Materials Advances

REVIEW

View Article Online
View Journal

Cite this: DOI: 10.1039/d5ma01203a

Electrochemical coupling of lignin-derived phenolic valorization and green hydrogen production: a minireview

Asad Ali, *[ab] Leif J. Jönsson, [c] Xiaoyan Ji, *[d] Lovisa Byström[ab] and Reverant Crispin*[abe]

Lignin, the most abundant aromatic biopolymer in nature, is composed of phenylpropane units and represents a promising renewable source of aromatic chemicals for industrial applications. The valorization of lignin into bio-based chemicals through electrolyzers and upgrading technologies holds significant potential for developing environmentally and economically sustainable biorefineries. This minireview explores electrochemical hydrogen production coupled with alternative oxidation reactions that can replace the oxygen evolution reaction (OER), alongside discussions of lignin's structure, solubility, analytical methods, and the challenges of electrochemical depolymerization. Among various strategies, the electrocatalytic oxidation of lignin-derived phenolics has emerged as an environmentally benign approach, utilizing renewable electricity to drive reactions under mild and controlled conditions. Key topics include the development of efficient electrocatalysts for phenolic conversion and lignin-assisted proton exchange membrane electrolysis. Emphasis is placed on achieving high electrocatalyst activity, stability, and selectivity for effective lignin oxidation. Furthermore, challenges related to catalyst design, electrode materials, electrocatalytic systems, and process optimization are critically examined, along with potential pathways for improvement. This minireview highlights the opportunities and challenges in advancing electrocatalytic lignin valorization and provides perspectives on future developments in catalyst design and proton exchange membrane electrolysis integration to promote sustainable biomass utilization in accordance with green chemistry principles.

Received 18th October 2025,
Accepted 15th January 2026

DOI: 10.1039/d5ma01203a

rsc.li/materials-advances

1. Introduction

The growing global population poses significant challenges to sustainable life on a planet with limited resources. The invention of sustainable technologies that allow effective use of renewable resources must go hand in hand with efforts to address the increasing dependence of society on nonrenewable petroleum, as well as the rising demand for fuels and chemicals.[1,2] Lignin, produced in large quantities through forestry and agricultural activities worldwide, stands out as an appealing, carbon-neutral, and non-edible starting material for the synthesis of bio-based materials and chemicals. Lignin, one of the three main organic constituents of the lignocellulose that makes up most of vascular plants. It holds significant potential as a feedstock for the synthesis of biobased products and represents the world's largest renewable source of aromatic building blocks.[3] Despite challenges arising from its complex and irregular structure, significant progress has been made in unlocking the value of this remarkable aromatic biopolymer. Advancements in innovative methodologies, including catalytic and biocatalytic depolymerization, are important for enabling the production of well-defined lignin-derived products with high yields.[4]

As lignin is considered the primary root of aromatic compounds, research aimed at improving its valorization processes has gained significant attention. Lignin depolymerization enables the production of various phenolic compounds.[5] Today, a range of chemical techniques are available for lignin depolymerization. Selective oxidation of the edges chains of lignin allows for the production of phenolic compounds, while preserving the integrity of its aromatic ring structure.[6] Additionally, the oxidation of functional groups on the edges chains

---

[a] Laboratory of Organic Electronics, Department of Science and Technology, Linköping University, Norrköping 60174, Sweden. E-mail: asad.ali@liu.se, reverant.crispin@liu.se
[b] Wallenberg Initiative Materials Science for Sustainability, Department of Science and Technology, Linköping University, Norrköping 60174, Sweden
[c] Department of Chemistry, Umeå University, Umeå, SE 901 87, Sweden
[d] Energy Engineering, Division of Energy Science, Luleå University of Technology, 97187, Luleå, Sweden. E-mail: xiaoyan.ji@ltu.se
[e] Wallenberg Wood Science Center, Department of Science and Technology, Linköping University, 601 74 Norrköping, Sweden

can yield aromatic alcohols, aldehydes, and ketones, with phenolic aromatic compounds receiving the most attention due to their high relevance.[7]

Over the past decade, electrochemical water splitting powered by renewable energy has emerged as a highly promising approach for producing high-purity hydrogen.[8,9] The sluggish kinetics of electrode reactions is particularly the four-electron oxygen evolution reaction at the anode, which incurs a substantial overpotential remain a major obstacle to the process.[10] Recently, the development of hybrid electrochemical water-splitting systems integrating thermodynamically favorable electro-oxidation reactions with hydrogen evolution at the cathode has enabled more energy-efficient hydrogen production.[11] Significant efforts have been devoted to leveraging advanced electrocatalysts and alternative anodic oxidation processes to attain very effective and economical hybrid water splitting for practical hydrogen production.[12]

Organic compounds can be electrocatalytically oxidized at the anode to get high value-added green chemicals and at the same time reduce the energy costs of hydrogen generation at the cathode. This approach put forward a promising method for coupling hydrogen production with the synthesis of valuable compounds.[13] From an economic perspective, if the selected feedstocks are readily available and inexpensive, their oxidation can yield high value-added chemicals, enabling the coproduction of upgraded electro-oxidation products and sustainable hydrogen fuel, provided energy conversion efficiency is optimized.[14]

Lignin depolymerization to produce high-value chemicals is an emerging and rapidly advancing field of research. In recent decades, numerous review articles have been published on lignin,[15,16] lignin solubility[17] and depolymerization.[18,19] However,

Asad Ali

Dr Asad Ali is a researcher in Linkoping university, Sweden. He received his PhD degree in chemical engineering and technology from Guangxi University, China, in 2022. Then he completed postdoctoral fellowship from the Division of Energy Engineering at Luleå University of Technology, Sweden. He has authored over 70 high-quality reviews and research articles. His research focuses on preparing nanomaterials and their applications for hydrogen production and biomass (lignin) conversion to valuable products.

Leif J. Jönsson

Prof. Leif Jönsson got PhD in Biochemistry from Lund University in 1994 on a thesis devoted to enzymes from lignin-degrading fungi. Postdoctoral studies in the USA and in Finland. Assistant professor and associate professor (docent, 2000) at Lund University/Lund Institute of Technology. Associate professor at Karlstad University 2001–2008. Professor at Umeå University 2008–presently, with laboratories at KBC Chemical-Biological Center in Umeå and at High Coast Innovation Park in Örnsköldsvik. Research on biorefining of lignocellulosic feedstocks, wood processing, industrial biotechnology, and enzymes involved in degradation of lignocellulosic biomass.

Lovisa Byström

Lovisa Byström is a PhD researcher in the Laboratory of Organic Electronics at Linköping University, working under the supervision of Prof. Reverant Crispin. Her research focuses on developing electrochemical deoxygenation protocols using flow-cell systems.

Reverant Crispin

Prof. Reverant Crispin is a Professor at the Laboratory of Organic Electronics at Linkoping University, leading the unit of Organic Energy Materials. He obtained his BS and PhD degrees from the University of Mons, Belgium, and started to develop his own research group at Linkoping University as Marie-Curie and ERC fellow. He was awarded the Tage Erlander and Goran Gustafsson prizes by the Swedish Academy of Science for the work on organic thermoelectrics. His research interest is the use of organic materials in energy devices such as fuel cells and electrolysers, batteries, thermoelectric and piezoelectric generators.

increasing attention is being directed toward the oxidative coupling of lignin-derived phenolic compounds and the simultaneous generation of green hydrogen at the anode and cathode, respectively. According to our survey, no review article has yet comprehensively addressed the lignin-derived phenolic compounds oxidation coupling with green hydrogen production.

The principal objective of this minireview is to provide an overview of current lignin valorization technologies, with particular emphasis on depolymerization strategies and hydrogen production. We present a prime overview of different lignin types, solubility aspects, and depolymerization processes. Furthermore, this minireview delves into key topics, including lignin-assisted electrolysis, direct lignin electrolysis, lignin monomer conversion, phenol oxidation, toluene oxidation, and the development of optimal electrocatalysts. The electrocatalytic oxidation of lignin phenolic monomers using renewable electricity is considered a flexible and sustainable process due to its ability to operate under mild conditions with precise control over the progress of the reaction. To enhance the direct application of this process, the advancement of more effective electrocatalysts with remarkable performance, selectivity, and stability are highly recommended. This critical review also examines key parameters including electrodes, catalysts, operational procedures, electrocatalytic systems, and additives, while addressing the challenges associated with the practical implementation of these technologies.

2. Lignin overview

This section will provide an overview of lignin, including an introduction to its structure, types of lignin, solubility, and depolymerization.

2.1 Lignin

Lignin, a phenylpropanoid complex polymer originated in the cell walls of vascular plants, has potential to serve as a major reservoir of renewable aromatic carbon atoms and is key for producing many bio-based chemicals, polymers, fuels, and materials. For instance, that any plants is composed of about lignin (15–25%), cellulose (38–50%) and hemicellulose (23–32%) (Fig. 1a and b). Lignin acts like a ''glue'' that binds cellulose and hemicellulose together, giving the plant rigidity, water resistance, and defense against microbial attack (Fig. 1c).

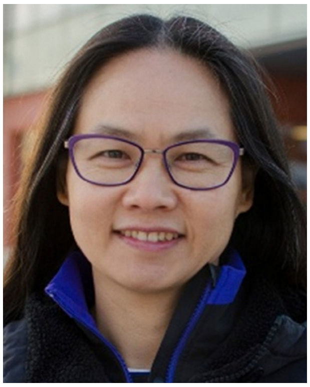
Comprising about 30% of the dry weight of lignocellulosic, the structure of lignin depends on the plant type.[20] Although other structural elements can occur, the three main lignin substructures are syringyl, guaiacyl, and *p*-hydroxyphenyl units. These substructures are derivative from combinatorial oxidative coupling of the corresponding *p*-hydroxyphenylpropene monolignols: sinapyl alcohol, which carries methoxy groups in positions 3 and 5, coniferyl alcohol, which carries a methoxy group in position 3, and *p*-coumaryl alcohol, which has no methoxy group (Fig. 1d).[21] Lignin from gymnosperms, such as conifers, is typically G-type lignin. Lignin from broadleaved trees (hardwood) is typically mixed GS lignin. Lignin subunits are interconnected with C–C and C–O–C (ether) bonds, among which β-O-4 ether bonds are the most common.[22] Whereas all monolignols are phenols, it is only a minor fraction of lignin subunits that are phenolic, as most phenolic hydroxyl groups have engaged in ether bond formation during the polymerization of monolignols to lignin. The phenolic groups in lignin are nevertheless important for its properties, affecting both solubility and reactivity.

Lignin is covalently bonded to hemicellulose, making lignin-carbohydrate complexes, and physically associated with cellulose, together creating a tightly integrated and recalcitrant structural network.[23] Thus, the method and conditions used to extract lignin will have a large impact on the structure, properties, and purity of the resulting lignin preparation. Common technical lignin preparations include hydrolysis lignin, kraft lignin (produced using the sulfate process), lignosulfonates (produced using the sulfite process), organosolv lignin, and soda lignin (Table 1). In an industrial context, chemical pulping procedures, such as the kraft process, the sulfite process, and the soda process, are the most common source of technical lignins.[24]

2.2 Lignin solubility

Lignin solubility is a critical factor in its characterization, extraction, and application across various domains. The use of solvents in industrial processes is indispensable due to their critical roles in dissolving solutes, facilitating separation and purification processes, and enhancing mass and heat transfer, among other functions.[29] Industrial operations often require substantial quantities of solvents, particularly when multiple types are needed to support various stages of the process. Consequently, solvent selection has a profound impact on the overall cost, safety, and environmental performance of a procedure.[30]

As a complex and heterogeneous aromatic polymer, the solubility of lignin is influenced by its basic structural properties, the preparation process, and the solvent system employed.



Xiaoyan Ji

Prof. Xiaoyan Ji got her PhD degree in Chemical Engineering in 2000 with more than 25 years of experience in research and development in the area of Chemical Engineering and Energy Engineering. She has taken part in projects in research groups in China, Sweden, Germany, and the US. Xiaoyan Ji started working at the division of Energy Science, Lulea University of Technology, in 2008. She created a research group on ''Advanced fluid materials for energy applications'', where CO_2 capture/separation, CO_2 electrochemical conversion, advanced electrolytes for batteries, and lignin conversion coupling H_2 production via electrochemical process are the focus.

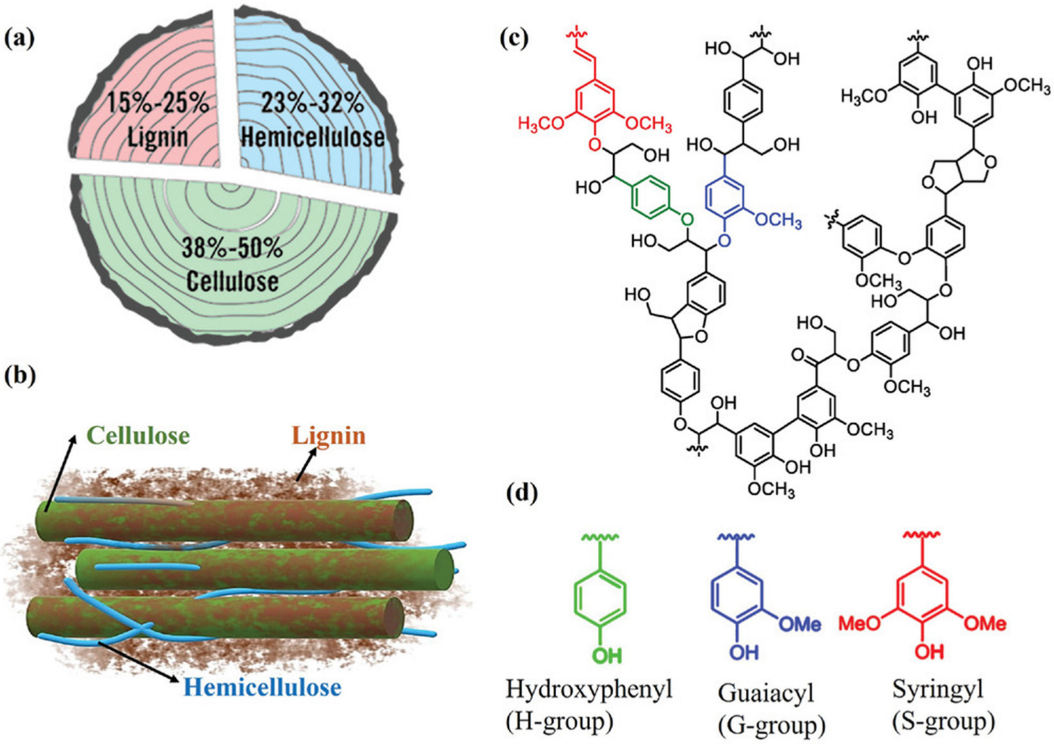


Fig. 1 (a) and (b) Schematic representations of lignin (lignin, cellulose, and hemicellulose are represented by red, green, and blue, respectively) are shown, while (c) and (d) depict the chemical structures of the corresponding monomeric units. Reprinted with permission from ref. 21. Copyright (2022), John Willy and Sons.

Table 1 Common types of technical lignin preparations

Lignin types	Extraction process	Chemicals, reagents	Optimum temperature (°C)
Hydrolysis-lignin[21]	Hydrolysis of cellulose and hemicelluloses, sulfur-free or sulfur-containing	Acids (commonly H_2SO_4), cellulolytic enzymes	Highly variable, typically in the range 150–230 °C.
Kraft-lignin[25]	Kraft process, sulfur-containing	NaOH + Na_2S	160–170
Lignosulfonates[26]	Sulfite process, sulfur-containing	HSO_3^-	140
Organosolv-lignin[27]	Solvent pulping, sulfur-free	Organic solvents, such as short-chain alcohols	150–200
Soda-lignin[28]	Soda process, a type of alkali pulping, sulfur-free	NaOH	150–170

The lignin present in the plant cell walls is highly insoluble due to its cross-linked structure and strong association with cellulose and hemicellulose. To render lignin soluble, it must be separated using chemical, thermal, or enzymatic processes, yielding technical lignins such as kraft, lignosulfonates, or organosolv lignins. The solubility of these industrial lignins varies significantly depending on their molecular weight, functional groups, and degree of condensation.[17] Although lignosulfonates are an exception, common solvents for lignin solubilization include aqueous alkaline solutions, organic solvents (*e.g.*, ethanol, dioxane, acetone), eutectic solvents and ionic liquids. Alkaline conditions enhance the solubility by ionization through deprotonation of phenolic hydroxyl groups and by breaking of ether and ester linkages, while organic solvents and ionic liquids disrupt the intermolecular interactions of lignin. Chemical modifications, such as acetylation or sulfonation, can further improve solubility.[31] Through sulfonation, lignosulfonates are typically water soluble even under non-alkaline conditions. Understanding and optimizing lignin solubility is essential for its valorization, enabling its conversion into bio-based materials, chemicals, and liquid fuels, thereby advancing the role of lignin in a circular bioeconomy.

2.3 Lignin depolymerization

Lignin depolymerization is a vital process for converting the complex and abundant aromatic polymer present in plant cell walls into valued chemicals and fuels.[32,33] However, the low reactivity of lignin and its complex structure significantly limit its potential applications, with the majority of it currently being burned for energy production.[18] Consequently, lignin depolymerization is regarded as one of the primary challenges to unlocking its full utilization.

Techniques are broadly categorized into chemical, biological, thermal, and catalytic approaches. Thermal processes, such as hydrothermal liquefaction and pyrolysis, generate a diverse range of products but often lack selectivity. Chemical methods, including alkaline and oxidative treatments, employ harsh conditions to cleave these bonds, though they may lead to over-oxidation or incomplete depolymerization.[34] Depolymerization, which utilizes metal catalysts offers higher specificity under milder reaction conditions. Processes like hydrogenolysis and oxidative catalysis produce phenolic monomers, dimers, and other valuable compounds. Reductive routes have also gained considerable attention for electrochemical depolymerization. Reductive depolymerization strategies, which typically operate under milder conditions, offer clear advantages such as improved selectivity toward hydrogenated monomers and reduced formation of oxygenated by-products.[35] Reductive catalytic fractionation and reductive catalytic depolymerization are two process topologies currently being investigated in pilot-scale installations, with the aim of upscaling to industrial-scale implementation, as reported in a recent study by Brent *et al.*[36] In addition, biological methods using lignin depolymerization enzymes such as laccases and peroxidases, offer an environmentally friendly but slower alternative.[37]

Recent advancements have focused on enhancing selectivity, yield, and sustainability. Integrating depolymerization processes into biorefineries could enable efficient lignin valorization, reducing reliance on fossil-derived aromatic compounds and fostering a circular bioeconomy. Kaur *et al.*[38] concluded that lignin depolymerization yields a diverse range of aliphatic and phenolic molecules, with the composition influenced by both the lignin's origin and the extraction method, as shown in Fig. 2.

J. Kim *et al.*[39] reported concentrated sulfuric acid hydrolysis lignin denoted as CSAHL was depolymerized using catalyst. Compared to CSAHL, Kraft lignin (KL) is more readily depolymerized. Fig. 3 presents the quantification results of thirteen

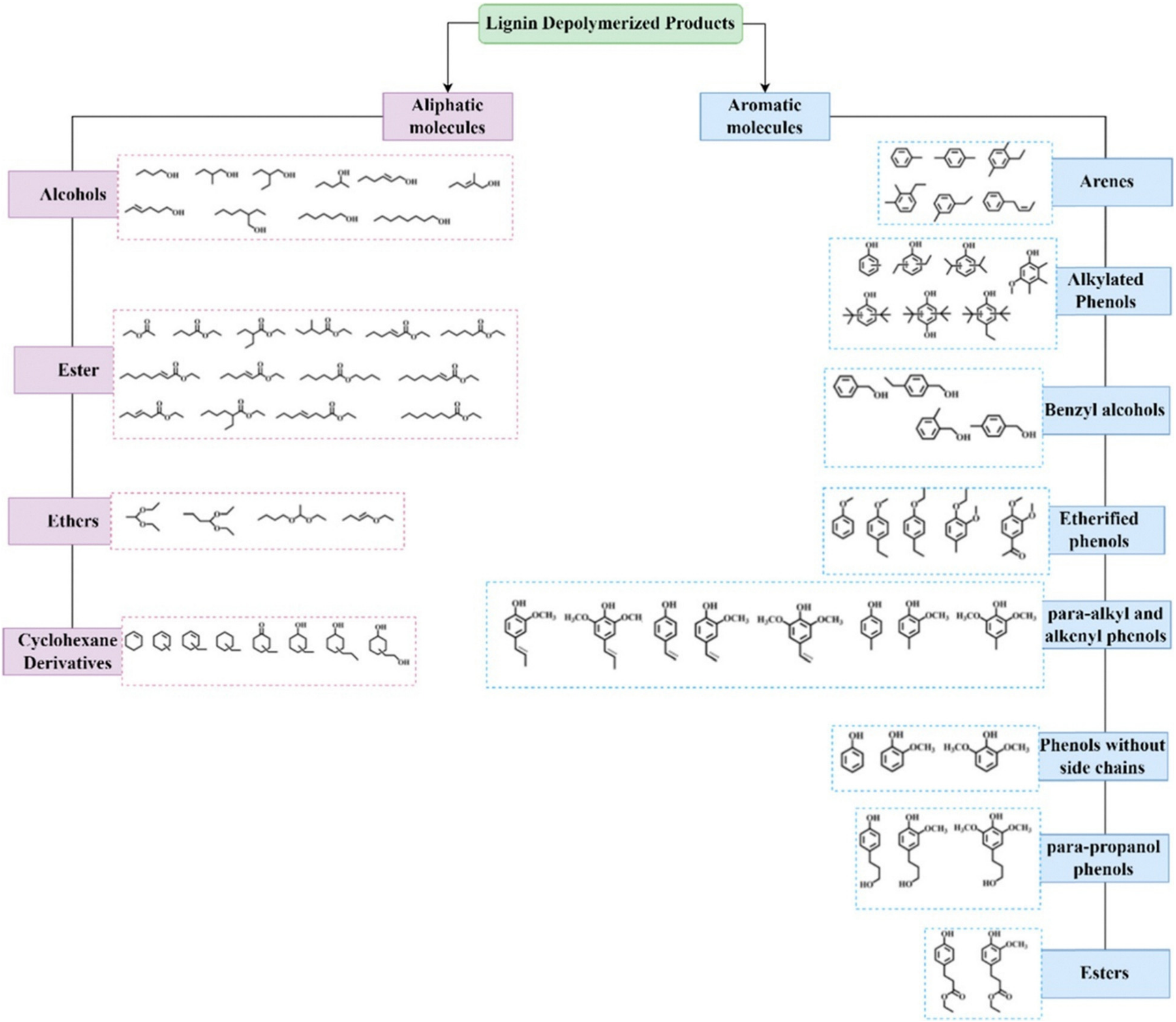


Fig. 2 Classification of lignin-depolymerized aliphatic and aromatic molecules. Reprinted with permission from ref. 38. Copyright (2025), American Chemical Society.

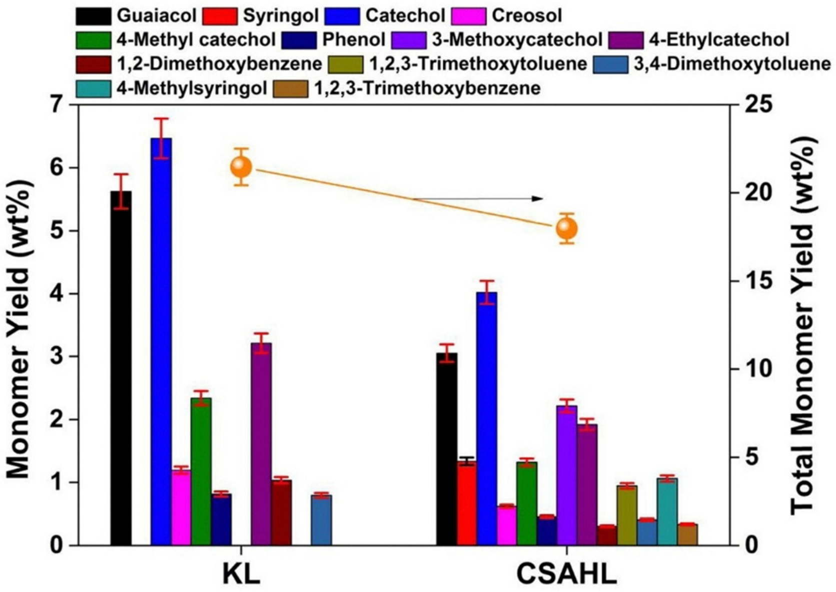


Fig. 3 Monomers yield derived from KL and CSAHL using catalyst. Reprinted with permission from ref. 39. Copyright (2017), Elsevier.

major compounds isolated from depolymerization products. The monomeric yields derived from base-catalyzed depolymerization were 21.5 wt% for KL and 17.9 wt% for CSAHL. Catechol and guaiacol were recognized as the primary aromatic compounds derived from both CSAHL and KL.

3. Direct lignin electrolysis

Direct lignin electrolysis is an emerging technique that utilizes electricity to transform lignin into valuable chemicals and fuels.[40] Traditionally appraised a low-value byproduct of the paper and pulp bioethanol industries, lignin contains a high density of energy-rich carbon–carbon and carbon–oxygen linkages, making it a promising feedstock for the production of sustainable chemicals.[41] In this process, lignin undergoes electrochemical oxidation at the anode of an electrolysis cell, where an applied electrical potential facilitates the selective cleavage of its linkages. The cathode complements this by carrying out reduction reactions, enabling energy-efficient operation.[42] The method is environmentally friendly, as it avoids the use of harsh chemical reagents and operates under relatively mild conditions. Direct lignin electrolysis produces valuable aromatic compounds, such as vanillin and syringaldehyde, while also generating hydrogen gas at the cathode, which can serve as a clean fuel. The selectivity of the process can be enhanced by optimizing catalysts, electrode materials, and reaction parameters.[43] This innovative approach aligns with green chemistry principles and offers a pathway to integrate renewable electricity into biorefineries. However, challenges such as the structural heterogeneity of lignin and the need for robust, efficient catalysts must be addressed to enable broader industrial adoption.[44] Electrochemical conversion of residual lignin driving out of biorefineries and pulp mills provides a sustainable alternate for producing industrial chemicals, offering greater control over the conversion process than thermochemical or catalytic methods, since the electrode potential and thus the reaction energetics can be precisely regulated.

According to Beliaeva *et al.*[45] electrolysis has emerged a highly effective alternative to conventional catalytic reforming techniques for hydrogen synthesis. Lignin electrolysis offers the potential to produce hydrogen with lower energy compared to conventional water electrolysis, while simultaneously repurposing lignin a low-cost biomass waste. Recent years have seen increasing research on the electrooxidation of lignin, especially utilizing nickel-based catalysts. Nickel is affordable metal, characterized by an extensive range of phase transitions and oxidation states, making it an ideal candidate for such applications. The electrooxidation of lignin and 2-phenoxyethanol compound that mimics the essential β-O-4 bond in lignin was investigated using a Ni/C catalyst.

The electrolysis of lignin contained alkaline slurry in continuous flow approach has been demonstrated for the first time using polymer electrolyte membrane-based reactors developed by Caravaca *et al.*[46] This innovative setup enables hydrogen production at the cathode with significantly lower potential (approximately 0.45 V) compared to traditional water electrolysis (Fig. 4a). The enhanced kinetics and conductivity provided by the polymeric membrane allow for optimal performance at elevated temperatures (below 90 °C), thereby maximizing electrolysis efficiency and hydrogen production. Cyclic voltammetry experiments reveal the electrooxidation of lignin at considerably lower voltage compared to potential required for oxygen evolution, highlighting its potential as an efficient process for hydrogen generation. In contrast to a commercial electrolyzer, Khalid *et al.*[6] investigated the electrooxidation of organosolv lignin in a 3D-printed reactor, employing platinum–nickel

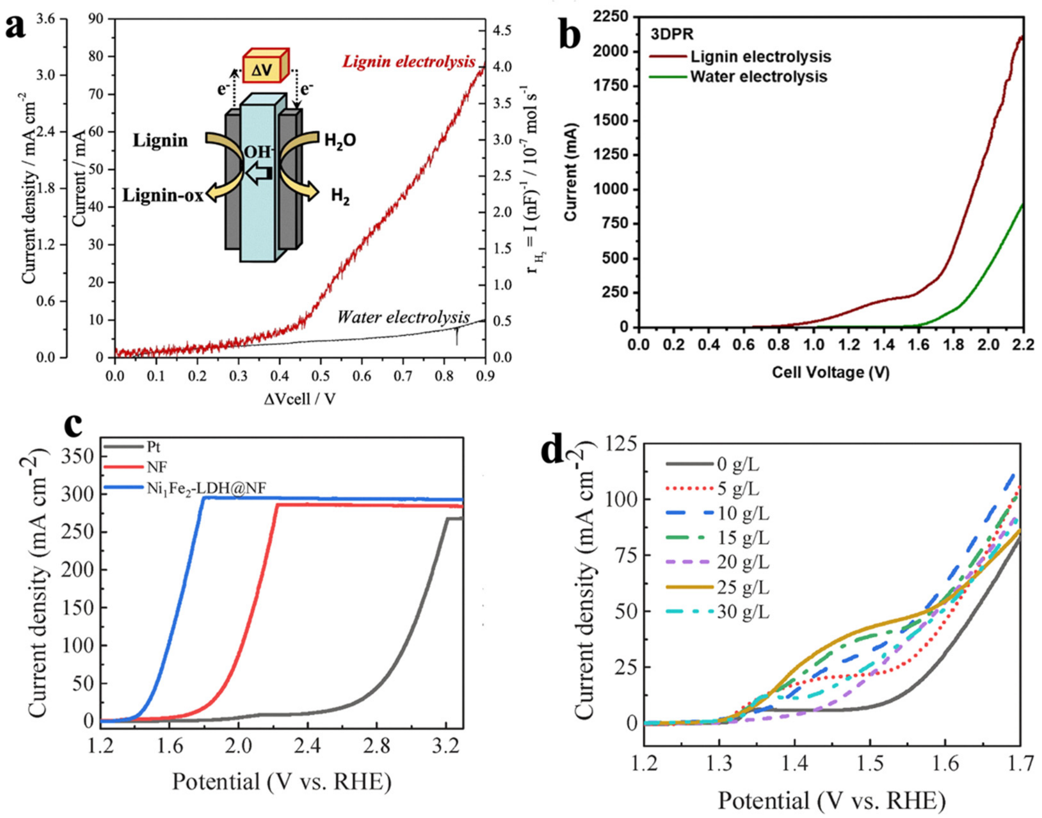


Fig. 4 (a) LSV curves of continuous lignin electrolysis and schematic illustration of reactor[46] (b) LSV curves for lignin and water electrolysis. Reprinted with permission from ref. 6. Copyright (2024), Elsevier. (c) LSV of lignin oxidation reaction (d) LSV of lignin oxidation reaction under different lignin concentrations. Reprinted with permission from ref. 7. Copyright (2024), Elsevier.

foam as both the cathode and the anode. The lignin electrolysis polarization curve significantly outperforms that of water electrolysis, exhibiting a current up to 2.8 times higher. The curve rises sharply from the starting voltage, achieving a maximum current of approximately 2100 mA. Interestingly, a voltage of 1.18 V was needed to sustain 100 mA current, compared to 1.77 V for water splitting at the same current (Fig. 4b). At the anode of the 3DPR, the lignin feed undergoes degradation, generating oxygenated species and releasing electrons. These electrons are subsequently used at the cathode to utilize water molecules and produce hydrogen. Notably, the cathode chamber of the 3DPR operates without electrolyte. Nevertheless, owing to the complex structure of lignin, elucidating a comprehensive reaction pathway based on charge transfer and redox processes remains a significant challenge. Ying *et al.*[7] combined computational and experimental approaches to investigate the relationship between lignin oxidation reaction kinetics and operating parameters in lignin-assisted water electrolysis for hydrogen production. They further demonstrated enhanced kinetics of the lignin oxidation reaction on a self-prepared, vertically produced nickel-iron layered double hydroxide nanosheet on nickel foam (Ni_1Fe_2-LDH@NF) electrode. The Ni_1Fe_2-LDH@NF electrode demonstrated exceptional activity, surpassing that of Pt and NF electrodes (Fig. 4c), thereby achieving significantly improved kinetics for the lignin oxidation reaction. Fig. 4d presents the LSV for the anodic lignin oxidation reaction at varying lignin concentrations.

The electrochemical oxidation of lignin using a cobalt core/platinum shell nanoparticle electrocatalyst was reported by Cabrera *et al.*[47] The findings indicates that the electrochemical oxidation of lignin generates valuable compounds such as apocynin and heptane. Certain oxidation products exhibit steadily increasing concentrations over time, suggesting that they are stable byproducts that do not undergo further transformation. In contrast, other products display a rise-and-fall concentration profile, indicating their involvement in subsequent chemical or electrochemical reactions. The identification of compounds such as 1,4-di-*tert*-butylphenol and 1,3-bis(1,1-dimethylethyl)benzene further suggests that hydroxyl radicals, most likely generated at the anode, act as key catalysts in the oxidative degradation process.

4. Electrocatalytic oxidation of phenolic compounds

The electrocatalytic oxidation of lignin-derived phenolic compounds at the anode offers an innovative approach to valorize biomass and address environmental challenges. Common

Table 2 Electrocatalytic phenolic oxidation to form valuable compounds

Phenolic compounds	Electrocatalysts	Electrolytes	Products	Ref.
Phenol	Ni_9S_8–$Ni_{15}O_{16}$/NF	1 M KOH	Benzoquinone	49
Phenol	NiFeB/CF	0.5 M H_2SO_4	Benzoquinone	50
Toluene	Graphite rod	Acetonitrile/HFIP	Benzaldehyde	51
Catechol	Pt/C@CP	0.3 M KOH	Benzoquinone	52
Benzyl alcohol	Carbon paper	Bu_4NBF_4 (0.20 mmol), CH_3CN/H_2O (1 : 1, 30 mL)	Benzaldehyde	53

phenolic compounds obtained from lignin include resorcinol, benzyl alcohol, toluene, catechol and phenol. During anodic oxidation, these compounds are transformed into valuable products such as, phenol oxidizes to benzoquinone and benzyl alcohol to benzaldehyde (Table 2). Concurrently, H^+ reduction at the cathode generates green hydrogen gas. Therefore, integrating electrocatalytic anodic oxidation with the production of high-value compounds from lignin derivatives offers a viable strategy to improve process economics, strengthen the linkage between the hydrogen and biorefinery sectors, and advance environmental sustainability.[48]

4.1 Phenol oxidation

para-Benzoquinone, which can be synthesized from the oxidation of phenol, is a versatile and essential compound with numerous applications, including its use as an industrial chemical feedstock for fungicides and dyes.[54] Additionally, *para*-benzoquinone is a favorable material for lithium-ion batteries due to its high theoretical specific capacity and voltage.[55,56] In the commercial market, *para*-benzoquinone holds significantly greater economic value compared to phenol, driven by its diverse and practical applications. Hydroquinone, another derivative of phenol, is a valuable compound widely utilized in cosmetics and pharmaceuticals.[57]

Liu *et al.*[58] reported a paired electrocatalytic approach for adipic acid production from lignin derivatives in a pH-asymmetric electrolyzer using water as the sole source of hydrogen and oxygen. Fig. 5a shows a schematic comparison between the current thermocatalytic method and the proposed paired electrolysis of lignin-derived aromatics to adipic acid. PtAu alloy catalysts are effective in reducing phenol into ketone-alcohol with 96% selectivity and 43% faradaic efficiency, whereas $CuCo_2O_4$ catalysts at the anode enable adipic acid production through ketone-alcohol oxidation with 85% yield and 84% faradaic efficiency. Theoretical and *in situ* electrochemical investigations reveal that the improved adsorption and activation of reactants on the cooperative bimetallic electrocatalysts are responsible for the superior catalytic efficiency. Even in a scaled-up two-electrode flow electrolyzer, 2.1 V cell voltage is needed to deliver a current of 2.5 A for gram-scale phenol to adipic acid electrosynthesis with a 38.5% yield and 70.2% selectivity, as well as excellent long-term stability over 200 h. This study provides a green and sustainable paired electrocatalytic strategy for adipic acid production.

Liu *et al.*[59] proposed a selective electrocatalytic phenol oxidation method for the production of *para*-benzoquinone based on experimental results (Fig. 5b). In the first electrochemical step, phenol is oxidized to phenoxy radicals *via* a single-electron transfer mechanism. Through spontaneous free radical resonance, these phenoxy radicals lead to C–O bond cleavage (step I). The highly reactive radicals subsequently couple with a hydroxyl group derived from water to form an unstable intermediate, identified as a hydroquinone tautomer (step II). Further oxidation of this intermediate at the anode yields *para*-benzoquinone in a highly selective manner (step III).

To achieve a feasible reaction of two phenol with one water molecule, Wu and co-workers.[60] developed an integrated electrochemical method that produced cyclohexanone and benzoquinone with 100% atom efficiency. In this approach, phenol undergoes simultaneous electrocatalytic oxidation and reduction as paired half-reactions. The study introduced nitrogen-doped hierarchically porous carbon-supported bimetallic FeRu catalysts as highly efficient anode materials. Their excellent performance is ascribed to the limited adsorption capacity of Fe single-atom-decorated Ru nanoparticles for benzoquinone, which prevents excessive oxidation of the target product.

4.2 Resorcinol oxidation

Lignin-derived resorcinol oxidation *via* water electrolysis is a favorable green approach for valorizing lignin into value-added products. We searched the recent literature, but no direct electrochemical systems have been reported in which resorcinol oxidation is coupled with hydrogen production. Most of the available literature focuses on the oxidation of resorcinol for wastewater treatment rather than as a value-added half-reaction paired with hydrogen generation in a hybrid electrolyzer. Therefore, this research would be highly novel if resorcinol oxidation is coupled with hydrogen production. In the following, we provide some details regarding the electrochemical oxidation of resorcinol.

The resorcinol oxidation is a complex process, and approaches based on different mechanisms are suggested in the literature. Ngamchuea and co-worker[61] evaluated the oxidation of resorcinol by CV measurements and DFT calculation. DFT results indicated that resorcinol oxidation proceeds *via* an electrochemically irreversible $1H^+/1e^-$ process, followed by the irreversible products of electrochemically inert polymers, consistent with all experimental observations. In alkaline solution, resorcinol oxidation was proposed to follow a similar mechanism, except without H^+ transfer, rendering the process pH independent. Consequently, an alternative polymer formation

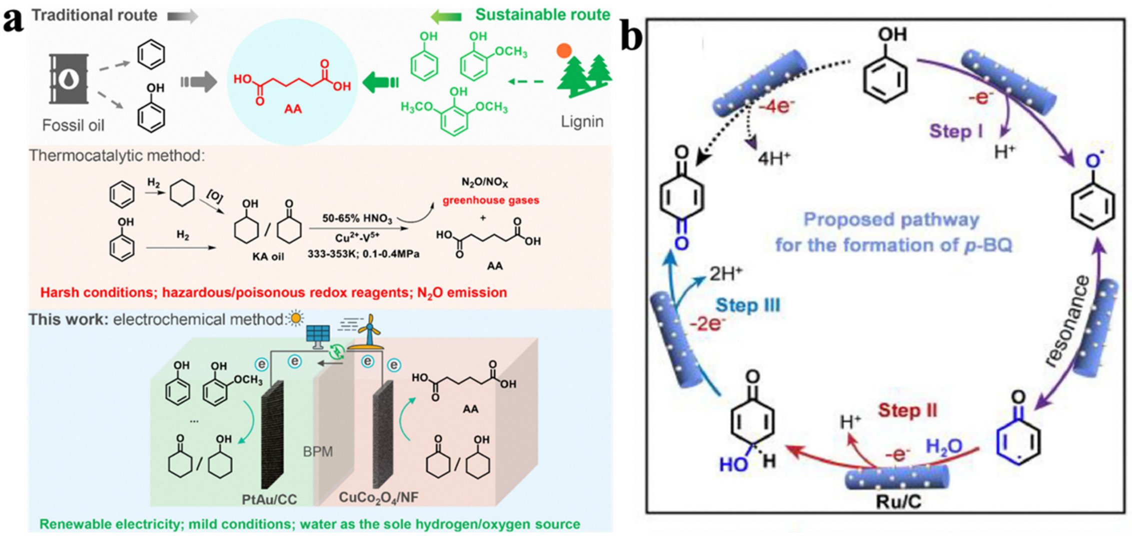


Fig. 5 (a) Comparison between the thermocatalytic method and the paired electrolysis of lignin-derived aromatics to adipic acid (AA) Reprinted with permission from ref. 58. Copyright (2024), American Chemical Society. (b) Proposed pathway for oxidation of phenol to *p*-benzoquinone. Reprinted with permission from ref. 59. Copyright (2024), Elsevier.

pathway *via* radical generation was explored computationally (Fig. 6a).

Fabri *et al.*[62] developed 3D-printed electrochemical setup incorporating sensors based on carbon black/polylactic acid (CB/PLA) filaments for the *in situ* detection of resorcinol in water. As shown in Fig. 6b, the treated electrode (red line) displays a distinct oxidation peak at approximately +0.715 V, along with a secondary, less intense peak at +1.15 V. The inset of Fig. 6b depicts the oxidation mechanism, which involves a two-electron, two-proton transfer. In contrast, the untreated electrode shows only the first oxidation peak at a higher potential (+0.95 V) and with much lower intensity (17.7 μA, roughly fourfold lower than the treated surface), highlighting the effectiveness of the treatment in enhancing resorcinol oxidation at the CB/PLA electrode surface.

4.3 Toluene oxidation

One of the most significant industrial processes today is the oxidation of toluene, which transforms this simple aromatic hydrocarbon into high-value compounds such as benzyl alcohol, benzaldehyde, benzoic acid, and benzoates.[63] The oxidation products are valuable compounds with broad applications in daily life, underscoring the importance of this process. Notably, toluene can be electrochemically oxidized to benzaldehyde with high selectivity, even in the absence of organic mediators or metal redox catalysts. The selectivity of this reaction is strongly influenced by the choice of carbon anode material and the applied current.[64]

The toluene oxidation to benzaldehyde is extremely challenging, as benzaldehyde is significantly more susceptible to oxidation than toluene. Seo *et al.*[51] analyzed the

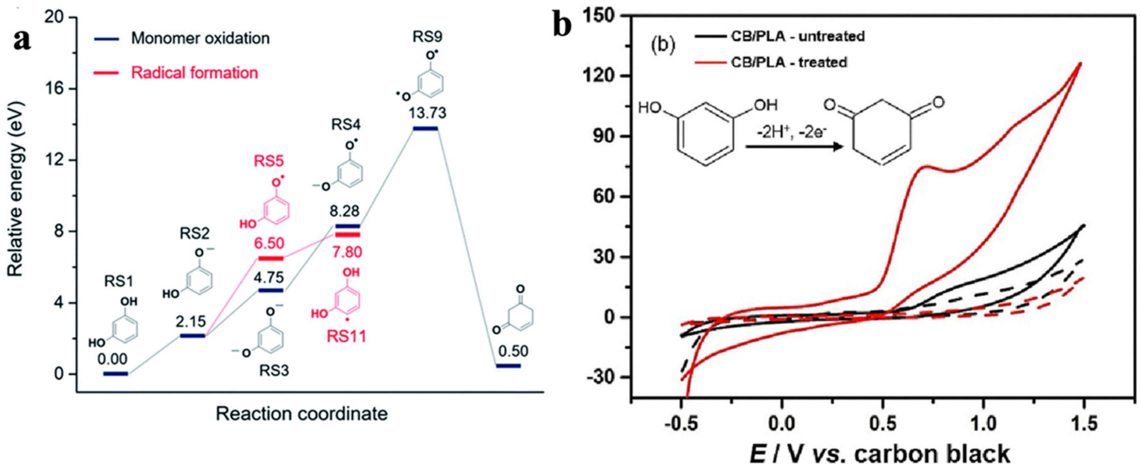


Fig. 6 (a) Potential energy diagram using the reaction energies of the possible mechanisms: radical monomer formation (red) and monomer oxidation (black). Reprinted with permission from ref. 61. Copyright (2024), The Royal Society of Chemistry. (b) Electrochemical oxidation of resorcinol. Reprinted with permission from ref. 62. Copyright (2023), Elsevier.

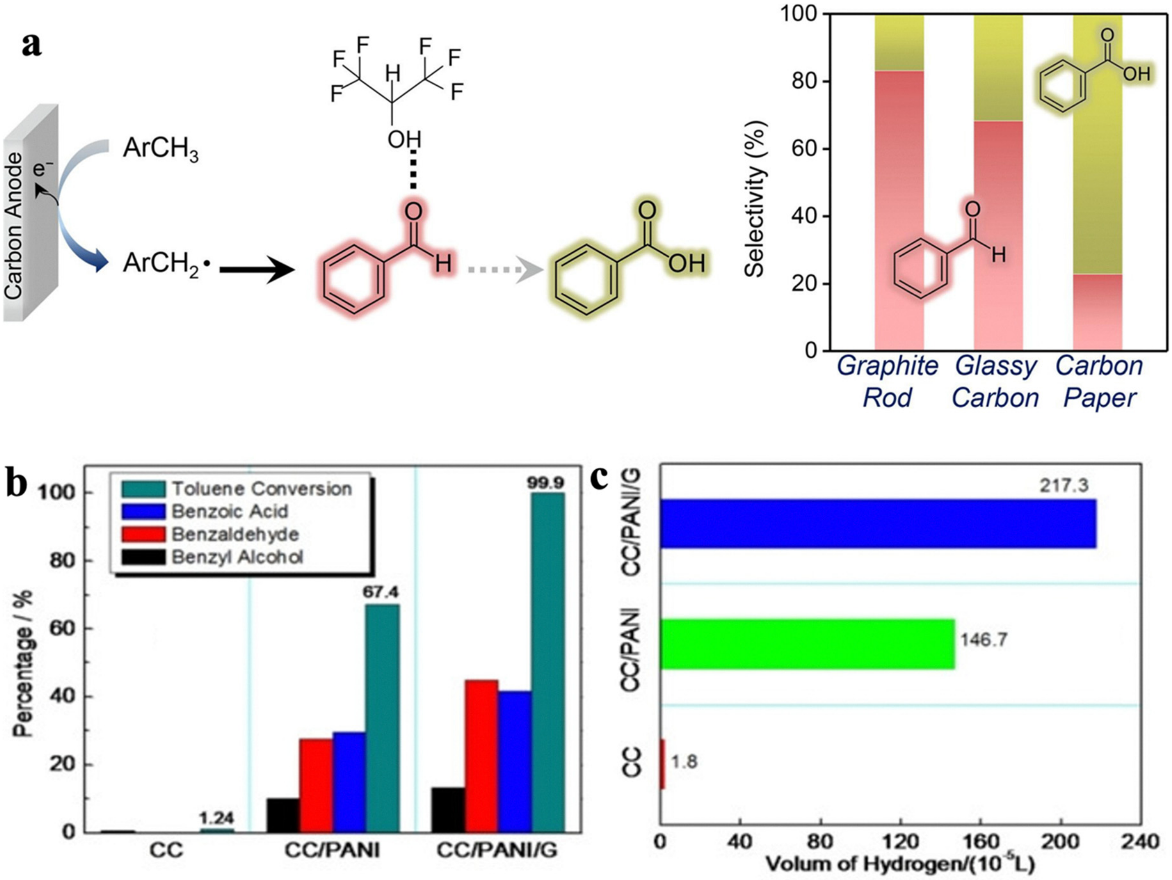


Fig. 7 (a) Electrochemical oxidation of toluene with selective control using graphite rod, glassy carbon, and carbon paper anodes. Reprinted with permission from ref. 51. Copyright (2020), Elsevier. (b) Yields of benzoic acid, benzaldehyde, and benzyl alcohol, along with the conversion of toluene methyl C–H bonds at CC, CC/PANI, and CC/PANI/G anodes during electrochemical toluene oxidation at a low applied voltage of 1.0 V. (c) Hydrogen volumes produced at the platinum cathode corresponding to CC, CC/PANI, and CC/PANI/G anodes during toluene conversion (10^{-5} L). Reprinted with permission from ref. 65. Copyright (2019), John Willy and Sons.

electrochemical toluene oxidation to benzaldehyde through direct electron transfer at a carbon anode (Fig. 7a). The electrode type and applied current were found to influence benzaldehyde selectivity, with a graphite rod achieving the highest value at 92%. This enhanced selectivity is attributed to the rod's large electrochemically active surface area and abundant defect sites, which preferentially adsorb benzaldehyde and suppress its further oxidation to benzoic acid. These findings demonstrate that readily available carbon anodes can be used to tune selectivity through the direct, non-mediated electrochemical oxidation of toluene. The approach not only offers high selectivity for benzaldehyde but also exhibits excellent stability in the reaction medium. Zhu *et al.*[65] developed a graphene-encased polyaniline nanoparticle film integrated with carbon cloth as an anodic electrocatalyst for the oxidation of methyl C–H groups in toluene. This system achieved an outstanding toluene conversion of 99.9% (Fig. 7b) at a low applied voltage of 1.0 V, with 86.6% of the methyl C–H groups selectively oxidized to benzoyl groups. Moreover, the process showed a strong correlation between high toluene methyl C–H conversion and enhanced hydrogen evolution at the cathode, yielding hydrogen production rates 120.7 times higher than those obtained with the unmodified carbon cloth (CC) anode (Fig. 7c).

4.4 Catechol oxidation

ortho-Benzoquinone, a key precursor in numerous chemical syntheses, is derived from catechol. Through a reversible reaction involving the release of two electrons, catechol can be converted into *o*-benzoquinone, which holds potential for fuel cell applications. Therefore, a highly efficient catalyst is essential to facilitate the conversion of catechol into *o*-benzoquinone.[66,67]

Kim *et al.*[52] proposed a spontaneous green hydrogen production device based on the catechol oxidation reaction, which simultaneously achieves saltwater desalination (Fig. 8). To optimize catechol degradation and maximize energy efficiency, the catholyte and anolyte pH values were adjusted to acidic and alkaline conditions, respectively. The electrochemical cell was divided into three compartments using two types of ion-exchange membranes: cation-exchange and anion-exchange. A sodium chloride buffer solution was introduced between the

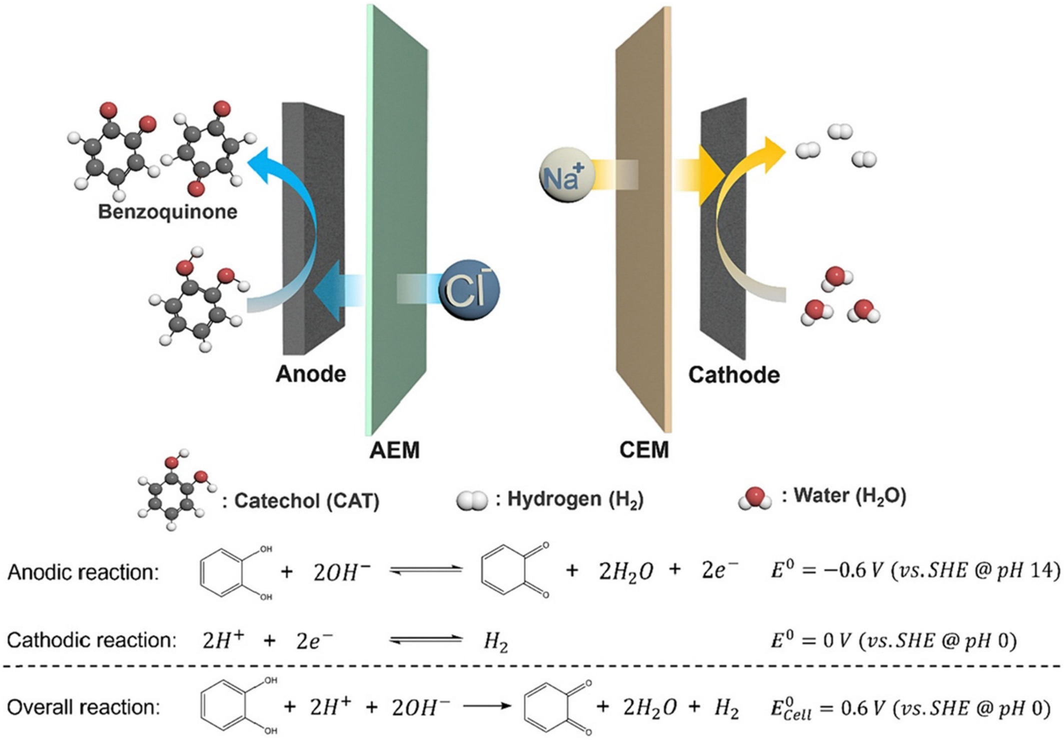


Fig. 8 Schematic illustration of desalination and redox reaction. Reprinted with permission from ref. 52. Copyright (2024), Elsevier.

membranes. Under these conditions, the system autonomously generated 4.2 mL h^{-1} of hydrogen while maintaining a constant current density of 5 mA cm^{-2} and an output power of 3.75 mA cm^{-2}, achieving a rapid desalination rate of 0.46 mg cm^{-2}·min.

4.5 Benzyl alcohol oxidation

Benzoic acid, a widely used intermediate in industrial manufacturing, is commonly produced through the oxidation of benzyl alcohol. However, traditional catalytic processes for alcohol oxidation often involve hazardous chemicals and harsh reaction conditions. In contrast, electrocatalytic alcohol oxidation utilizes less hazardous reagents and offers significant advantages in terms of reaction conditions. Under mild conditions, the electrooxidation of benzyl alcohol is considered a more environmentally friendly alternate to conventional methods for synthesizing benzoic acid.[68,69]

Wan *et al.*[70] investigated the benzyl alcohol oxidation performance of the N–Mo–Ni/NF electrode using a three-electrode configuration. Fig. 9a shows the linear sweep voltammetry curves of the N–Mo–Ni/NF electrode in electrolytes with and without 0.1 M benzyl alcohol. In the absence of benzyl alcohol, a voltage of 1.59 V (*vs.* RHE) is required to reach a current density of 100 mA cm^{-2} for the oxygen evolution reaction. In contrast, the presence of 0.1 M benzyl alcohol significantly enhances the current density, requiring only 1.338 V (*vs.* RHE)

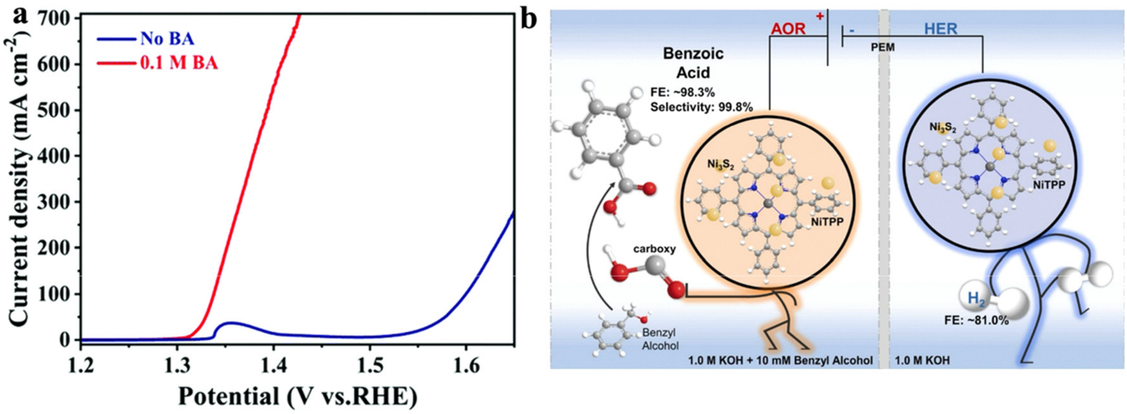


Fig. 9 (a) LSV curves of N–Mo–Ni/NF. Reprinted with permission from ref. 70. Copyright (2022), The Royal Society of Chemistry. (b) Schematic diagram of electrochemical alcohol oxidation to benzoic acid and hydrogen production. Reprinted with permission from ref. 71. Copyright (2024), Elsevier.

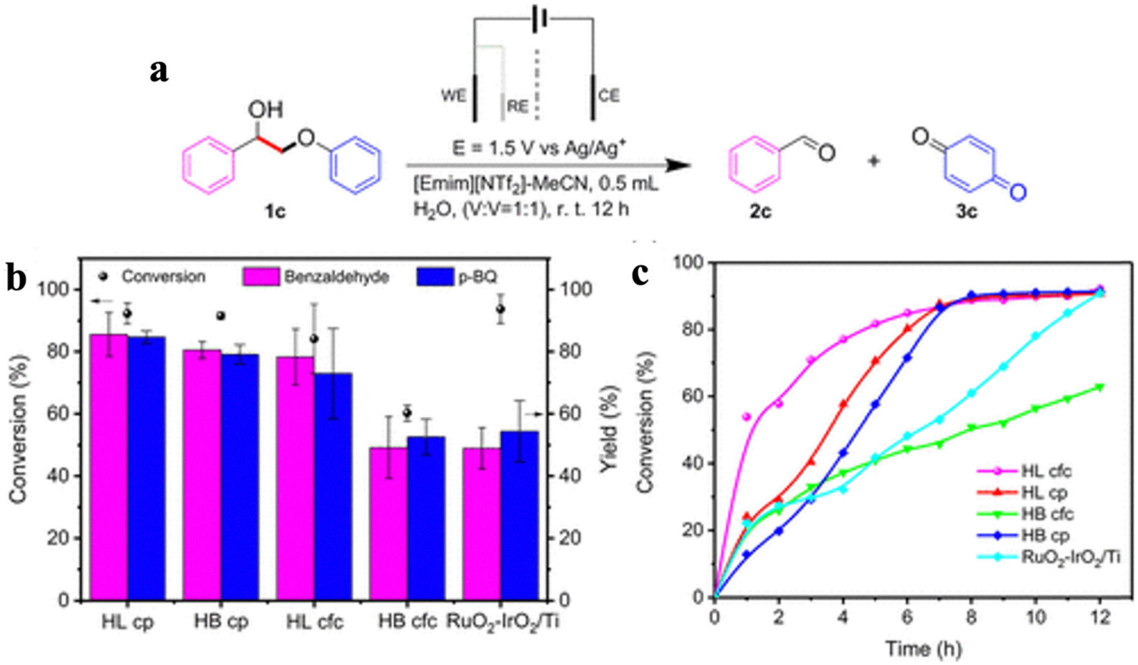


Fig. 10 (a) Electrocatalytic oxidation of the carbon–carbon bond. (b) Conversion rates and product yields obtained with different catalysts under identical conditions. (c) Reaction time profiles for various catalysts. Reprinted with permission from ref. 72. Copyright (2024), American Chemical Society.

to achieve 100 mA cm^{-2}. These results highlight the improved catalytic performance of the electrode in the presence of benzyl alcohol.

Begildayeva *et al.*[71] developed a highly selective and tunable electrocatalyst by combining single-phase Ni_3S_2, produced *via* pulsed laser ablation in liquids, with varying amounts of the nickel tetraphenylporphyrin (NiTPP) complex. The optimal composition, NiS-NiTPP10%, exhibited the highest activity and minimal overpotential. This catalyst significantly promoted alcohol oxidation, achieving a benzoic acid production rate of 2.23 mM h^{-1} cm^{-2} with 99.8% selectivity, 98.3% faradaic efficiency, and complete mass balance. The system operated at a reduced cell voltage of 193 mV compared to conventional water electrolysers and was effectively implemented in a NiS-NiTPP10%‖NiS-NiTPP10% electrolyser, enabling simultaneous hydrogen evolution and value-added benzoic acid production (Fig. 9b). This configuration reached faradaic efficiencies of 81% and 99%, with corresponding production rates of 0.42 and 4.03 mM h^{-1} cm^{-2}, respectively.

4.6 Phenolic dimers oxidation

The development of effective electrocatalysts for the oxidation of lignin-derived dimers *via* water splitting offers significant potential for chemical production and renewable energy applications. Researchers have demonstrated that tailored electrocatalysts can selectively oxidize lignin-derived dimers into high-value compounds using H-cell and flow cell systems. Flow cell configurations enhance scalability and efficiency through integrated water splitting, paving the technique for industrial purposes in biomass depolymerization and sustainable energy systems.

Liu *et al.*[72] explored the electrooxidation of lignin model compounds using a variety of commercially available electrode materials, including hydrophobic carbon fiber cloth (HB cfc), Hydrophilic carbon fiber cloth (HL cfc), Hydrophilic carbon paper (HL cp), Hydrophobic carbon paper (HB cp), and precious metal RuO_2–IrO_2@Ti, with the common ionic liquid electrolyte [Emim][NTf_2] (Fig. 10a). Remarkably, readily accessible carbon-based materials exhibited conversion ratios comparable to or even exceeding those of noble metal electrodes. This finding demonstrates that all five materials can degrade the lignin model compound to varying extents (Fig. 10b). A key observation is the production of benzaldehyde as the main byproduct, which can only result from the breaking of C–C bonds. This suggests that carbon materials have the potential for oxidative C–C bond splitting, a property traditionally attributed to noble metals. Among hydrophilic carbon electrodes, HL cfc exhibits superior catalytic performance, achieving the highest conversion rate within 6 hours, as evidenced by the reaction–time curves (Fig. 10c).

5. Conclusion and future perspectives

This critical review highlights recent advances in lignin valorization *via* electrocatalytic oxidation and related approaches, providing a comprehensive understanding of lignin's potential as a sustainable feedstock for chemical production. Key topics, such as electrochemical hydrogen production coupled with alternative oxidation reactions and types, structure, solubility, and depolymerization of lignin, have been thoroughly discussed to establish a foundational understanding of its complexity. The review highlights the adaptability and sustainability of lignin-assisted and direct lignin electrolysis, as well as the electrocatalytic conversion of lignin monomers, such as oxidation of resorcinol, benzyl alcohol, toluene, catechol and phenol. Electrocatalytic oxidation of phenolic lignin-derived monomers using renewable electricity emerges as a promising technology due to its mild reaction environments and tunable process parameters. Catalytic processes capable of producing high yields and selective products from pre-isolated lignin or lignocellulose could significantly advance the biorefinery concept. Oxidation pathways are strongly influenced by the type of electrocatalyst, its electronic structure, morphology, porosity, and surface chemistry. Electrocatalysts with high surface area and hierarchically porous structures, such as carbon felt, can modulate the adsorption energies of phenolic compounds and their intermediates, thereby enhance performance and enable targeted selectivity. Carbon-based materials function both as anodes and as support for catalysts. Surface properties also play a critical role. Furthermore, factors such as flow cell design, electrolyte composition, and ion-exchange membranes are key in regulating overall process performance and selectivity.

However, several challenges remain for lignin valorization *via* electrocatalytic oxidation and related approaches.

(1) Ionic liquids have shown strong potential to facilitate the oxidative conversion of lignin-derived phenolics into valuable aromatic platform chemicals. However, the broader potential of electrolytes such as ionic liquids for lignin processing remains far from fully realized. Future studies should focus on designing ionic liquids tailored to specific lignin substrates and oxidation pathways, enabling more scalable and energy-efficient processes. To fully leverage lignin as a renewable resource for green chemistry and sustainable energy applications, further research is needed to improve electrocatalytic systems, develop innovative ionic-liquid formulations, and address remaining challenges in product separation.

(2) Electrocatalyst fouling caused by polymeric intermediates is a major issue that reduces performance. Advances in novel catalyst materials, such as carbon-based electrodes, hybrid systems, and nanostructured materials, hold promise for enhancing product yields, improving selectivity, and reducing energy consumption. Developing effective and selective electrocatalysts tailored specifically for oxidation of lignin-derived monomers should be a top priority.

(3) The feed complexity associated with lignin oxidation and the challenges of product separation remain major barriers to scalable implementation. In addition to investigating oxidized lignin, researchers should prioritize strategies that address feed heterogeneity and develop product-separation technologies that are low-cost, energy-efficient, and environmentally sustainable. Furthermore, considering factors such as lignin type, the distribution of lignin-derived phenolic compounds, and physicochemical properties including viscosity and conductivity, there is a clear need for the design of novel reactor systems, particularly advanced flow-cell configurations tailored to the specific requirements of lignin processing.

(4) Scaling up lignin depolymerization processes from laboratory to industrial scales remains a critical challenge. For scalability, explicitly compare reactor configurations (H-cell, flow cell, 3D-printed) in terms of mass transfer efficiency and industrial applicability. Current research often lacks the complexity of large-scale operations, necessitating comprehensive characterization of scaled-up processes to ensure economic viability, process efficiency, and reproducibility. This effort will require cutting-edge analytical techniques and real-time monitoring systems, supported by interdisciplinary collaboration among chemists, engineers, material scientists, and industry stakeholders. Strengthening communication between academia and industry will be crucial for transforming laboratory-scale breakthroughs into scalable and practical solutions.

(5) Most of the available literature focuses on the oxidation of resorcinol for wastewater treatment rather than as a value-added half-reaction paired with hydrogen generation in a hybrid electrolyzer. Therefore, this research would be highly novel if resorcinol oxidation is coupled with hydrogen production.

(6) In addition, cross-membrane transport remains a significant challenge. Therefore, future research should prioritize the development and systematic evaluation of membranes that can effectively suppress species crossover while maintaining high ionic conductivity and chemical stability.

These collaborative efforts pave the way for a sustainable future in lignin valorization, enabling the production of green chemicals and the generation of renewable energy.

Author contributions

Asad Ali: writing original review article, conceptualization, investigation. Leif J. Jönsson: writing review and editing. Xiaoyan Ji: writing review, supervision. Lovisa Byström: editing. Reverant Crispin: writing review and editing, supervision, funding acquisition.

Conflicts of interest

The authors declare that they have no competing or financial interests.

Data availability

No primary research results, software or code have been included and no new data were generated or analysed as part of this review.

Acknowledgements

A. A., R. C., L. B. thanks the Knut and Alice Wallenberg foundation (Wallenberg Wood Science Center, WWSC), Wallenberg Initiative Materials Science for Sustainability (WISE), the Norrköping Fund for Research and Development, Swedish Government Strategic Research Area in Materials Science on

Advanced Functional Materials at Linköping University Faculty Grant SFO-Mat-LiU no. 2009-00971. X. J. thanks for the financial support from Horizon-EIC and Pathfinder Challenges, grant number 101070976. X. J. and L. J. thanks for the financial support from Bio4Energy.

References

1 R. Ding, J. Chen, Y. Chen, J. Liu, Y. Bando and X. Wang, Unlocking the potential: machine learning applications in electrocatalyst design for electrochemical hydrogen energy transformation, *Chem. Soc. Rev.*, 2024, **53**, 11390–11461.

2 A. Ali, A. Laaksonen, G. Huang, S. Hussain, S. Luo, W. Chen, P. K. Shen, J. Zhu and X. Ji, Emerging strategies and developments in oxygen reduction reaction using high-performance platinum-based electrocatalysts, *Nano Res.*, 2024, **17**, 3516–3532.

3 H. Liu, Y. Guan, L. Yan, Y. Zheng, C. Si and L. Dai, The development of lignin towards a natural and sustainable platform for optical materials, *Green Chem.*, 2024, **26**, 9281–9294.

4 Z. Yu, W. Kong, W. Liang, Y. Guo, J. Cui, Y. Hu, Z. Sun, S. Elangovan and F. Xu, Heterogeneously Catalyzed Reductive Depolymerization of Lignin to Value-Added Chemicals, *ChemSusChem*, 2024, e202401399.

5 Y. Tong, T. Yang, J. Wang, B. Li, Y. Zhai and R. Li, A review on the overall process of lignin to phenolic compounds for chemicals and fuels: From separation and extraction of lignin to transformation, *J. Anal. Appl. Pyrolysis*, 2024, 106663.

6 M. Khalid, B. S. De and S. Shahgaldi, Electrocatalytic lignin oxidation for hydrogen and fine chemical co-production using platinized nickel foam in a 3D printed reactor, *DeCarbon*, 2024, **6**, 100074.

7 Z. Ying, H. Sun, J. Cao, X. Zheng, B. Dou and G. Cui, Lignin oxidation reaction kinetics and its conversion into high-value chemicals over self-prepared electrode during lignin-assisted water electrolysis for hydrogen production, *Renewable Energy*, 2024, **237**, 121746.

8 A. Ali, F. Long and P. K. Shen, Innovative strategies for overall water splitting using nanostructured transition metal electrocatalysts, *Electrochem. Energy Rev.*, 2022, **5**, 1.

9 A. Ali and P. K. Shen, Nonprecious metal's graphene-supported electrocatalysts for hydrogen evolution reaction: fundamentals to applications, Carbon, *Energy*, 2020, **2**, 99–121.

10 A. Ali and P. K. Shen, Recent progress in graphene-based nanostructured electrocatalysts for overall water splitting, *Electrochem. Energy Rev.*, 2020, **3**, 370–394.

11 T. Wang, L. Tao, X. Zhu, C. Chen, W. Chen, S. Du, Y. Zhou, B. Zhou, D. Wang and C. Xie, Combined anodic and cathodic hydrogen production from aldehyde oxidation and hydrogen evolution reaction, *Nat. Catal.*, 2022, **5**, 66–73.

12 T. Gao, Q. An, X. Tang, Q. Yue, Y. Zhang, B. Li, P. Li and Z. Jin, Recent Progress in Energy-Saving Electrocatalytic Hydrogen Production *via* Regulating Anodic Oxidation Reaction, *Phys. Chem. Chem. Phys.*, 2024, **26**, 19606–19624.

13 T. Wang, X. Cao and L. Jiao, Progress in hydrogen production coupled with electrochemical oxidation of small molecules, *Angew. Chem.*, 2022, **134**, e202213328.

14 D. Si, M. Wang, X. Yang, C. Wang, K. Shi, B. Huang, L. Chen and J. Shi, Hydrogen anode/cathode co-productions-coupled anode alcohol selective oxidation and distinctive H/e transfer pathways, *Appl. Catal., B*, 2023, **331**, 122664.

15 F. G. Calvo-Flores and J. A. Dobado, Lignin as renewable raw material, *ChemSusChem*, 2010, **3**, 1227–1235.

16 L. A. Z. Torres, A. L. Woiciechowski, V. O. de Andrade Tanobe, S. G. Karp, L. C. G. Lorenci, C. Faulds and C. R. Soccol, Lignin as a potential source of high-added value compounds: A review, *J. Cleaner Prod.*, 2020, **263**, 121499.

17 E. Melro, L. Alves, F. E. Antunes and B. Medronho, A brief overview on lignin dissolution, *J. Mol. Liq.*, 2018, **265**, 578–584.

18 Z. Sun, B. Fridrich, A. De Santi, S. Elangovan and K. Barta, Bright side of lignin depolymerization: toward new platform chemicals, *Chem. Rev.*, 2018, **118**, 614–678.

19 N. Zhou, W. W. Thilakarathna, Q. S. He and H. V. Rupasinghe, A review: depolymerization of lignin to generate high-value bio-products: opportunities, challenges, and prospects, *Front. Energy Res.*, 2022, **9**, 758744.

20 C. Crestini, H. Lange, M. Sette and D. S. Argyropoulos, On the structure of softwood kraft lignin, *Green Chem.*, 2017, **19**, 4104–4121.

21 U. Ail, J. Nilsson, M. Jansson, I. A. Buyanova, Z. Wu, E. Björk, M. Berggren and X. Crispin, Optimization of Non-Pyrolyzed Lignin Electrodes for Sustainable Batteries, *Adv. Sustainable Syst.*, 2023, **7**, 2200396.

22 L. Shuai, M. T. Amiri and J. S. Luterbacher, The influence of interunit carbon–carbon linkages during lignin upgrading, *Curr. Opin. Green Sustainable Chem.*, 2016, **2**, 59–63.

23 D. Tarasov, M. Leitch and P. Fatehi, Lignin–carbohydrate complexes: properties, applications, analyses, and methods of extraction: a review, *Biotechnol. Biofuels*, 2018, **11**, 269.

24 O. Yu and K. H. Kim, Lignin to materials: A focused review on recent novel lignin applications, *Appl. Sci.*, 2020, **10**, 4626.

25 D. D. S. Argyropoulos, C. Crestini, C. Dahlstrand, E. Furusjö, C. Gioia, K. Jedvert, G. Henriksson, C. Hulteberg, M. Lawoko, C. Pierrou, J. S. M. Samec, E. Subbotina, H. Wallmo and M. Wimby, Kraft Lignin: A Valuable, Sustainable Resource, Opportunities and Challenges, *ChemSusChem*, 2023, **16**, e202300492.

26 T. Aro and P. Fatehi, Production and Application of Lignosulfonates and Sulfonated Lignin, *ChemSusChem*, 2017, **10**, 1861–1877.

27 B. Wang, X. J. Shen, J. L. Wen, L. Xiao and R. C. Sun, Evaluation of organosolv pretreatment on the structural characteristics of lignin polymers and follow-up enzymatic hydrolysis of the substrates from Eucalyptus wood, *Int. J. Biol. Macromol.*, 2017, **97**, 447–459.

28 M. Chen, Y. Li, H. Liu, D. Zhang, Q. S. Shi, X. Q. Zhong, Y. Guo and X. B. Xie, High value valorization of lignin as

environmental benign antimicrobial, *Mater. Today Bio*, 2023, **18**, 100520.

29 Q. Ma, C. Yu, Y. Zhou, D. Hu, J. Chen and X. Zhang, A review on the calculation and application of lignin Hansen solubility parameters, *Int. J. Biol. Macromol.*, 2024, **256**, 128506.

30 E. I. Evstigneyev and S. M. Shevchenko, Structure, chemical reactivity and solubility of lignin: a fresh look, *Wood Sci. Technol.*, 2019, **53**, 7–47.

31 J. V. Vermaas, M. F. Crowley and G. T. Beckham, Molecular lignin solubility and structure in organic solvents, *ACS Sustainable Chem. Eng.*, 2020, **8**, 17839–17850.

32 C. Chio, M. Sain and W. Qin, Lignin utilization: A review of lignin depolymerization from various aspects, *Renewable Sustainable Energy Rev.*, 2019, **107**, 232–249.

33 G. T. Beckham, C. W. Johnson, E. M. Karp, D. Salvachúa and D. R. Vardon, Opportunities and challenges in biological lignin valorization, *Curr. Opin. Biotechnol*, 2016, **42**, 40–53.

34 R. Roy, M. S. Rahman, T. A. Amit and B. Jadhav, Recent advances in lignin depolymerization techniques: A comparative overview of traditional and greener approaches, *Biomass*, 2022, **2**, 130–154.

35 N. Karanwal, S. Kim, Y. Liyanage, D. K. Lee and J. Kim, Highly efficient electro-reductive conversion of lignin into aromatics and cyclohexenes, *Appl. Catal., B*, 2025, 125851.

36 B. Daelemans, B. Sridharan, P. Jusner, A. Mukherjee, J. Chen, J. K. Kenny, M. Van Dael, K. Vanbroekhoven, P. J. Deuss and M. L. Stone, From lignin to market: a technical and economic perspective of reductive depolymerization approaches, *Green Chem.*, 2025, **27**, 13160–13178.

37 L. T. Nguyen, D. P. Phan, A. Sarwar, M. H. Tran, O. K. Lee and E. Y. Lee, Valorization of industrial lignin to value-added chemicals by chemical depolymerization and biological conversion, *Ind. Crops Prod.*, 2021, **161**, 113219.

38 P. Kaur, J. Wang, X. Li, R. Karinen, G. Papanikolaou, P. Lanzafame, G. Centi and Y. Li, Valorization of Lignin and Its Derived Molecules by Electrocatalytic Oxidation, *ACS Sustainable Chem. Eng.*, 2025, **13**, 16214–16231.

39 M. J. Hidajat, A. Riaz, J. Park, R. Insyani, D. Verma and J. Kim, Depolymerization of concentrated sulfuric acid hydrolysis lignin to high-yield aromatic monomers in basic sub-and supercritical fluids, *Chem. Eng. J.*, 2017, **317**, 9–19.

40 T. Hibino, K. Kobayashi, M. Nagao and S. Teranishi, Hydrogen production by direct lignin electrolysis at intermediate temperatures, *ChemElectroChem*, 2017, **4**, 3032–3036.

41 X. Du, W. Liu, Z. Zhang, A. Mulyadi, A. Brittain, J. Gong and Y. Deng, Low-energy catalytic electrolysis for simultaneous hydrogen evolution and lignin depolymerization, *ChemSusChem*, 2017, **10**, 847–854.

42 J. González-Cobos, M. S. Prévot and P. Vernoux, Electrolysis of lignin for production of chemicals and hydrogen, *Curr. Opin. Electrochem.*, 2023, **39**, 101255.

43 X. Du, H. Zhang, K. P. Sullivan, P. Gogoi and Y. Deng, Electrochemical lignin conversion, *ChemSusChem*, 2020, **13**, 4318–4343.

44 M. Zirbes, L. L. Quadri, M. Breiner, A. Stenglein, A. Bomm, W. Schade and S. R. Waldvogel, High-temperature electrolysis of kraft lignin for selective vanillin formation, *ACS Sustainable Chem. Eng.*, 2020, **8**, 7300–7307.

45 K. Beliaeva, N. Grimaldos-Osorio, E. Ruiz-López, L. Burel, P. Vernoux and A. Caravaca, New insights into lignin electrolysis on nickel-based electrocatalysts: Electrochemical performances before and after oxygen evolution, *Int. J. Hydrogen Energy*, 2021, **46**, 35752–35764.

46 A. Caravaca, W. E. Garcia-Lorefice, S. Gil, A. de Lucas-Consuegra and P. Vernoux, Towards a sustainable technology for H2 production: Direct lignin electrolysis in a continuous-flow Polymer Electrolyte Membrane reactor, *Electrochem. Commun.*, 2019, **100**, 43–47.

47 O. Movil-Cabrera, A. Rodriguez-Silva, C. Arroyo-Torres and J. A. Staser, Electrochemical conversion of lignin to useful chemicals, *Biomass Bioenergy*, 2016, **88**, 89–96.

48 J. Wang, Y. Li, C. Hummel, G. Huang, X. Ji, E. Demiröz, A. Urakawa, S. Huang, R. Zhao and J. Lercher, Electrocatalytic Production of a Liquid Organic Hydrogen Carrier with Anodic Valorization of the Process: Review and Outlook, *Energy Fuels*, 2024, **39**, 132–165.

49 C. He, D. Pan, K. Chen, J. Chen, Q. Zhang, H. Zhang, Z. Zhang and Z. Wen, Energy-Efficient Co-production of Benzoquinone and H2 Using Waste Phenol in a Hybrid Alkali/Acid Flow Cell, *Angew. Chem., Int. Ed.*, 2024, **63**, e202407079.

50 A. Ali, G. Huang, J. Zhu, A. Laaksonen and X. Ji, Selective Electrocatalytic Oxidation of Phenol to Benzoquinone *via* Water Splitting Using a Nonprecious Metal-Based Electrocatalyst, *Adv. Energy Sustainability Res.*, 2025, 2500108.

51 B. Seo, W. H. Lee, Y. J. Sa, U. Lee, H.-S. Oh and H. Lee, Electrochemical oxidation of toluene with controlled selectivity: The effect of carbon anode, *Appl. Surf. Sci.*, 2020, **534**, 147517.

52 N. H. Kim, B. Kim, Y. S. Kim, A. R. Mule and C. H. Chung, A hybrid electrochemical system for spontaneous green-hydrogen production with simultaneous desalination using catechol oxidation, *Desalination*, 2024, **580**, 117541.

53 D. Wang, P. Wang, S. Wang, Y.-H. Chen, H. Zhang and A. Lei, Direct electrochemical oxidation of alcohols with hydrogen evolution in continuous-flow reactor, *Nat. Commun.*, 2019, **10**, 2796.

54 P. Silakari and P. Piplani, p-Benzoquinone as a privileged scaffold of pharmacological significance: A Review, *Mini-Rev. Med. Chem.*, 2020, **20**, 1586–1609.

55 Z. Luo, L. Liu, Q. Zhao, F. Li and J. Chen, An insoluble benzoquinone-based organic cathode for use in rechargeable lithium-ion batteries, *Angew. Chem.*, 2017, **129**, 12735–12739.

56 J. Yang, P. Xiong, Y. Shi, P. Sun, Z. Wang, Z. Chen and Y. Xu, Rational molecular design of benzoquinone-derived cathode materials for high-performance lithium-ion batteries, *Adv. Funct. Mater.*, 2020, **30**, 1909597.

57 G. S. Buzzo, A. C. B. Rodrigues, R. F. De Souza, J. C. M. D. Silva, E. L. Bastos, E. V. Spinacé, A. Neto and M. H. M. T. Assumpção, Synthesis of hydroquinone with co-generation of electricity from phenol aqueous solution in a

proton exchange membrane fuel cell reactor, *Catal. Commun.*, 2015, **59**, 113–115.

58 F. Liu, X. Gao, Z. Guo, E. C. Tse and Y. Chen, Sustainable Adipic Acid Production *via* Paired Electrolysis of Lignin-Derived Phenolic Compounds with Water as Hydrogen and Oxygen Sources, *J. Am. Chem. Soc.*, 2024, **146**, 15275–15285.

59 F. Liu, H. Dong, S. Zhong, X. Wu, T. Wang, X. Wang, Y. Liu, M. Zhu, I. M. Lo and S. Zhan, Selective electrocatalytic transformation of highly toxic phenols in wastewater to *para*-benzoquinone at ambient conditions, *Water Res.*, 2024, **251**, 121106.

60 R. Wu, Q. Meng, J. Yan, H. Liu, Q. Zhu, L. Zheng, J. Zhang and B. Han, Electrochemical strategy for the simultaneous production of cyclohexanone and benzoquinone by the reaction of phenol and water, *J. Am. Chem. Soc.*, 2022, **144**, 1556–1571.

61 K. Ngamchuea, B. Tharat, P. Hirunsit and S. Suthirakun, Electrochemical oxidation of resorcinol: mechanistic insights from experimental and computational studies, *RSC Adv.*, 2020, **10**, 28454–28463.

62 J. Fabri, L. R. Silva, J. S. Stefano, J. F. Pereira, D. R. Cocco, R. A. Muñoz and D. P. Rocha, In situ electrochemical determination of resorcinol using a fully 3D printed apparatus, *Microchem. J.*, 2023, **191**, 108810.

63 Y. Lv, A. Kong, H. Zhang, W. Yang, Y. Chen, M. Liu, Y. Fu, J. Zhang and W. Li, Electrocatalytic oxidation of toluene into benzaldehyde based on molecular oxygen activation over oxygen vacancy of heteropoly acid, *Appl. Surf. Sci.*, 2022, **599**, 153916.

64 F. Valentini, G. Ferracci, P. Galloni, G. Pomarico, V. Conte and F. Sabuzi, Sustainable highly selective toluene oxidation to benzaldehyde, *Catalysts*, 2021, **11**, 262.

65 Y. Zhu, H. Wang, K. Jin and J. Gong, Nanopolyaniline Coupled with an Anticorrosive Graphene as a 3D Film Electrocatalyst for Efficient Oxidation of Toluene Methyl C—H Bonds and Hydrogen Production at Low Voltage, *Chem. – Eur. J.*, 2019, **25**, 6963–6972.

66 B. Vellaichamy, S. K. Ponniah and P. Prakash, An in-situ synthesis of novel Au@ NG-PPy nanocomposite for enhanced electrocatalytic activity toward selective and sensitive sensing of catechol in natural samples, *Sens. Actuators, B*, 2017, **253**, 392–399.

67 M. F. Islam, R. H. Rakib, K. A. Alamry, M. M. Rahman and M. A. Hasnat, Electrocatalytic oxidation of catechol using IrOx-ITO electrode in aqueous medium, *J. Electroanal. Chem.*, 2022, **907**, 116031.

68 Z. Li, J. Zhang, X. Jing, J. Dong, H. Liu, H. Lv, Y. Chi and C. Hu, A polyoxometalate@ covalent triazine framework as a robust electrocatalyst for selective benzyl alcohol oxidation coupled with hydrogen production, *J. Mater. Chem. A*, 2021, **9**, 6152–6159.

69 G. Liu, X. Zhang, C. Zhao, Q. Xiong, W. Gong, G. Wang, Y. Zhang, H. Zhang and H. Zhao, Electrocatalytic oxidation of benzyl alcohol for simultaneously promoting H 2 evolution by a Co 0.83 Ni 0.17/activated carbon electrocatalyst, *New J. Chem.*, 2018, **42**, 6381–6388.

70 J. Wan, X. Mu, Y. Jin, J. Zhu, Y. Xiong, T. Li and R. Li, Nitrogen-doped nickel-molybdenum oxide as a highly efficient electrocatalyst for benzyl alcohol oxidation, *Green Chem.*, 2022, **24**, 4870–4876.

71 T. Begildayeva, J. Theerthagiri, A. Min, C. J. Moon and M. Y. Choi, Density-controlled metalloporphyrin with mutated surface *via* pulsed laser for oxidative refining of alcohols to benzoic acid and H2 production using linear tandem electrolysis, *Appl. Catal., B*, 2024, **350**, 123907.

72 G. Liu, Z. Zhai, Y. Lu, J. Lu, Y. Wang, S. Liang, H. He and L. Jiang, Electrocatalytic Cleavage of C–C Bonds in Lignin Models Using Nonmetallic Catalysts at Ambient Conditions, *Chem Bio Eng.*, 2024, **1**, 357–365.