysis has concentrated on combining gas production (such as water splitting) with hydrogen production alongside organic oxidation. Studies exploring the simultaneous transformation of two different organic substances within a single electrocatalytic device to yield two valuable products are notably scarce. By doing so, they first enhance the overall energy utilization efficiency. Second, coupled systems hold the potential to convert organic molecules into valuable products

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simultaneously, e.g., process intensification. Finally, they can further facilitate the industrialization of electrocatalytic oxidation/reduction of different organic molecules.[303] However, compared to simpler half-reactions, paired electrolysis introduces greater complexity and several significant challenges,[304] including (1) ensuring that the reaction conditions are compatible for both the anode and cathode processes, (2) limitations on the types of reactions that can be conducted due to the compatibility of the reactants, products, electrolytes, and solvents involved, and (3) the need to develop methods for separating products that are both efficient and cost-effective.

5.1.1. HER. Noble-metal-based electrocatalysts coupled with HER have been utilized for the full oxidation of small alcohols to CO_2, ensuring total proton utilization. Even though his approach allows for the complete utilization of protons, partial oxidation is preferred to yield valuable products.[305] The electrosynthesis of high-value-added 1,1-diethoxyethane (DEE) from ethanol was successfully made with high selectivity and efficiency by coupling it with hydrogen production. This was achieved through the utilization of an effective bifunctional catalyst based on PtIr nanowires.[306]

The electrocatalytic oxidation of polyhydric alcohols demands a more careful design of the electrocatalyst due to the risk of overoxidation, which can lead to the cleavage of the C−C bond. Additionally, the required cell voltage is significantly lower than that of conventional water splitting, typically below 1 V. By designing a NiMo nitride electrocatalyst, which decreased the cell voltage by approximately 260 mV compared to water splitting, effective glycerol oxidation was achieved, resulting in the anodic production of formate and the H_2 production at the cathode with high FEs, 95 and 99.7%, respectively.[307] Analogously, the coupling of HER with HMF oxidation also facilitates the improvement of energy efficiency of the overall electrolysis, leading to a significant reduction of the cell voltage by 200 mV compared to conventional water splitting.

Zhao and his team have reported an interesting coupling by simultaneously performing the oxidation of HMF to 2,5-furandicarboxylic acid at the anode and HER at the cathode by utilizing double-layer hydroxides based on CoFe@NiFe as an electrocatalyst. The overall reaction achieves a current density of 38 mA cm^{-2} at 1.40 V, leading to 100% selectivity to 2,5-furandicarboxylic acid and a nearly 100% FE, accompanied by high yields of hydrogen, reaching 901 μmol cm^{-2}.[308] Furthermore, high yields of H_2 at the cathode and value-added products at the anode were reached in the HMF oxidation reaction over co-doped Ni_3S_2 electrocatalysts on the NF substrates. In this study, it was demonstrated how very high current densities can be achieved starting from a very low potential thanks to an optimized electrocatalyst based on $Co_{0.4}NiS$@NF.[309]

5.1.2. CO_2RR. Replacing OER at the anode with the electrocatalytic oxidation of biomass-derived molecules and coupling it with the carbon dioxide reduction reaction (CO_2RR) can significantly enhance the overall efficiency. Such integration can also enhance the sustainability and efficiency of chemical transformations, using CO_2 as a feedstock to generate value-added products. For instance, integrating CO_2 electroreduction with the conversion of biomass-derived intermediates can potentially yield a range of valuable chemicals and fuels, offering the dual benefit of mitigating CO_2 emissions while utilizing renewable biomass. This paired approach not only addresses environmental concerns but also contributes to the circular economy by creating more efficient use of resources.

Nam et al.[310] reported an example of HMF-CO_2 coupled electrochemical system. In this system, nickel oxide nanoparticle catalysts based on 3D transition metal NPs NiO, Mn_3O_4, and Co_3O_4 were used. Operating at a current density of 2 mA cm^{-2} for 3 h and a cell voltage of 2.5 V, the system achieved a 36% conversion of HMF at the anode and produced formic acid at the cathode with an 81% yield. These results highlight the potential for not only generating polymeric materials but also producing liquid fuels.

Instead, through the use of catalysts based on PdOx/ZIF-8 as cathode and PdO as anode, it was possible to obtain the simultaneous production of CO and organic acids from CO_2 and HMF, respectively.[311] The favorable thermodynamics of HMF oxidation have also been utilized for electrocatalytic ammonia production using Ru(III) PEI@MWCNT catalysts. This approach achieved stable electrolysis over 27 h at a current density of 0.50 mA cm^{-2}, with the cell voltage decreasing from 1.56 to 1.34 V compared to OER.[312] The examples discussed above illustrate successful attempts to enhance emerging electrocatalytic technologies by coupling them with the electrocatalytic oxidation of small bioderived molecules.

Liu et al.[313] pair the cathodic electrochemical CO_2 reduction with the anodic electrochemical 5-hydroxymethylfurfural oxidation to co-produce high-value chemicals efficiently while significantly reducing the energy requirements (Figure 4).

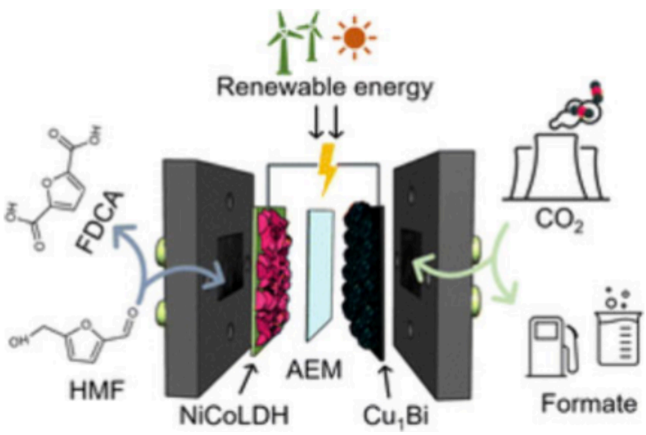

Figure 4. Paired cell: the cathodic electrochemical CO_2 reduction with the anodic electrochemical 5-hydroxymethylfurfural oxidation. This figure was reproduced with permissions from ref 313. Copyright 2023 Royal Society of Chemistry.

Utilizing single-atom Cu-doped Bi as the cathode catalyst and NiCo layer doubled hydroxides (NiCo LDH) as the anode catalyst, this system demonstrates exceptional functionality. Concurrently, the NiCo LDH anode achieves efficient electrooxidation of HMF to 2,5-furandicarboxylic acid with a faradaic efficiency exceeding 95% at low potential. This approach not only underscores the efficiency and cost-effectiveness of utilizing electrocatalytic processes for CO_2 reduction and biomass valorization but also demonstrates significant potential for reducing energy demand in chemical production.

However, utilizing raw biomass, such as lignin or its high molecular weight products, could be a highly attractive option for commercial-scale applications. Significant research efforts

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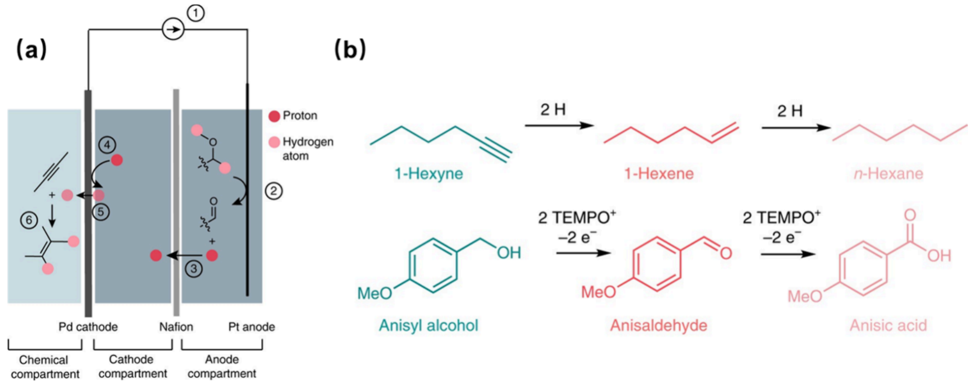

Figure 5. (a) Configuration of a triple-compartment cell for paired electrolysis is outlined as follows: (1) An electric current is directed through the palladium. (2) At the platinum anode, alcohol undergoes oxidation to form an aldehyde, facilitated by an electron-transfer mediator, while releasing protons. (3) These protons then traverse a Nafion proton-exchange membrane. (4) At the palladium foil cathode, the protons are converted into adsorbed hydrogen atoms. (5) These hydrogen atoms migrate through the palladium lattice to reach the other side of the foil. (6) Hydrogen atoms then add across an unsaturated bond, completing the hydrogenation process. (b) Paired reaction mechanisms. This figure was reproduced with permissions from ref 304. Copyright 2018 Springer Nature.

are required to design electrocatalysts capable of reducing the cell voltage compared to OER while also achieving high faradaic efficiency and product selectivity by employing feed streams of varying composition and purity.

5.1.3. Organic Components. The coupling of electrocatalytic oxidation and reduction reactions for lignin derivatives remains an area with limited literature. Liu et al.[314] demonstrate the possibility of synthesis of adipic acid from lignin-derived phenolic compounds via coupled electrolysis using bimetallic catalysts. They used an electrolyzer capable of controlling separately the pH in both anodic and cathodic compartments. In the cathode, phenol was hydrogenated into various ketone−alcohol compounds using a PtAu alloy catalyst, achieving yields of 92% with a FE of 43%. Simultaneously, in the anode, ketone−alcohols were oxidized to adipic acid using a $CuCo_2O_4$-based catalyst, attaining yields of 85% and an FE of 84%. This study demonstrated that the approach of a two-electrode flow-bipolar membrane electrolyzer efficiently promotes the electrosynthesis of adipic acid from phenol. The process achieved a yield of 38.5% and a selectivity of 70.2%, operating at a cell voltage of just 2.1 V and achieving a current of 2.5 A. Moreover, the electrolyzer exhibited stable performance over 200 h at a constant current of 2.5 A, underscoring its potential for practical, long-term applications. This study not only demonstrates the feasibility of coupling oxidation and reduction reactions within a single electrolyzer but also paves the way for future advancements in the sustainable synthesis of valuable chemicals from lignin derivatives.

Wu et al.[208] reported for the first time the simultaneous electrocatalytic reduction and oxidation of phenol to produce cyclohexanone and benzoquinone, respectively. Using nitrogen-doped hierarchically porous carbon-supported NiPt bimetallic nanoparticles as the cathode catalyst and FeRu bimetallic nanoparticles as the anode catalyst, they achieved selectivities higher than 99.9% for both cyclohexanone and benzoquinone. This coupled system demonstrated enhanced electrocatalytic performance, with an overall electron efficiency of 87.7%, surpassing conventional single-electrode electrocatalytic reduction or oxidation of phenol. The integrated system operated at a constant current density, optimizing the performance of the two half-cells. At controlled current densities of 7.5 mA/cm^2, the selectivities for cyclohexanone and benzoquinone consistently exceeded 99.9%, effectively preventing excessive reduction and oxidation of the desired products along 90 h of reaction. Additionally, conducting the two desired reactions simultaneously on separate electrodes reduced the electrical energy demand to less than half that of the half-cells operating independently. This efficiency is attributed to the electrons and protons needed for the cathodic reaction being supplied by the anodic reaction.

Sherbo et al.[304] provide a compelling example with their work on paired electrolysis within an electrochemical cell (Figure 5). This innovative approach facilitates the simultaneous production of valuable chemicals, 4-methoxybenzyl alcohol to 4-methoxybenzaldehyde, with the concomitant formation of 1-hexene from 1-hexyne under ambient conditions using electricity. The reactions are efficiently separated and facilitated by a dense palladium membrane, which allows hydrogen atoms to permeate and hydrogenate 1-hexyne. Over 5 h, the system achieves quantitative conversion and maintains a high selectivity of ≥95% for both products, showcasing the potential of electrosynthesis for efficient and waste-free chemical production.

Zhang et al.[315] present a notable example with their innovative use of paired electrosynthesis in an electrochemical cell (Figure 6). This approach harnesses water as both the source of oxygen and hydrogen to simultaneously produce valuable chemicals, converting 5-hydroxymethylfurfural to 2,5-furandicarboxylic acid and reducing *p*-nitrophenol to *p*-aminophenol under ambient conditions. The process is facilitated by the versatile NiB_x catalyst, which serves both as the anode and cathode, allowing for the efficient separation and conversion of substrates. The system allows hydrogen atoms to permeate through and hydrogenate the organic substrates, employing a dense palladium membrane. In 5 h experiments, the cell demonstrates an exceptional conversion efficiency, maintaining a high selectivity of ≥99% for both reactions. This result exemplifies the capabilities of paired electrosynthesis for sustainable and zero-waste chemical production.

Zhang et al.[147] used 1 M KOH + 50 mM FF as both cathode and anode electrolytes to study electrocatalytic oxidation and hydrogenation of FF in a H-cell. The electrocatalytic hydrogenation product was furyl alcohol, and the oxidation

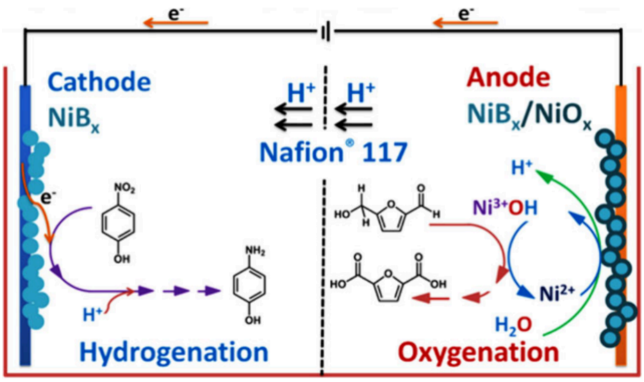

Figure 6. Paired electrolysis setup for converting *p*-nitrophenol to *p*-aminophenol and HMF to FDCA. This figure was reproduced with permissions from ref 315. Available under a CC BY-NC-ND 4.0 license (https://creativecommons.org/licenses/by-nc-nd/4.0/). Copyright 2019 Peili Zhang. Published by Wiley-VCH Verlag GmbH & Co. KGaA.

product was furylic acid with almost 100% selectivity, and the FE of FF conversion can reach 97−99%.

5.2. Reactors/Electrolyzers. *5.2.1. Types of Reactors/Electrolyzes.* Due to the different electrolyte conditions required for electrocatalytic hydrogenation and oxidation, they are typically made within a divided cell, which is separated by a membrane to control ion transport. The type of cell goes from more simple configurations, such as H-cells, to more realistic and industrial-relevant configurations, such as flow cells and zero-gap. However, often, the H-cell (the most used) does not provide reliable information for the other types of cells, including in terms of electrocatalyst selection, because the factors controlling the behavior are different.[316]

The most commonly used device in the laboratory is the H-cell, which is conveniently used to explore the effect of various factors on the reaction, but there are limitations in the current densities, resulting in low overall product conversion. Using a flow cell can reduce the distance between the counter electrode and the working electrode, decreasing the reaction resistance and thus improving the mass transfer of the reactants. The zero-gap electrolyzer retains the excellent properties of the flow cell with high mass transfer efficiency and can avoid the use of liquid electrolytes.[317]

In recent years, electrocatalytic palladium membrane reactors (ePMRs) have played an important role in the field of electrocatalytic hydrogenation and oxidation. ePMRs have the outstanding advantage of allowing good control of reaction conditions, such as freeing solvent selection in the hydrogenation chamber from the limitations of proton solvents, thus achieving higher substrate solubility while alleviating problems such as low FE and complex product separations.[157] Han et al.[318] reported for the first time a four-compartment device hydrogenation strategy using ePMR. This pioneering electrocatalytic double hydrogenation method utilizes water and formaldehyde as the hydrogen source, which allows the simultaneous hydrogenation and oxidation of the same organic substrate on both sides of the electrolytic cell. This approach not only saves voltage input but also achieves a theoretical maximum FE of 200%. In the work of Stankovic et al.,[319] 0.1 M FF in *tert*-butanol (*t*-BuOH) was used as the hydrogenation chamber electrolyte, 1 M H_2SO_4 solution was the anode electrolyte, and FF was converted to 2-methyltetrahydrofuran (MTHF) by electrocatalytic hydrogenation with high selectivity of 76% using a Pd membrane reactor. In contrast, the selectivity dropped to below 35% when using a H-cell. In their preceding study,[320] it was found that *t*-BuOH could inhibit byproduct formation and improve product selectivity, but it was inapplicable to the conventional H-cell.

5.2.2. PEM Electrolysis for LOHC Hydrogenation. *5.2.2.1. Benzene.* The coupling benzene hydrogenation and water electrolysis in PEM electrolyzers was first studied by Itoh et al.[321] They proposed that the positive voltage from the benzene hydrogenation (0.17 V) would decrease the external voltage requirement from 1.23 V of water electrolysis to a lower value.[13] Nafion 117 was roughened by sandpaper prior to soaking it in a Pt precursor solution. Then, the sample was reduced by treating with $NaBH_4$. Afterward, Rh coating was applied in the same way to realize a Rh−Pt electrode. Both water and benzene were humidified and fed with carrier gases prior to being fed to a finite-gap cell operating at 25−70 °C.

5.2.2.2. Toluene. Direct toluene hydrogenation toward methylcyclohexane was proposed in 2015 by Mitsushima et al.,[322] where the toluene hydrogenation voltage was 0.15 V. Different from the work of Itoh et al.,[321] toluene was fed to the electrolyzer without dilution. Nafion 212 membrane was selected as PEM, and a zero-gap electrolyzer cell was utilized. For this configuration, the performance of PtRu/C was found to be higher than Pt/C, where toluene is hydrogenated without HER up to 450 mA cm^{-2} at 2 V cell voltage.

Takano et al.[323] used a similar electrolysis setup. Given that the PEM cells usually do not include a reference electrode, the Pt/C catalyst on the anode can be implemented as a pseudoreference electrode. Subsequently, the catalysts of Pt/C, Rh/C, Ru/C, and PtRu/C were tested. It was hypothesized that better performance of PtRu/C catalyst could be due to dual functions such as the high catalytic activity of the rich adsorbed hydrogen on Pt and the strong toluene adsorption by Ru. Matsuoka et al.[322] used a high surface active area (25 cm^2) membrane electrode assemblies. By recirculating the cathode stream, the toluene concentration was decreased from 100 to 7.6% with PtRu/C catalyst. Other Pt alloy catalysts (Pt_3M, M = Rh, Au, Pd, Ir, Cu, and Ni) were investigated by Imada et al.[324] and Pt_3Rh/C performed better than commercial Pt/C.

Non-platinum catalysts were investigated by Inami et al.[325] in a finite-gap system with Nafion 117 membrane. Within Ru, Rh, Pd, Ir, and Au supported on Ketjenblack (KB), Ru/KB showed superior performance at low loadings. The synergy between Ru and Ir in alloy catalyst was further explained by the same group,[326] as well as the effect of different carbon supports.[327] A spontaneous deposition method was also applied by the same group for the selective deposition of Ir on Ru nanoparticles, allowing for control over the surface structure.[328]

5.2.2.3. Mass Transport. Rate-limiting factors of direct toluene hydrogenation were investigated in a PEM system containing a reversible hydrogen electrode. Polarization properties showed that the mass transfer for the cathode and the electron transfer process for the anode were crucial.[159]

In the work on optimization of the flow channel of the electrolyzer, superior performance of porous carbon (with no flow field) was reported. In comparison to parallel, interdigit, and serpentine channels, porous carbon performed better due to enhanced toluene transport and minimized charge transfer resistance, leading to higher efficiency and lower voltage requirements.[329]

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Nagasawa et al.[330] investigated the effect of PtRu/C catalyst loading on mass transfer. Thicker catalyst layers limited the mass transfer, whereas thin layers had an insufficient amount of catalyst. The optimum loading was found to be 1.4−1.6 mg cm^{-2}.

During direct methylcyclohexane (MCH), water is dragged from the anode to the cathode due to electro-osmosis phenomena. Shigemasa et al.[331] visualized this phenomenon with a transparent cell, showing the porous transport layer (PTL) at the cathode. In the following work of Reyna-Pena,[332] hydrogen bubbles inside the PTL were observed using X-ray computed tomography. Rib−channel and flat flow field plates (FFP) were compared. The rib−channel configuration was beneficial for reduced pressure drop and easy bubble removal even though hydrogen bubbles were trapped under the ribs. However, current efficiency was lower considering the higher distance of toluene feed to the catalyst layer. Flat FFPs, on the other hand, lower the distance to active sites, which can improve the toluene conversion.

5.2.2.4. Combining Electro- and Heterogeneous (Thermal) Catalysis. Nagasawa et al.[333] made use of H_2 bubbles to further increase the conversion by doping PTLs with Pt catalyst. This technology, called "direct MCH", is implemented by ENEOS, Chiyoda, and QUT.

5.2.2.5. Polycyclic Hydrocarbons. Polycyclic aromatic hydrogenation on PEM flow cells was studied by Tsyganok et al.[181] Reactions were performed in an electrochemical reactor configured with a Nafion 324 membrane. Sulfur-resistant tungsten disulfide (WS_2) on glassy carbon electrodes and Raney nickel cathodes were studied. The reactants were dissolved in a solution of ionic liquids butyl-3-methylimidazolium tetrafluoroborate ($BMIM{\cdot}BF_4$) and hexafluorophosphate ($BMIM{\cdot}PF_6$) and water, which served to provide high solubility, high conductivity, and protons for the electrochemical hydrogenation process. Current efficiency values and conversions were found to be insufficient.

6. CHALLENGES AND PERSPECTIVES

Even though intensive research has been conducted from the components (catalysts, electrolytes, and membranes), to the processes and reactors, there are still challenges to be addressed, and more work needs to be carried out to improve the performance. As the core, catalysts play an essential role in both ECH and ECO, and their challenges and perspectives were primarily discussed in this section.

6.1. Challenges and Perspectives of Electrocatalysts for ECH. *6.1.1. Stability and Durability of Catalysts.* One of the major challenges in ECH is the stability and durability of catalysts. Many catalysts, especially those based on transition metals and their compounds, can deactivate due to several factors: poisoning, surface oxidation, and structural degradation under harsh reaction conditions.

The support plays a crucial role in the stability of ECH electrocatalysts. This objective can be achieved by increasing the specific surface area, tuning the electronic structure, and optimizing adsorption behavior through surface functionalization.[334,335] Another strategy is to introduce stabilizers or dopant elements into the catalyst structure to enhance resistance to degradation, thereby maintaining the catalyst's stable performance over a long period.[175,336]

6.1.2. Selectivity Issues. Selectivity is another key challenge in ECH, especially when dealing with complex organic molecules. It is essential to attain high selectivity for the target product while minimizing side reactions to achieve an efficient and economically viable process. The reaction selectivity in ECH largely depends upon the adsorption energies of the reactants, hydrogen atoms, and products. Therefore, the selectivity of ECH reactions is greatly influenced by the surface properties and electronic structure of the catalyst, which can be tuned by modifying the electrocatalyst.

To improve selectivity, researchers have focused on tailoring the electronic and geometric structure of catalysts. This goal can be achieved through alloying, doping, or the design of nanostructured catalysts with specific active sites that favor certain reaction pathways.[106,116,337] Additionally, modifying reaction conditions, such as temperature, pressure, and solvent choice, can also help to enhance selectivity by influencing the reaction kinetics and the adsorption behavior of reactants on the catalyst surface.[113]

6.1.3. Scale-Up Challenges. While significant progress has been made in the development of catalysts for ECH at the laboratory scale, scaling up these processes for industrial applications presents numerous challenges. One of the primary difficulties is maintaining the activity, selectivity, and stability of catalysts when transitioning from small-scale experiments to large-scale production. The performance of a catalyst can be significantly affected by changes in reactor design, feedstock purity, and process conditions.

Moreover, the synthesis and processing of catalysts on a large scale can introduce additional challenges. For instance, the reproducibility of nanostructured catalysts, which often exhibit excellent performance at the lab scale, can be difficult to achieve when produced in bulk quantities. Additionally, the cost and availability of catalyst materials can become limiting factors as the demand increases for large-scale applications.

6.1.4. Recent Advances and Innovations. Despite the challenges, recent advances in catalyst design and fabrication have shown promise in addressing some of the limitations associated with ECH. The development of hybrid and composite catalysts, which combine the advantages of different materials, has led to improvements in both catalytic activity and stability. Furthermore, the exploration of novel catalytic materials, such as metal−organic frameworks (MOFs)[120,338] and single-atom catalysts,[339−341] has opened up new avenues for enhancing selectivity and durability in ECH. These materials offer unique structural features and active sites that can be precisely tuned to target specific reactions, making them highly attractive for future development in electrocatalysis.

6.1.5. Advances in In Situ Characterization Techniques. In situ characterization allows for real-time observation of changes in catalyst structure and morphology, as well as the formation of reaction intermediates, revealing transient reaction mechanisms. *In situ* X-ray absorption near edge structure (XANES) can identify changes in catalyst sites during the ECH process. Wang et al.[342] used an *in situ* XANES electrochemical cell to reveal the promotion of competitive adsorption of acetylene relative to hydrogen on optimized Cu particle catalysts (Figure 7).

In situ Fourier transform infrared spectroscopy (FTIR) can be used to identify adsorbed species and observe the formation of reaction intermediates on the catalyst surface during the ECH process. Zhou et al. successfully tuned the electronic properties of PtNi nanoparticles through B-doping and utilized *in situ* FTIR to track the ECH of guaiacol on the catalyst.[343]

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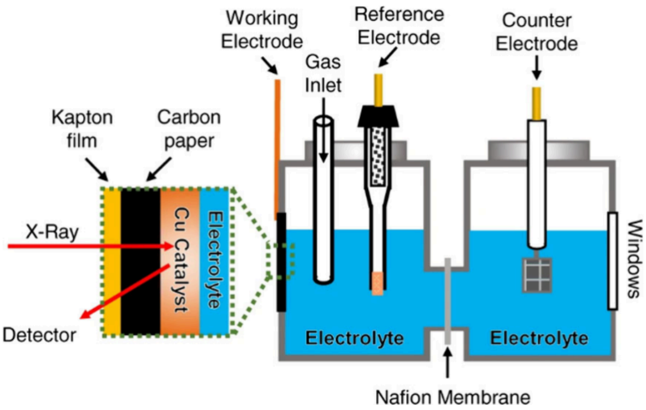

Figure 7. Schematic illustration of an *in situ* XANES electrolytic cell. This figure was reproduced with permission from ref 342. Available under a CC-BY 4.0 license (http://creativecommons.org/licenses/by/4.0/). Copyright 2021 Suheng Wang.

6.1.6. Potential Directions for Research. As the field of ECH continues to evolve, several promising research directions are emerging that could significantly enhance the efficiency, selectivity, and sustainability of this technology. One critical area of focus is the design and development of new catalyst materials that are both highly active and durable. The exploration of earth-abundant and non-toxic materials is essential to make ECH more economically viable and environmentally friendly. For example, further studies on transition-metal-based catalysts, such as iron, cobalt, and nickel, could yield catalysts with improved performance while reducing reliance on rare and expensive noble metals.

Another promising direction is the use of advanced computational methods and machine learning to predict and optimize catalyst performance.[130] By integrating theoretical modeling with experimental data, researchers can accelerate the discovery of novel catalyst compositions and structures with tailored properties for specific reactions. This approach not only shortens the development cycle but also provides deeper insights into the underlying mechanisms of ECH.

6.1.7. Emerging Trends and Technologies. The development of advanced catalysts is at the heart of the evolving field of ECH. Several emerging trends and technologies are focused on creating more efficient, durable, and scalable catalysts that can meet the demands of industrial applications.

6.1.7.1. Single-Atom Catalysts (SACs). One of the most promising trends is the development of SACs. These catalysts consist of individual metal atoms dispersed on a support material, offering maximum atom utilization and unique active sites. SACs are gaining attention due to their ability to catalyze specific reactions precisely and with high efficiency and selectivity. In the ECH processes, SACs have shown the potential to improve reaction rates while minimizing the use of expensive metals, making them an attractive option for both academic research and industrial applications. Their application extends to selectively hydrogenating complex organic molecules, which is a significant challenge in traditional catalysis.

6.1.7.2. Metal–Organic Frameworks (MOFs). MOFs represent another cutting-edge technology in catalyst development. They are highly porous materials composed of metal ions coordinated to organic ligands, creating a flexible and tunable structure. These materials can be designed to feature specific active sites and pore sizes, which can accommodate reactants and promote selective hydrogenation reactions. The versatility of MOFs makes them ideal candidates for ECH, where their structural properties can be optimized for different reaction environments. Moreover, MOFs (or the materials obtained from their pyrolysis) can support other active catalytic species, enhancing their stability and reusability in continuous processes.

6.1.7.3. Doped and Functionalized Carbon Materials. Doping carbon materials with heteroatoms (such as nitrogen, sulfur, or boron) or functionalizing their surfaces with various groups is another promising strategy. These modifications can significantly alter the electronic properties of carbon catalysts, enhancing their interaction with reactants and improving catalytic performance. For instance, nitrogen-doped graphene has shown enhanced catalytic activity in hydrogenation reactions, attributed to the altered electron distribution and increased active sites. These doped carbon materials are not only cost-effective but also offer a sustainable alternative to traditional metal catalysts, especially in applications requiring large-scale production.

6.1.7.4. In Situ Characterization and Real-Time Monitoring. Advancements in *in situ* characterization techniques, such as *in situ* FTIR and X-ray absorption spectroscopy, are providing deeper insights into catalyst behavior during ECH. These techniques allow for real-time monitoring of reaction intermediates and catalyst surface changes, enabling researchers to fine-tune catalyst design and reaction conditions for optimal performance. The integration of these analytical tools into industrial systems could lead to more efficient and adaptive ECH processes, ensuring consistent quality and performance across large-scale applications.

6.2. Challenges and Perspectives of Electrocatalysts for ECO.

6.2.1. Challenges. Despite these advancements, a leading anode remains elusive in both glucose and furanic compound electro-oxidation. Moreover, the studies are more challenging due to the irreproducibility of some reported results, hindering progress and the development of effective anodes for the ECO applications. Despite extensive research on ECO, there is a notable absence of specific studies dedicated to the electro-oxidation of lignin-derived molecules, and the support of current studies regarding mechanistic insights is minimal. On the basis of the above, the design of the anodes for ECO of lignin-derived molecules requires a great effort from the scientific community. Although, as reported at the beginning of this paragraph, the literature is limited to the total electrocatalytic oxidation of organic molecules even structurally similar to lignin derivatives, such as phenols, studies on the modification of the used electrocatalysts as well as on the modulation of the reaction conditions could represent a starting point for the development of anodes.

6.2.2. Perspectives. To realize efficient electrocatalysts, it is important to improve the intrinsic catalytic activity of active sites and maximize the active site availability. Adjusting the electronic structure of catalyst active sites via heterojunction construction, facilitating electronic transfer between the active site and substrate, introducing heteroatomic doping, and creating vacancies make it possible to improve the catalytic activity. Through these strategies, a better adsorption/desorption process between the reagents and the electrocatalysts could be achieved by improving the overall thermodynamic efficiency of the reaction. Another critical factor is to maximize the number of active sites, which is important for electrooxidation processes including multielectronic organic substances. The use of a 3D structure can lead to major exposure of active sites, enhancing catalytic performance.[73]

6.2.3. Two Special Electrocatalysts. The electrocatalytic behavior of two different classes of electrocatalysts employed in the complete oxidation of phenols, based on TiO_2 nanostructures and boron-doped diamond (BDD) structures, deserves to be analyzed to guide the design of anodes for the selective oxidation of lignin-derived molecules. Different electrochemical systems based on TiO_2 have been used in the last decades for the degradation of phenols due to their high catalytic activity, chemical stability, and durability.[344−346] The use of such anodes leads to a decrease in the consumption of power for oxygen formation due to the high oxygen evolution potential on TiO_2.[347] Anodes based on titanium-supported coating of noble metal oxides induce a pathway of phenol oxidation that leads to the formation of quinone-like species, followed by further oxidation to organic acids favored at low potential and high phenol concentration. However, this last condition can induce the polymerization of these compounds.[348] Jin et al. highlight the importance of 3D space in TiO_2/activated carbon fibers (ACF) and TiO_2/ACF−graphite anodes to increase the contact area between phenol and electrode.[349] The high capability to adsorb hydroxyl radicals induced by the presence of TiO_2 nanostructures compared to ACF−graphite anodes leads, besides CO_2, also a set of aromatic intermediates, such as hydroquinone, pyrocatechol, and benzoquinone, which can undergo a further hydroxylic radicals attack to form maleic acid and formic acid. The observed behavior suggests that the limitation of the adsorption capacity, for example, on a two-dimensional (2D) TiO_2 structure, which provides only restricted adsorption sites,[347] could prevent the complete mineralization of the aromatic intermediates formed, favoring the partial oxidation products. Moreover, the chemical doping of TiO_2 2D nanostructures could affect the nature of the generated active surface oxygen species.

Boron-doped diamond thin film electrode (BDD), due to the wide potential windows in aqueous and non-aqueous solutions, good stability and corrosion resistivity have also been widely employed for the complete electrochemical oxidation of phenols in acidic media.[350] The high local concentration of hydroxyl radicals on the BDD surface leads to the total oxidation of phenol to CO_2 operating at high current density and low phenol concentration. Also, in this case, the partial oxidation of phenol to other aromatics compounds, e.g., benzoquinone, hydroquinone, and catechol, is observed at low current density and high phenol concentration. Thus, the local concentration of oxygen species represents a key parameter, which can be controlled through a chemical modification of the electrocatalyst as well as the operating conditions, e.g., applied potential and the concentration of oxidizable species.[349]

6.3. Challenges and Perspectives from Other Aspects.

6.3.1. Electrolytes. For an ideal electrolyte, it must first have excellent conductivity to effectively shuttle charges between electrodes, so as to promote the electrocatalytic reaction. In addition, the electrolyte needs to have high solubility to effectively dissolve the organic substrate and improve the high dispersion of reactants, thereby improving the reaction rate and ensuring a more efficient catalytic process. Also, the electrolyte needs to be stable in the electrocatalytic process and cannot react unnecessarily with reactants or products to avoid product pollution. It is also necessary to consider the environmental friendliness of electrolytes and avoid the use of toxic substances to minimize the impact on the environment. The recycling of electrolytes is another concern to reduce costs. All these requirements make it challenging to develop advanced catholytes. Even though ILs/DESs have been proposed as promising electrolytes, their relatively high cost, the limited studies on their environmental impact, as well as their recycling are essential concerns, which need further investigation. Also, in general, adjusting the electrolytes to improve the performance was always studied together with the specific catalysts, and how to clarify the role and contribution of electrolytes themselves is worthy of study. Also, for anolytes, high concentrations can exacerbate the oxidation process, leading to significant carbon loss and reduced selectivity of the target product. As a result, most studies were conducted with low electrolyte concentrations to achieve high product selectivity. However, industrial production demands high product concentrations, which is beneficial for reducing the cost of product separation. Therefore, it is essential to select a suitable electrolyte to improve the FE and the selectivity of the target product, which is crucial for the industrial application of electrocatalytic oxidation of biomass molecules.

6.3.2. Others. From the aspect of electrocatalytic regeneration of LOHC by hydrogenation, the main challenges are to improve the process performance and achieve a long-term stable operation. Also, producing renewable LOHC is another concern. Concerning the membrane, the long-term durability of ion-exchange membranes under operational conditions is still mostly untested, particularly for applications with organic molecules. Increased crossover of reactants and byproducts over time can diminish overall system efficiency. Finally, for the overall device, similar to its components of catalysts and novel electrolytes, there are challenges in scaling up, such as the optimization of electrolyzer design, energy management, and cost control, calling for long-term research and development.

7. CONCLUSION

This review summarizes the research progress related to this new concept of electrocatalytic production of liquid organic hydrogen carriers with anodic valorization of the process. At the same time, it presents the challenges and opportunities, but also the complexity of the many aspects to be taken into account. The review also offers clues to open new directions in the highly active area of electrocatalytic technologies for the low-carbon production of fuels and chemicals.

Specifically, the electrocatalytic processes, including the reaction processes of hydrogenation and oxidation and the main components of electrocatalysts for cathodes and anodes, membranes, and electrolyte solutions, are briefly introduced. Subsequently, the electrocatalytic hydrogenation of liquid organic hydrogen carriers and electrocatalytic anodic oxidation are analyzed with respect to advances in terms of the single components: catalysts, membranes, and electrolyte solutions. Then, aspects related to the reactor and processes, as well as system integration and intensification, are commented together with the paired processes and reactors. Finally, the challenges and prospects are highlighted to show how this direction represents one of the crucial technologies for the future, even the many issues still to be solved. We hope, however, that this review, which derives from the joint contributions of the

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various researchers in the frame of the EU project EPOCH (grant 101070976), provides a firm foundation for developing the framework of electrocatalytic production of liquid organic hydrogen carrier with anodic valorization of the process, promoting the development and application of green hydrogen.

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■ NOMENCLATURE

BCN = boron−nitrogen co-doped carbon
BDD = boron-doped diamond
CAL = cinnamaldehyde
CNT = carbon nanotube
CO_2RR = carbon dioxide reduxtion reaction
DER = direct electro-reduction
DES = deep eutectic solvent
ePMR = electrocatalytic palladium membrane reactor
ECH = electrocatalytic hydrogenation
ECO = electrocatalytic oxidation
EHDC = electrochemical hydrodechlorination
EPOCH = electrocatalytic production of liquid organic hydrogen carrier and chemicals from lignin (EU project)
FDCA = 2,5-furandicarboxylic acid
FE = faradaic efficiency
FF = furfural
HER = hydrogen evolution reaction
HMF = 5-hydroxymethylfurfural
IL = ionic liquid
LDH = layered double hydroxide
LOHC = liquid organic hydrogen carrier
MCH = methylcyclohexane
MOF = metal−organic framework
OER = oxygen evolution reaction
PBI = polybenzimidazole
PCET = proton-coupled electron transfer
PFSA = perfluorosulfonic acid
PIL = proton ionic liquid
PTL = porous transport layer
RHE = reference hydrogen electrode
SAC = single-atom catalyst
SAP = sulfonated aromatic polymer
TOF = turnover frequency
XANES = X-ray absorption near edge structure

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