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Review

Electrocatalytic Lignin Oxidation

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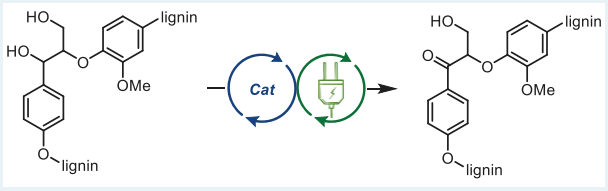
ABSTRACT: Electrocatalytic processes in organic chemistry have recently seen a resurgence of interest. When coupled to renewable feedstocks, electrochemical transformations can provide an alternative to conventional synthetic methods. Thus, developing methods for the selective degradation of lignin, the largest known natural source of aromatic rings, to simpler aromatic hydrocarbons is of high importance. This review summarizes and highlights recent achievements and challenges for electrocatalytic lignin oxidation and provides an overview, foundation, and reference for further method development.



KEYWORDS: *electrocatalysis, oxidation, lignin, β-O-4, degradation*

1. INTRODUCTION

One of the greatest global environmental sustainability challenges facing modern society is anthropogenic climate change from fossil fuel usage.[1] Although fossil fuel-derived hydrocarbons enabled the industrial revolution, the concomitant production of carbon dioxide (CO_2) and other waste products in the atmosphere impact human health and the environment.[2] In 2019, global CO_2 emissions from fossil fuel usage continued with the same trend of the previous six decades, climbing to an all-time high in recorded history.[3] In this context, decreasing societal reliance on fossil fuels is valuable.

The biopolymer lignin is an attractive alternative feedstock for commodity chemical productions.[4] Lignin offers the most abundant aromatic functional groups in nature, making lignin a potent renewable source of chemicals containing electron-rich aromatic rings (Figure 1A).[5] However, lignin as a resource is vastly underutilized.[4−6,8−10] Even with the large demand from the pulp and paper industry, the majority of lignin is simply being burned to produce heat.[7]

The prevailing lignin degradation literature focuses on two major types of lignin: Kraft lignin and organosolv lignin.[11] Kraft lignin is an industrial lignin obtained from the Kraft pulp process, which accounts for about 85% of the total lignin production around the world.[12] Kraft lignin contains sulfur and thus suffers from a foul smell and side reactions in subsequent processes.[13] Its degradation products often include sulfur as well and require additional functional group manipulations to produce common commodity chemicals. In contrast, organosolv lignin is sulfur-absent. Its selective deconstruction (the so-called "lignin first" strategy)[14] retains the native functionality of the lignin polymer and produces a series of highly valuable methoxy-substituted aromatic chemicals. However, the technology to convert the sulfur-free high-quality lignin to useful products is still lacking.[13] This review focuses on method development for the degradation of organosolv lignin.

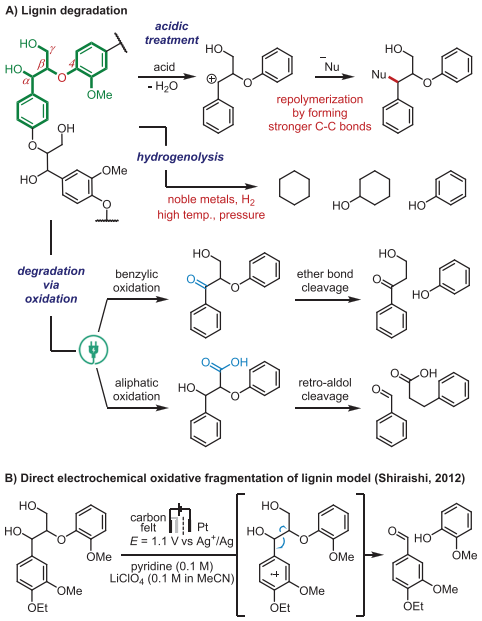


Figure 1. Lignin degradation.

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Organosolv lignin is deceptively difficult to break down due to its structure. It features an irregular pattern of methoxy-substituted aromatic groups that are linked together via aliphatic C−C and C−O bonds.[15] Despite the large number of weak C−O connections in its structure, lignin cannot be hydrolyzed under acidic conditions (Figure 1A).[16] Its tolerance to strong acids is precisely what makes plant cell walls durable and impermeable to harsh conditions, facilitating plant defense and survival. This aspect conversely makes its depolymerization extremely challenging.[16]

The most extensively explored and developed "lignin first" strategies for lignin degradation can be divided into two categories: hydrogenolysis and selective deconstruction. Lignin degradation by hydrogenolysis involves the use of noble metals, high temperature, high pressure, and hydrogen gas (Figure 1A).[17] In general, this approach gives mixtures of phenols, cyclic alcohols, cycloalkanes, etc.[17] The latter tactic features the selective deconstruction of lignin via oxidation−reduction sequences under mild conditions, which are aimed at the high-yield production of defined aromatic molecules (Figure 1A).[8] Notably, the direct cathodic reduction of lignin has also appeared in the literature. For example, Lessard and co-workers reported reductive lignin degradation back in the 1990s.[18] However, the scope of this review is centered on the second approach, i.e., lignin oxidation methods.

The β-O-4 connection accounts for around two-thirds of the linkages in native lignin and is consequently a good target for selective deconstruction methodologies.[19] The β-O-4 linkage contains two hydroxyl groups, a benzylic alcohol on the C_α and an aliphatic alcohol on the C_γ (Figure 1A). The selective oxidation of these alcohols affords a good electron acceptor, enabling facile fragmentation with high selectivity.[10] Benzylic oxidation produces an aromatic ketone as the intermediate to realize selective reductive C−O cleavage (Figure 1A).[20] Oxidation of an aliphatic alcohol instead gives a carboxylic acid and finally delivers benzyl aldehyde derivatives and aliphatic acids by a retro-aldol reaction (Figure 1A).[21]

Electrochemical oxidation, in principle, can provide the following four advantages in the context of lignin depolymerization. First, lignin oxidation can be operated in an environmentally friendly manner without the usage of stoichiometric molecular oxidants and the generation of the corresponding waste. Second, precise potential control provides a high selectivity for the desired deconstruction. Third, decomposition under galvanic conditions allows for a tunable and temporally controlled lignin degradation process.[22] Fourth, the electrochemical oxidation of lignin can proceed with the simultaneous generation of hydrogen gas, which can be used for the electrocatalytic hydrogenation of lignin and its intermediates.[23] Indeed, studies on electrochemical biomass conversion date back several decades, with an excellent summary in the pioneering monograph "The Electrochemistry of Biomass and Derived Materials" by Chum and Baizer.[24]

Recently, a few studies of electrochemical lignin oxidation focused on direct electrolysis. For example, Shiraishi and co-workers investigated the direct electrochemical oxidation of two β-O-4 lignin models at a carbon felt anode (Figure 1B).[25] Potential-controlled electrolysis in the presence of pyridine-derived bases delivered benzyl aldehyde and phenol as fragmentation products. The key mechanistic step of this direct oxidative lignin fragmentation is the selective generation of an arene radical cation, which undergoes C−C cleavage in the presence of a base. Recently, Waldvogel and co-workers applied the same principle on Kraft lignin and developed a series of direct electrochemical degradation methods for selective vanillin production using a nickel-based anode under high temperature conditions.[26]

Many efforts have largely focused on electrocatalysis to improve reaction selectivity and efficiency.[27] There are numerous possible electrocatalytic strategies that could be applied to lignin oxidation, but three modes[28] are the most prevalent in the lignin oxidation literature. First, a freely diffusing small molecule redox species can participate as the electrocatalyst to accelerate electron transfer between the anode and lignin (Figure 2, type I). Second, a macromolecular enzyme initiated by an electrochemically generated species serves as a catalyst (Figure 2, type II). Third, the electrode material is itself electrocatalytic, or discrete electrocatalysts are affixed onto the electrode surface (Figure 2, type III). The scope of this contribution is to review advances in these three electrocatalyst embodiments. This review summarizes the current state of the art and provides a reference for novel method development for electrocatalytic lignin oxidation.

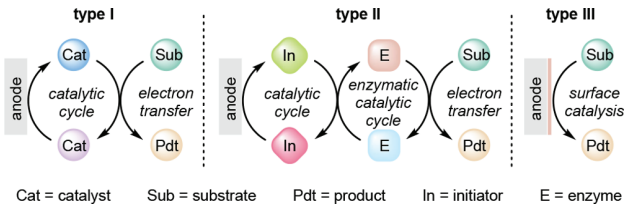

Figure 2. Classifications of electrocatalytic lignin oxidation.

2. SMALL MOLECULES AS ELECTROCATALYSTS

Nitroxyl radicals are one type of widely studied molecules to promote electrochemical oxidations.[29] Both aminoxyl radicals and imidoxyl radicals in the form of TEMPO (2,2,6,6-tetramethylpiperidine-*N*-oxyl) and PINO (phthalimide-*N*-oxyl), respectively, are of particular interest.[29] This section details TEMPO-mediated and PINO-catalyzed electrochemical lignin oxidation and discusses the reaction selectivity and mechanisms.

2.1. TEMPO-Mediated Electrochemical Oxidation.

TEMPO displays two redox transitions in the potential range from −2 to +2 V vs SCE, indicating a possibility of acting as an electrocatalyst with multiple redox states. First, TEMPO can operate as a hydrogen atom abstractor (Figure 3A, top). The generated hydroxylamine (TEMPOH) can be oxidized back to TEMPO electrochemically to release a proton (−0.62 V vs SCE).[30] Despite an abundance of targeted studies on the TEMPO−TEMPOH redox couple, only a few reactions utilizing TEMPO as an oxidant have been reported due to its weak ability to drive hydrogen atom abstraction ($BDE_{TEMPO-H}$ = 71 kcal/mol).[31] Second, TEMPO can act as a catalyst precursor and generate active oxidizing species via oxidation (Figure 3A, bottom). TEMPO undergoes a facile one-electron oxidation to its oxoammonium ion (approximately 0.49 V vs SCE), which readily reacts with alcohols to produce corresponding aldehydes, ketones, and carboxylic acids.[29] Both TEMPO and the oxidizing intermediate oxoammonium salt are isolable, which facilitates the mechanistically guided development of TEMPO-mediated oxidation strategies. A recent review by Stahl and co-workers summarizes electrochemical alcohol oxidation that is mediated

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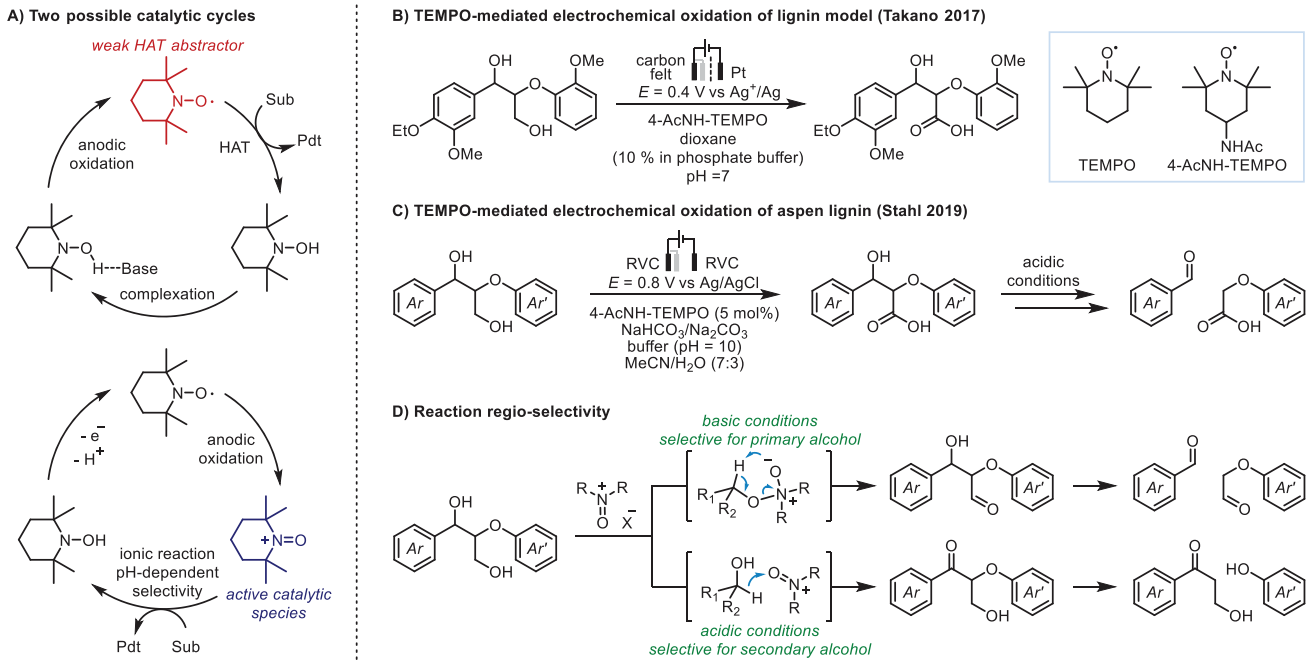

Figure 3. TEMPO-mediated electrochemical lignin oxidation.

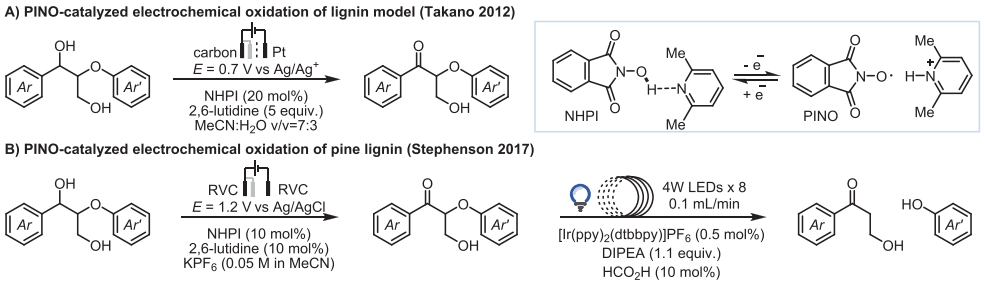

Figure 4. PINO-catalyzed electrochemical lignin oxidation.

by TEMPO.[29] This review focuses on its application on lignin models and native lignin.

In 1983, Semmelhack reported the first example of the TEMPO-mediated electrochemical oxidation of a series of alcohols, including a monomeric lignin model, i.e., anisyl alcohol.[32] In the presence of 5 mol % TEMPO as a catalyst precursor, anisyl alcohol was converted to anisyl aldehyde in an 83% yield. In 2017, Takano and co-workers investigated the TEMPO-mediated electrochemical oxidation of dimeric β-O-4 model substrates (Figure 3B).[33] They observed that the electrolyte strongly influenced the chemoselectivity of the oxidation between primary and secondary alcohols. In a MeCN/H_2O solvent mixture with $LiClO_4$, benzylic oxidation was favored but with a low yield (2−11%). In contrast, in a dioxane/phosphate buffer, aliphatic oxidation became dominant and gave a higher yield (72%−93%). Additionally, the catalytic efficiency of 4-acetamido-TEMPO (4-AcNH-TEMPO) was higher than that of TEMPO.

Recently, Stahl and co-workers further optimized the reaction conditions and expanded the substrate scope to native lignin extracted from poplar wood (Figure 3C).[21] Similarly, the chemoselective oxidation of the primary alcohols in lignin employs 4-AcNH-TEMPO as an electrocatalyst precursor and provides the corresponding carboxylic acids in moderate to high yields. Interestingly, the authors found that MeCN/H_2O media with a $NaHCO_3/Na_2CO_3$ buffer (pH = 10) gave a better selectivity for the primary alcohol and higher yields. Further treatment of the oxidized lignin under acidic conditions resulted in the depolymerization of the material into characterized aromatic monomers in a nearly 30 wt % yield.

The chemoselectivity of TEMPO-mediated oxidation appears to be impacted by the acidity or basicity of the reaction solution. In general, acidic media gives secondary alcohol oxidation selectivity, while basic environments deliver primary alcohol oxidation products. Stahl and co-workers suggested the following rationale for these results (Figure 3D).[21] Under basic conditions, the oxoammonium mediates alcohol oxidation by an inner-sphere mechanism that favors the reaction with the less sterically hindered primary alcohol. In contrast, under acidic conditions, the oxoammonium promotes alcohol oxidation via a bimolecular hydride transfer mechanism that strongly favors the reaction with the secondary benzylic alcohol in lignin. In contrast, under basic conditions, the oxoammonium mediates alcohol oxidation by an inner-sphere mechanism that favors the reaction with the less sterically hindered primary alcohol. Notably, Stahl and co-workers have also disclosed an aerobic benzylic oxidation of lignin using TEMPO under acidic conditions, supporting their explanations on the reaction

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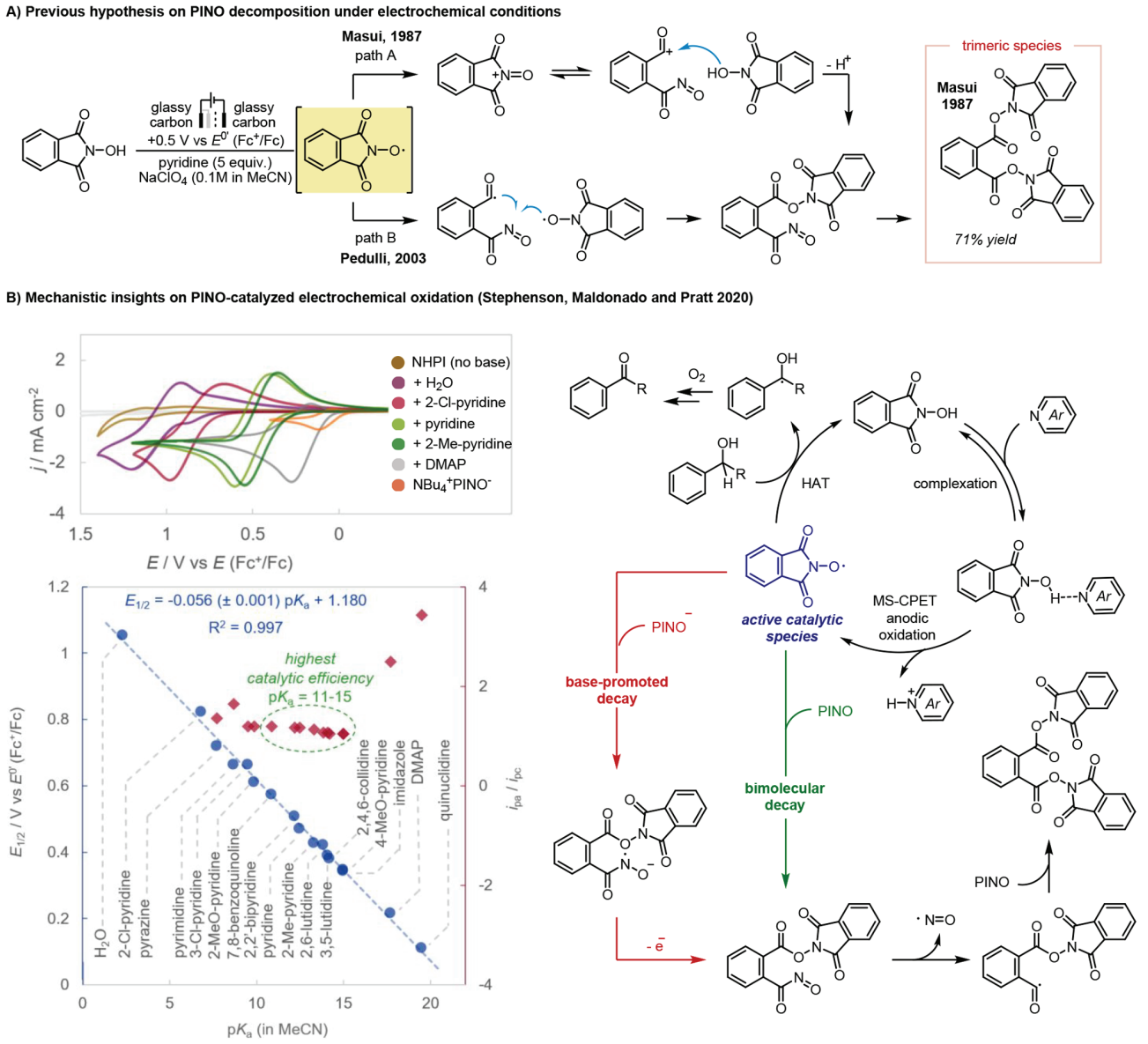

Figure 5. PINO decomposition under electrochemical conditions. Reproduced from ref 41. Copyright 2021, American Chemical Society.

selectivity.[20e] In principle, a similar reaction selectivity should be possible in an acidic solution using an electrochemical method. However, the electrochemical oxidation of lignin models or native lignin under acidic conditions has not yet been demonstrated.

2.2. PINO-Catalyzed Electrochemical Oxidation. Imidoxyl radicals feature carbonyl groups in the positions adjacent to the *N*-oxyl functional group.[29] The most prominent member of this class is PINO. PINO is short-lived and is often generated in situ by an oxidation of its precursor *N*-hydroxyphthalimide (NHPI) in the presence of a base (Figure 4A). Due to a relatively high bond dissociation energy (BDE_{NHPI} = 88 kcal/mol),[31] PINO is a potent hydrogen atom transfer (HAT) electrocatalyst for oxidation reactions, particularly for allylic, benzylic, and other weak C−H bonds. The BDE of NHPI matches closely with the bond strength of benzylic hydrogens in substrates like lignin (BDE = ∼85 kcal/mol).[34] Accordingly, after Masui and co-workers reported the first PINO-catalyzed electrochemical oxidation of benzylic alcohols,[35] several subsequent studies focused on the oxidation of lignin.

In 2012, Takano and co-workers explored the NHPI/PINO redox mediator for the electrochemical oxidation of lignin model substrates (Figure 4A).[36] In this reaction, 2,6-lutidine shifted the redox response of NHPI/PINO toward more negative potentials, affording better selectivity control. The electrolysis of lignin model substrates with NHPI in the presence of this base gave 88−92% yields. They also provided a comparison of the action of NHPI/PINO against that of the direct electrochemical oxidation of lignin models. The data indicated poor selectivity and yields (5−40%) for the direct electrochemical oxidation, demonstrating that PINO is a superior reagent for lignin oxidation.

In 2017, Stephenson and co-workers integrated a similar electrochemical strategy with photochemical reductive C−O cleavage, resulting in a one-pot two-step lignin degradation approach (Figure 4B).[37] The PINO-catalyzed electrolysis of a

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variety of β-O-4 model substrates enabled selective benzylic oxidation and provided moderate to high yields. The resulting crude mixture from the electrochemical oxidation was directly treated with irradiation in a continuous flow with a 0.5 mol % iridium complex $[Ir(ppy)_2(dtbbpy)](PF_6)$ as a photocatalyst without any intermediate purification to give aromatic ketones and phenols as products. In addition, pine lignin was also amenable to this approach and provided >1 wt % monomers.

Although PINO is a promising catalyst, PINO-catalyzed electrochemical oxidation generally requires a high catalyst loading (10−20 mol %) to offset the concomitant PINO decomposition.[37−39] The first study on PINO decomposition in an electrochemical context appeared in 1987 and indicated a trimeric species as the major decomposition product (Figure 5A, path A).[40] The paper suggested an ionic path featuring the nucleophilic attack of an oxoammonium ion. Later, Pedulli and co-workers suggested a radical pathway involving the coupling of PINO and the acyl radical that arises from the C−N fragmentation of another molecule of PINO (Figure 5A, path B).[31] However, those assumptions have never been experimentally corroborated due to the challenge of studying short-lived PINO-based intermediates. Nevertheless, these hypotheses strongly influenced subsequent strategies involving PINO-catalyzed oxidation.

Recently, Stephenson, Maldonado, Pratt, and co-workers detailed a mechanistic study on PINO-catalyzed oxidation.[41] Using voltammetric analysis and computational calculations, this study provided insights into the mechanism of the generation and decomposition of PINO under electrochemical conditions. Cumulative cyclic voltammetry suggested that the formation of PINO from NHPI in the presence of base occurs by the formation of a complex with the base. The formal standard potential $E^{0\prime}$ for the oxidation of NHPI-base complexes is dependent on the pK_a values of the bases. Across a pK_a range from 2 to 19, the linear least-squares fit yielded a slope of 56 ± 1 mV per pK_a unit, which is consistent with the Nernst factor (59 mV/pK_a) and suggests that the oxidation event operates via a multiple-site concerted proton−electron transfer (MS-CPET) mechanism (Figure 5B). The catalytic efficiency of the NHPI/base complexes, which is dependent upon the reversibility of the electrochemical oxidation, depends on the strength of the base, reaching a maximum at a pK_a range of ∼12−15 (Figure 5B). Consequently, the oxidation of benzyl alcohol achieved full conversion only when bases spanning a pK_a range of 12−15 were used.

Taken together with computational support, the reported data indicate a base-promoted mechanism, which is presented in Figure 5B. The reaction starts with the formation of a hydrogen bonded complex between NHPI and the base. The electrochemical oxidation of the NHPI−base complex occurs by proton-coupled electron transfer. Specifically, an electron moves from NHPI to the anode, and a proton moves from NHPI to the base. With stronger bases, the oxidation requires a lower applied potential to reach the same current, i.e., the same reaction rate. The oxidatively generated PINO abstracts the benzylic hydrogen from the lignin substrate and gives a benzylic radical intermediate, which is rapidly trapped by oxygen to form the aromatic ketone product. Notably, this process results in the generation of the hydrogen peroxyl radical, which can oxidize NHPI or the lignin substrate by a radical chain mechanism. Most importantly, the reaction can be terminated not only by hydrogen peroxyl radical coupling but also by base-promoted PINO decomposition. PINO has two operative decomposition pathways in solution. In the presence of weak bases (pK_a < 15), a second-order bimolecular reaction is dominant, where two PINO species dimerize into a species that can be further oxidized. In the presence of stronger bases (pK_a > 15), a second decomposition pathway is operative—the reaction between deprotonated NHPI and PINO to produce a dimerized redox-active species.

The identification of the base effect and the PINO decomposition mechanisms suggest a new viewpoint to advance PINO-catalyzed electrochemical oxidations. Previous efforts on designing PINO-derived HAT catalysts have largely focused on adjusting the bond dissociation free energy (BDFE) to improve the reactivity. In contrast, an approach to improving catalysis through an extension of the effective catalytic lifetime of PINO by obviating the degradation pathways has not been a focus of research efforts. On the basis of the results presented herein, we suggest that these two aspects (BDFE and decomposition) have to be considered in concert to design more effective *N*-oxyl catalysts for C−H oxidation reactions.

Lignin oxidation has also been explored in photoelectrochemical systems. Photoelectrochemistry utilizes incident optical energy to drive electrochemical reactions.[42] Such processes are based principally on the photogeneration of electron−hole pairs within a semiconductor photoanode. Photoelectrochemical cells have been intensively studied for water splitting and CO_2 reduction coupled to water oxidation for the formation of solar fuels,[43,44] but there is little precedent for using photoelectrochemical platforms for the oxidation of organic compounds.[45] In 2020, Sherman, Yoo, Leem, and co-workers described a photoelectrochemical PINO-catalyzed lignin oxidation reaction (Figure 6).[46] Their system was based on a

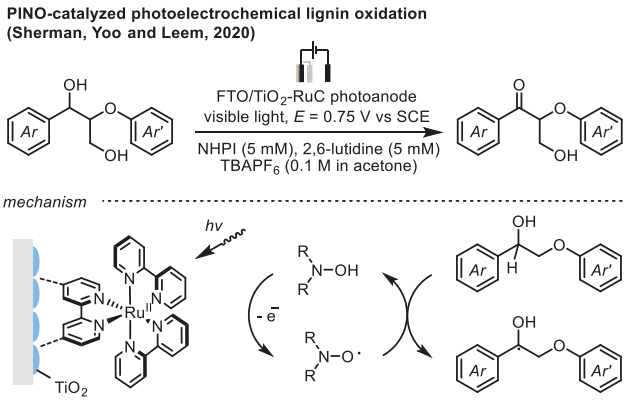

Figure 6. PINO-catalyzed photoelectrochemical lignin oxidation.

TiO_2 photoanode, a surface-bound Ru(II)-based photocatalyst, and a homogeneous NHPI catalyst precursor and was capable of degrading both lignin models and native lignin. The role of the ruthenium polypyridyl complex RuC immobilized on the photoanode surface was both to sensitize the TiO_2 and cause the subsequent RuC^{*+} species to oxidize NHPI to generate PINO, which ultimately gives the benzylic oxidation product. In this case, NHPI replaces the role of iodide in a conventional dye-sensitized photovoltaic cell. From an energy usage perspective, this work illustrates the possibility of a clean and "green" lignin oxidation process and provides a new perspective for the design of PINO-catalyzed lignin oxidation methods.

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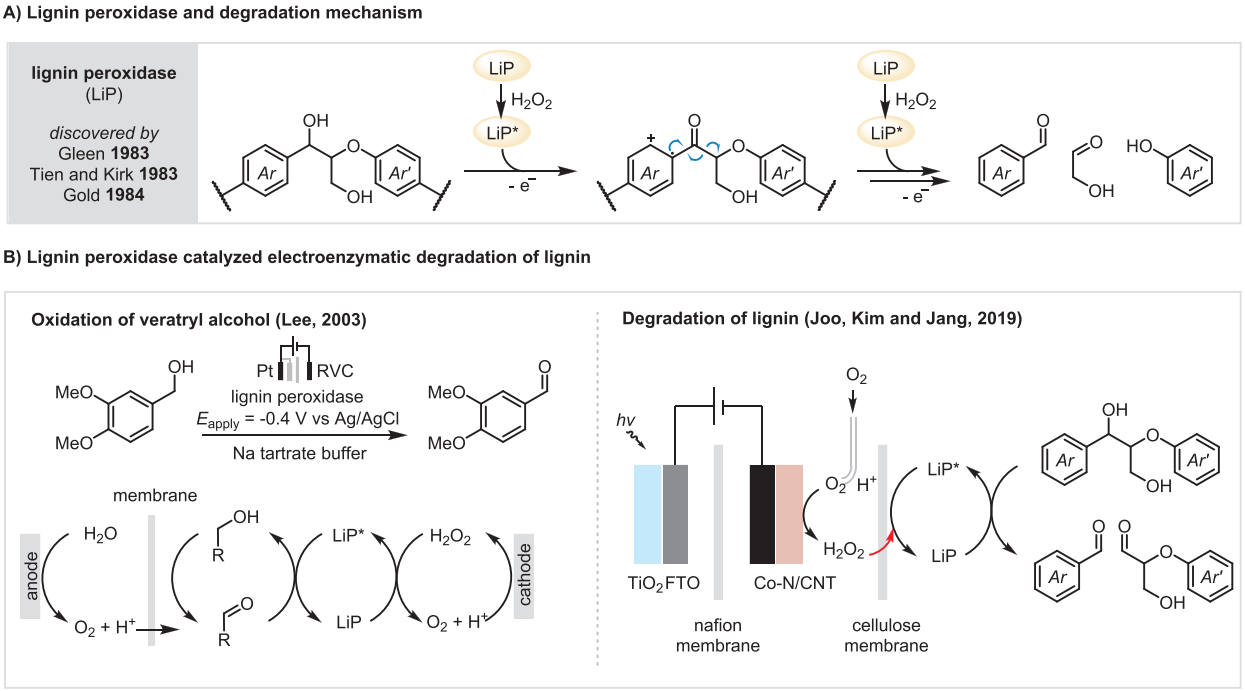

Figure 7. Lignin peroxidase-catalyzed oxidative degradation of lignin.

3. ENZYMES AS ELECTROCATALYSTS

Although lignin is highly resistant to chemical degradation, nature has evolved elegant strategies to decompose the biomass generated by living organisms.[47] Microorganisms, including fungi and bacteria, have been selectively degrading lignin for more than 300 million years.[48] Lignin-degrading basidiomycetes, collectively known as white rot fungi, have been shown to efficiently and selectively depolymerize, degrade, and mineralize plant lignocellulose, including cellulose, hemicellulose, and lignin.[49] These white rot fungi play an important role in the carbon cycle[47] and thus attract considerable interest in the development of bio-based sustainable processes, such as selective lignin depolymerization.

The white rot fungus *Phanerochaete chrysosporium* has been the most extensively studied system for lignocellulose biodegradation since its discovery in the 1980s.[50] Specifically, the lignin biodegradation process that occurs in *P. chrysosporium* is catalyzed by two extracellular peroxidases: lignin peroxidase (LiP, EC 1.11.1.14) and manganese peroxidase (MnP, EC 1.11.1.13).[49] These enzymes are responsible for directly or indirectly generating highly reactive free radicals that can ultimately achieve lignin degradation, although the exact mechanisms remain unclear.[51] This section details recent efforts on electroenzymatic catalysis for lignin depolymerization using these two peroxidases.

3.1. Lignin Peroxidase-Catalyzed Electroenzymatic Oxidation. Lignin peroxidase is interesting because of its exceptional ability to catalyze the oxidative degradation of structurally diverse organic biopolymers such as lignin.[52] Mechanistically, activated lignin peroxidase has a sufficiently positive standard potential to oxidize nonphenolic veratryl-type aromatic rings in lignin substructures to radical cations (Figure 7A).[53] In nonphenolic alkyl aryl β-O-4-linked lignin model dimers, the resulting homolytic C−C bond cleavage leads to the formation of a benzaldehyde derivative and a phenol when the C−O bond is subsequently broken.[53] Although LiP-catalyzed lignin oxidation is efficient, the biocatalytic system requires hydrogen peroxide as an external oxidant, which is a critical limitation for scaling up this system.[54]

In 2003, Lee and co-workers disclosed an electroenzymatic oxidation of the lignin model veratryl alcohol using lignin peroxidase (Figure 7B).[54] The premise was to electrochemically reduce oxygen in the presence of an acid and generate hydrogen peroxide in situ, thereby activating LiP. The activated LiP* then oxidized 2 equiv of veratryl alcohol to produce veratryl aldehyde. Notably, the anode is separated from the electrochemical cell by an internal membrane to avoid any crossover. At the same time, the anode provides protons by oxidizing water. Potential control was critical to achieve a higher yield, as the lignin peroxidase exhibits a better stability and higher catalytic efficiency within a specific range of hydrogen peroxide concentrations.

In 2019, Joo, Kim, and Jang described a photoelectrobiochemical system for lignin degradation (Figure 7B).[55] The reaction integrated a TiO_2 photocatalyst, an atomically dispersed Co-based electrocatalyst, and an enzymatic catalyst, i.e., lignin peroxidase. Oxygen reduction occurred at the cathode with the assistance of the Co−N/CNT catalyst, generating hydrogen peroxide. Hydrogen peroxide traveled through the cellulose membrane into the third compartment and promoted the lignin peroxidase catalytic cycle. The system enables lignin dimer cleavage with a 94% conversion.

3.2. Inspiration from Manganese Peroxidase: Mn−Schiff Complex-Catalyzed Electrochemical Oxidation. Another lignin-degrading enzyme isolated from *P. Chrysosporium*, manganese peroxidase (MnP), was reported one year after the discovery of LiP.[56] Initially, MnP was considered only as an assistant enzyme in the process of lignin biodegradation.[57] However, subsequent studies suggested that several fungi, which do not exhibit LiP activity but are nevertheless strong producers of MnP, cause the selective degradation of wood lignin.[57] MnP in a mixture of surfactant Tween 80, Mn(II), a Mn-chelating organic acid, and a hydrogen peroxide-generating system results

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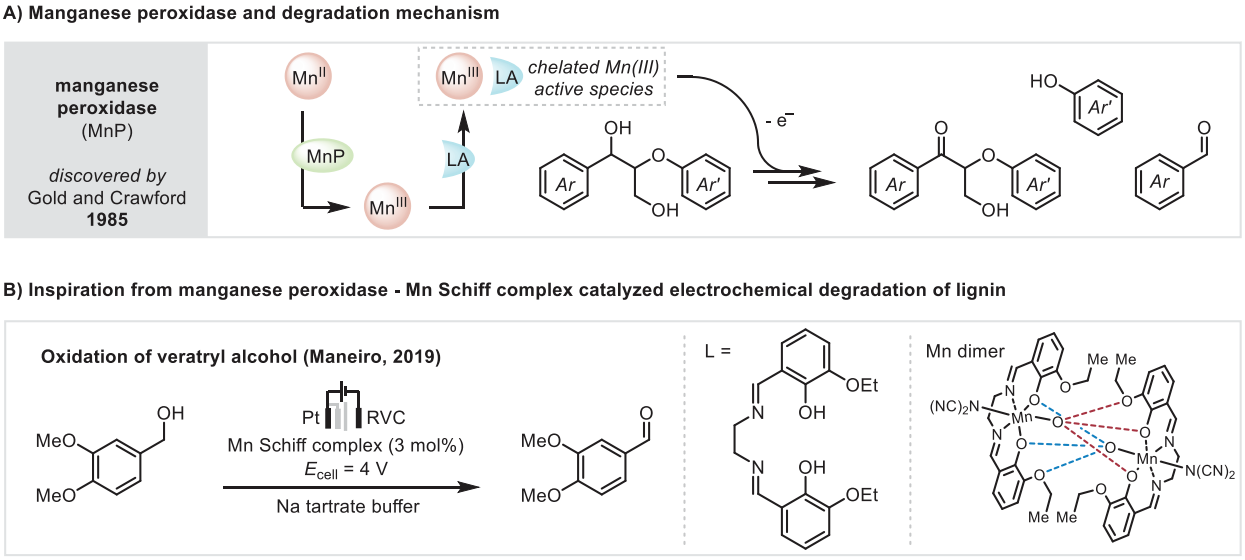

Figure 8. Manganese peroxidase-catalyzed lignin oxidative degradation of lignin.

in the depolymerization of lignin.[57] Mechanistically, MnP catalyzes the oxidation of Mn(II) to Mn(III); an ionic species that is stabilized by chelation with organic carboxylates, such as oxalate, malate, lactate, and malonate (Figure 8A). The chelated Mn(III) then oxidizes phenolic rings in lignin to phenoxyl radicals, leading to the decomposition of these structures.

Accordingly, a series of Mn-based complexes have been developed as oxidative catalysts.[58] Manganese(III) Schiff base complexes have been shown to be effective catalysts for the oxygenation of both saturated and unsaturated hydrocarbons.[59,60] Strongly chelating oxygen−nitrogen−nitrogen−oxygen (ONNO) Schiff base ligands are able to stabilize the manganese ion in various oxidation states since the two donor atoms of the chelating Schiff base exert opposing electronic influences. The phenolate oxygen is a hard donor that is known to stabilize the higher oxidation state of the metal ion, whereas the imine nitrogen is a softer donor with a tendency to stabilize the lower oxidation state.[61]

In 2019, Maneiro and co-workers developed a "MnP-like" catalytic system for the electrochemical oxidation of the lignin model veratryl alcohol using manganese−Schiff base complexes (Figure 8B).[61] In the paper, seven manganese−Schiff complexes with basic ligands were synthesized and evaluated. The tetragonally elongated octahedral geometry for the manganese coordination sphere and the global μ-aquo dimeric structure were characterized by X-ray crystallography. Among the seven prepared catalysts, complex $Mn_2L_2(H_2O)_2(N(CN)_2)_2$ behaves as the most efficient oxidative electrocatalyst to convert the lignin model veratryl alcohol to veratryl aldehyde with a turnover number of 85.

4. HETEROGENEOUS ELECTROCATALYSIS

Metal oxide electrodes have been widely studied for lignin oxidation reactions because of their innate high electrocatalytic activities for organic oxidations.[22,62−67] Specifically, metal oxide interfaces offer the possibility of inner-sphere electron-transfer pathways that can facilitate lignin oxidation relative to graphitic carbon electrodes. The earliest published effort in this direction dates to just after the second World War when Brooks and co-workers demonstrated the electrochemical oxidation of butanol-based organosolv lignin[68] in a 1% NaOH solution using an oxidized lead (Pb) electrode.[62]

Electrode fouling caused by polymerization and accumulation at the electrode−electrolyte interface complicates heterogeneous electrocatalysis. Thus, research in this vein has not focused extensively on mechanistic details or the improvement of the conversion efficiency.[63] This section provides a few examples of developments in electrode-catalyzed lignin oxidation literature within the past 20 years.

In 2000, Parpot and co-workers investigated the electrochemical oxidative degradation of kraft lignin in batch and flow cells on platinum (Pt), gold (Au), nickel (Ni), copper (Cu), dimensionally stable anodes (DSA), and lead dioxide (PbO_2) electrodes.[63] The authors chose vanillin production as the standard to perform kinetic analyses. They discovered that the conversion and chemical yields were dependent mainly on the applied current density and the partial pressure of oxygen at the interface. Conversely, the electrode identity influenced the attainable reaction rates when all other conditions were held constant. Empirically, current-controlled electrolysis proved more effective and consistent than potential-controlled electrolysis.

In 2017, Li and co-workers reported a study on the electrochemical degradation of bamboo lignin using a cell comprised of a Cu cathode and a Pb/PbO_2 anode in a sodium hydroxide solution.[64] In the electrocatalytic process, the electrooxidation of lignin generated intermediates and small molecular compounds at the anode. Meanwhile, chemisorbed hydrogen participated in the hydrogenation reduction of the intermediates at the cathode. After 2 h of electrolysis, 24 different products were confirmed by gas chromatography−mass spectrometry, of which vanillin (36.06 g per kilogram of lignin), syringaldehyde (57.30 g per kilogram of lignin), and *p*-coumaric acid (29.64 g per kilogram of lignin) were the major monomer fragments. Li and co-workers later reported the electrochemical degradation of corn stover lignin using the same methodology in 2018.[57] Electrolysis of this lignin yielded several products, including *trans*-ferulic acid (22.40 g per kilogram of lignin), vanillin (11.09 g per kilogram of lignin), 3-hydroxy-4-methoxyphenyl-ethanone (2.37 g per kilogram of lignin), syringaldehyde (10.04 g per kilogram of lignin), acetosyringone

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(6.95 g per kilogram of lignin), and 4-methoxy-3-methylphenol (38.83 g per kilogram of lignin).

Furthermore, Li and co-workers integrated a Pb/PbO_2 anode with a nickel plate cathode for the electrochemical degradation of cornstalk lignin in 2020.[66] As above, the process was performed in an aqueous sodium hydroxide solution and featured electrocatalytic hydrogenation at the Ni cathode. Twelve compounds were identified by gas chromatography−mass spectrometry (GC-MS), including valuable products such as toluene (36.1 g per kilogram of lignin), anisole (9.5 g per kilogram of lignin), *o*-xylene (14.4 g per kilogram of lignin) and *m*-xylene (11.7 g per kilogram of lignin).

In 2018, Li and co-workers developed a $Ti/SnO_2−Sb_2O_3/\alpha$-PbO_2/β-PbO_2 anode for the electrochemical oxidation of lignin.[22] The electrolysis of rice straw lignin was performed in a sodium hydroxide solution at 35−55 °C. At ambient pressure, rice straw lignin was directly oxidized at the anode, followed by a subsequent reduction at the metal (titanium−iron or titanium−tin) cathodes. This process demonstrated the breakdown of the chemical linkages among phenylpropyl units in rice straw lignin and afford 16 aromatic compounds, which contained aromatic ketones (4.09 g per kilogram of lignin), aromatic aldehydes (1.53 g per kilogram of lignin), and aromatic acids (23.92 g per kilogram of lignin).

In 2010, Chen and co-workers reported IrO_2-catalyzed electrochemical lignin oxidation.[67] In their report, four different iridium dioxide (IrO_2)-based electrodes ($Ti/SnO_2−IrO_2$, $Ti/RuO_2−IrO_2$, $Ti/Ta_2O_5−IrO_2$, and $Ti/TiO_2−IrO_2$) were systematically studied for their stability and electrocatalytic activity toward the degradation of lignin to vanillin and vanillic acid. The results showed that the $Ti/Ta_2O_5−IrO_2$ electrode exhibited the highest activity for O_2 evolution but the lowest activity for lignin oxidation. The $Ti/RuO_2−IrO_2$ electrode displayed the highest stability and the highest reactivity for lignin degradation among the four IrO_2-based electrodes. Vanillin and vanillic acid were identified as the primary products by high-performance liquid chromatography (HPLC).

The same group further demonstrated that the $Ti/TiO_2NT/PbO_2$ electrode was also promising for the treatment of lignin wastewater and the production of value-added chemicals.[69] The authors fabricated PbO_2 nanoparticles supported on TiO_2 nanotubes (the TiO_2NT/PbO_2 electrode) for the electro-oxidative degradation of kraft lignin. TiO_2 nanotubes led to a higher PbO_2 loading per geometric area, a higher catalytic efficiency, and a longer operational lifetime compared to those of previous reports. The prepared electrode produced vanillin and vanillic acid from kraft lignin.

5. CONCLUSIONS AND OUTLOOKS

Lignin is a promising yet underutilized natural source of aromatic chemicals. The development of methods to deconstruct lignin has a long history. Although some advances in electrocatalyst design, enzymatic system development, and electrode fabrication have been made, an optimal and technologically viable lignin electrolysis method has yet to be realized. Among the three types of electrocatalytic systems covered in this review, small organic molecule-catalyzed lignin oxidation has emerged as a front-runner for further development due to a better understanding of its detailed mechanism in comparison to complicated enzymatic catalysis or surface catalysis. This review summarizes the cumulative insights to date on the design of electrocatalytic systems for lignin oxidation and will hopefully stimulate further work in this area. The challenges and possible directions for each type are discussed below.

Novel abiotic electrocatalyst design is one direction where advances must continue. A better homogeneous electrocatalyst for effecting lignin oxidation must satisfy the following four criteria. First, the catalyst must be highly reactive, as lignin processing is anticipated to operate on an immense scale wherein catalyst loading would become a primary consideration for process cost and practicality. Second, the catalyst must be a long-lived species and provide a durable catalytic ability. Third, the catalyst must be highly selective, targeting specific positions in lignin to avoid side reactions. Fourth, the catalyst and its derivatives must be easily accessible to study and compare their redox response, catalytic efficiency, and other properties. To date, no electrocatalyst has adequately satisfied all these constraints.

The maturation of biologically inspired enzymatic catalysts for lignin oxidation should also be pursued. Only a few examples have been reported, perhaps due to the challenge of operating an enzyme in a desired pathway under electrochemical conditions. Such advances will require a better understanding of the mechanisms of enzyme operation in practical conditions (e.g., solvent and temperature). Furthermore, enzymes are often unstable outside a narrow range of temperature and pH values and it is difficult to achieve long-term durability. Engineering highly active enzymes without adversely impacting their innate properties is desirable. The further involvement of chemical biologists and biochemical researchers will be helpful.

Furthermore, identifying and validating novel electrode designs will be useful. The realization of the dimensionally stabilized anode motif was crucial to the success of chlor-alkali cells. Lignin electrolysis poses similar challenges (e.g., extreme potentials and caustic electrolyte solutions) but with an even greater premium on balancing activity and the efficient transport of protons and hydrogen atoms. The work to date shows that metal oxides are promising, but only a small fraction of the available compositional space for metal oxides has been explored. Recent advances in metal oxide anodes[22,62−67] for water oxidation suggest that nonintuitive multinary oxide compositions could prove useful and should be explored. Similarly, the advantages and limitations of the various possible structural motifs of electrodes (e.g., planar versus porous) should be identified and described.

Finally, despite the promising results presented herein, several challenges remain to move from the model systems to lignin polymers. First, native lignin is highly insoluble in organic solvents; thus, the development of a method for soluble lignin separation is still necessary. Second, a large amount of different products may cause isolation issues, and the development of highly a selective degradation method is critical. Third, lignin processing is anticipated to operate on an immense scale, and the application of continuous flow technology to these reactions should be pursued.

Although it has a long history spanning more than 75 years, electrochemical lignin oxidation is more relevant than ever. We anticipate that breakthrough electrochemical strategies for lignin valorization will be the key to "greening" chemical production processes and fostering a sustainable future.

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Notes

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