Research
Environmental Engineering—Review

Electrochemical Biorefinery Towards Chemicals Synthesis and Bio-Oil Upgrading from Lignin

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ABSTRACT

Recalcitrance and the inherent heterogeneity of lignin structure are the major bottlenecks to impede the popularization of lignin-based chemicals production processes. Recent works suggested a promising pathway for lignin depolymerization and lignin-derived bio-oil upgrading via an electrochemical biorefinery (a process in which lignin valorization is performed via electrochemical oxidation or reduction). This review presents the progress on chemicals synthesis and bio-oil upgrading from lignin by an electrochemical biorefinery, relating to the lignin biosynthesis pathway, reaction pathway of lignin electrochemical conversion, inner-sphere and outer-sphere electron transfer mechanism, basic kinetics and thermodynamics in electrochemistry, and the recent embodiments analysis with the emphasis on the respective feature and limitation for lignin electrochemical oxidative and reductive conversion. Lastly, the challenge and perspective associated with lignin electrochemical biorefinery are discussed. Present-day results indicate that more work should be performed to promote efficiency, selectivity, and stability in pursuing a lignin electrochemical biorefinery. One of the most promising developing directions appears to be integrating various types of lignin electrochemical conversion strategies and other existing or evolving lignin valorization technologies. This review aims to provide more references and discussion on the development for lignin electrochemical biorefinery.

1. Introduction

Despite traditional fossil fuels, coal, oil, and natural gas still dominate the entire energy network globally. Unfortunately, fossil fuels reserves in nature will be depleted by 2069–2088 [1,2]. Additionally, these primary energy combustion processes usually release large amounts of toxic gas, seriously destroying ecosystem balance and threatening human health [3]. Overall, the energy crisis and environmental pollution resulted from over-reliance on conventional fossil fuels have become alarming. As such, the energy transition from conventional fossil fuels with insufficient reserves to renewable resources with carbon-neutrality and sustainability, is imminent.

As a natural organic carbon source, lignocellulosic biomass provides a sustainable option to eliminate our reliance on these fossil fuels with the key advantages of carbon neutrality and widespread abundance. This biomass mainly consists of cellulose (40%–50%), hemicellulose (15%–30%), and lignin (15%–30%) [4]. Currently, the utilization of cellulose and hemicellulose has been well promoted but lignin produced in the pulp industry, is usually used as low-value waste or burning for energy [5,6]. It has been reported that about 50 million tonnes of lignin was generated as waste in pulp and paper industry each year. Regrettably, only 2% of lignin was adopted for commercialization while most of lignin was abandoned or burned. Undeniably, as the second most abundant biomass component, such low-value utilization of lignin would lead to a serious waste of resources and great disposal costs. Lignin is rich in aromatic functional groups, which can be converted into high value-added aromatic monomers [7]. Overall, lignin valorization into high value-added chemicals not only achieves waste

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utilization but also decreases the requirement for fossil fuels, suggesting an outstanding potential for energy crisis alleviation and environmental protection [3,7].

Considerable effort has been directed to convert lignin into valuable chemicals. Depolymerization approaches mainly include (hydro)thermal treatment, acid/base catalysis, catalytic oxidation, catalytic reduction, and so forth [7,8], which provide a viable pathway to convert lignin into high value-added chemicals. Still, some potential limitations need to be overcome. Thermal depolymerization of lignin has been extensively studied to produce bio-oil, but the high temperatures and subsequent need for upgrading of bio-oil with its high oxygen content need to be overcome. Lignin oxidation depolymerization occurs under mild conditions. But the new C–C bonds would be formed attributing to the recondensation caused by the uncontrollability of radical intermediates, carbocations in the C_α site of lignin substrate and quinone methide, resulting in a low product selectivity. Catalytic reduction can effectively inhibit the recondensation of lignin fragments by utilizing endogenous or exogenous hydrogen to stabilize radical intermediates and thus enhance the yield and selectivity of the products. In particular, high H_2 pressure is inevitable. However, using hydrogen arising from fossil fuels would reduce the sustainability of the catalytic reduction technique. Likewise, acid/base-catalyzed depolymerization may be accompanied by issues of catalyst poisoning and recovery. These methods are outstanding for lignin valorization into chemicals, but more work should be continuously conducted to overcome these limitations to promote the large-scale application of lignin valorization via these techniques.

Lately, an electrochemical biorefinery (a process in which lignin valorization is performed via electrochemical oxidation or reduction) has emerged as a strategy to achieve lignin valorization under milder conditions. The advantages include: ① electrons as cleaning oxidant to substitute stoichiometric molecular oxidant for lignin depolymerization, ② hydrogen energy production or *in situ* generated green hydrogen for the upgrading of lignin derivatives, ③ lower energy requirement to pair with cathodic half reactions like hydrogenation/hydrogenolysis of oxygenates due to that oxygen evolution reaction is substituted by lignin oxidation reaction, ④ high product selectivities adjusted by potential control, ⑤ milder operating conditions, ⑥ an electrode as the catalyst to avoid separation of catalyst, and ⑦ renewable energy such as photovoltaic, wind energy, solar energy, and hydraulic energy is used as the electricity supply [9–15]. Notably, the implement of renewable energy as electricity supply on industrial scale is still a huge challenge since the nature of renewable energy can make it unreliable, indicating that it cannot be directly incorporated into the power grid [16,17]. Although energy storage systems can mitigate intermittency (from wind and solar), operating costs are greatly elevated [16,17], and the benefits of electrochemistry have been balanced against sometimes high electricity costs. Many works about lignin electrochemical conversion have been performed, Du et al. [13] and Wijaya et al. [18] reviewed the progress on lignin valorization by electrocatalytic oxidation and hydrogenation, respectively. Still, a comprehensive understanding on lignin biosynthesis pathway, lignin electrochemical oxidation/reduction reaction pathway, electron transfer mechanism, and kinetics information in term of lignin electrochemical biorefinery, is lacking.

This review aims to provide more information for novel strategy development and accelerate commercialization process of lignin electrochemical biorefinery. This study first dissects the biosynthesis pathway and electrochemical oxidation/reduction reaction pathways for lignin. Then, the inner-sphere and outer-sphere electron transfer mechanism and basic kinetics and thermodynamics in electrochemistry are elucidated. Subsequently, the state-of-the-art advance in lignin electrochemical biorefinery are summarized and analyzed. Finally, the challenge

and perspective associated with lignin electrochemical conversion are discussed.

2. Biosynthesis pathway and primary structure of lignin

Lignin can be considered as a complex phenolic polymer, formed by free radical polymerization (i.e., lignification) of syringyl (S), guaiacyl (G), and *p*-hydroxyphenyl (H) units (Fig. 1) [19–21]. These polymerization reactions initiated by laccase and peroxidase enzymes involve the combination or termination of two free radicals, also called a supramolecular self-assembled chaos [20]. The structure imparts the plant cell wall with rigidity and barrier to prevent microbial attack [22]. The aromatic units are derived from the corresponding monolignols: that is, sinapyl alcohol, coniferyl alcohol, and *p*-coumaryl alcohol, which are synthesized by the core phenylpropanoid pathway, a multi-enzyme biochemical network (Fig. 1) [19,23]. The proportion of monolignols significantly varies with plant taxonomy (Table S1 in Appendix A). Detailed information about core phenylpropanoid pathway and monolignols proportion in various native lignins are described in Section S1 in Appendix A.

Given the monolignol's diversity, conjugated π-system and random polymerization of various many inter-unit linkages are formed during lignin biosynthesis (Fig. 1), mainly involving the C–O–C and C–C bonds [24,25]. The relative amounts of these and their bond dissociation energies in various types of lignin show significant differences (Table S2 in Appendix A). For example, the β-O-4 proportion (50%–65%) in hardwood lignin is much higher than that (43%–50%) in softwood lignin. A reasonable explanation is that the C_5 positions in the G units of softwood lignin provide more opportunities for free radical coupling, which result in a higher degree of condensation [21]. Consequently, large numbers of C–C bonds such as β-5 and 5–5 are built. In contrast, the C_5 positions in hardwood lignin are restricted and ascribed to the high proportion of S units, preventing the probability of C–C free radical coupling [26]. Some noncanonical subunits like ferulate and tricin are also involved in the construction of grass lignin [27]. In term of lignin valorization, various high value-added chemicals can be acquired including vanillin and syringaldehyde. For native lignin, the highly efficient cleavage of β-O-4 bond in lignin is regarded as the core step because of its abundance and relatively lower Bond dissociation energy (BDE) value versus other bonds (Table S2). However, C–C linkages are the majority for some technical lignin like kraft lignin, alkaline lignin, and organosolv lignin [20,28], indicating that the cleavage of C–C bonds is crucial in such cases.

3. Reaction pathway in lignin electrochemical conversion

3.1. Oxidation reaction pathway in lignin electrochemical conversion

Electrochemical oxidation (ECO) can be divided into two cases: that is, direct oxidation and indirect oxidation. Direct oxidation involves the direct de-electron reaction (i.e., direct electron transfer between lignin and electrode) of lignin while indirect oxidation refers to that the electron transfer between lignin and electrode and is achieved by oxidizing reagent or redox species. Nonetheless, the essence of depolymerization is the electron transfer between the lignin substrate and electrode [12]. Oxidation reaction pathways of lignin are categorized as four types (Fig. 2) [29]. Types I and II involve direct oxidation of lignin and indirect reaction of lignin mediated by reactive oxygen species (ROS), respectively. Types III and IV are associated with the indirect reaction of lignin mediated by electrocatalytic redox species including small molecules and enzyme.
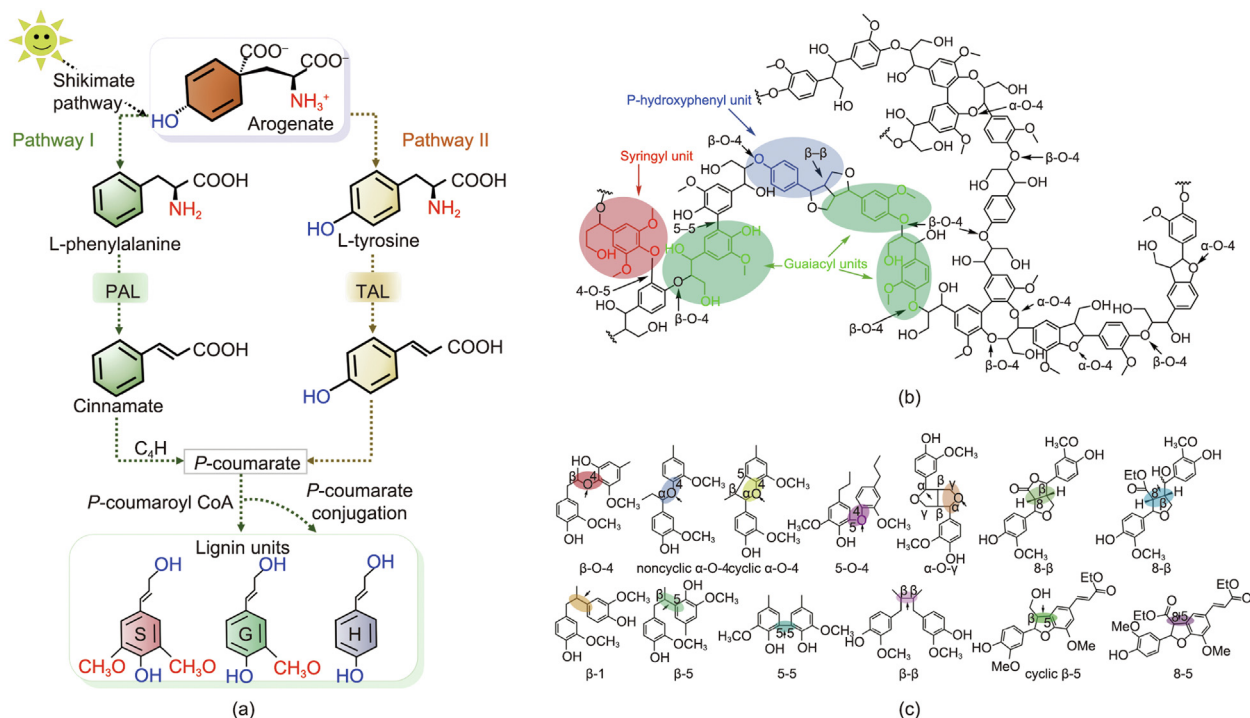
Fig. 1. (a) Core phenylpropanoid pathway. PAL: phe ammonia-lyase; TAL: tyrosine ammonialyase; CoA: coenzyme a. Reproduced from Ref. [19] with permission. (b) Typical lignin structure and (c) linkages between the primary units of lignin. Reproduced from Ref. [25] with permission.
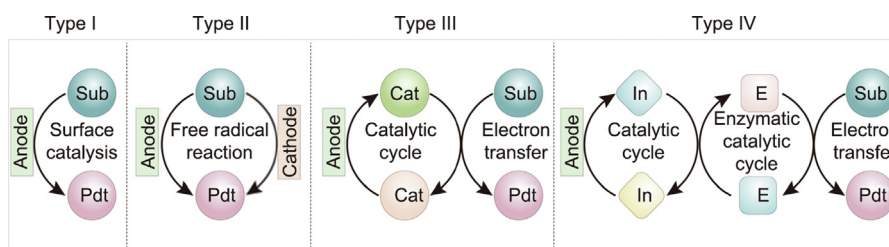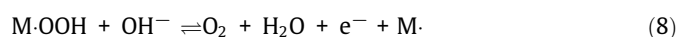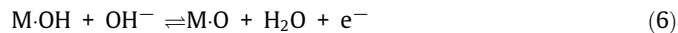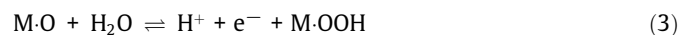

Fig. 2. Typical types of lignin ECO. Sub: substrate; Pdt: product; Cat: catalyst; In: initiator; E: enzyme. Reproduced from Ref. [29] with permission.

### 3.1.1. Direct reaction pathway and indirect reaction pathway mediated by ROS

For surface catalysis reactions of lignin, either the electrocatalyst is directly used as the electrode or the electrocatalyst is supported on the electrode surface for lignin depolymerization. Direct reaction of lignin relates to the direct electron transfer between lignin and the electrode. Nonetheless, it is well-known that lignin depolymerization at the anode is usually accompanied by water electrolysis (i.e., oxygen evolution reaction (OER), as depicted in Eqs. (1)–(9)), in which these intermediates chemically adsorbing active oxygen (O_{ads}) and physically adsorbing active oxygen ($\cdot OH$) generated by oxygen evolution reaction OER play a vital role in lignin indirect oxidation mediated by ROS [13,30,31].

$$M\cdot + H_2O \rightleftharpoons M\cdot OH + H^+ + e^- \tag{1}$$

$$M\cdot OH \rightleftharpoons H^+ + e^- + M\cdot O \tag{2}$$

$$M\cdot O + H_2O \rightleftharpoons H^+ + e^- + M\cdot OOH \tag{3}$$

$$M\cdot OOH \rightleftharpoons H^+ + e^- + M\cdot + O_2 \tag{4}$$

$$OH^- + M\cdot \rightleftharpoons M\cdot OH + e^- \tag{5}$$

$$M\cdot OH + OH^- \rightleftharpoons M\cdot O + H_2O + e^- \tag{6}$$

$$M\cdot O + OH^- \rightleftharpoons M\cdot OOH + e^- \tag{7}$$

$$M\cdot OOH + OH^- \rightleftharpoons O_2 + H_2O + e^- + M\cdot \tag{8}$$

$$M\cdot O + M\cdot O \rightleftharpoons O_2 + 2M\cdot \tag{9}$$

in which Eqs. (1)–(4) corresponds to the reaction process in an acidic medium and Eqs. (5)–(8) corresponds to the reaction process in an alkaline medium. Eq. (9) corresponds to the thermal desorption of oxygen. Additionally, M· corresponds to an active site or a bond to the anode electrode surface.

Chemically adsorbing active oxygen O_{ads} and electrode metal oxide (M·O) formed by OER play a crucial role in the selective indirect oxygenation reaction of lignin [13]. Detailed reactions are presented in Eqs. (10) and (11). When current was loaded on the reactor, lignin was adsorbed on the active site of the electrode. Then, formed M/M·O during OER process was used as a redox couple to oxidize lignin into low molecular weight products (electrochemical conversion), achieving the oxygen atom transfer from H_2O to lignin products and reducing the potential of H_2 generation at the cathode [13,31]. Conversely, physically adsorbing active

oxygen ·OH is not conducive to product-directed regulation even mineralizing lignin into carbon dioxide (electrochemical combustion). Nonetheless, electrochemical conversion and electrochemical combustion are determined by electrode activity [13]. For active electrodes like IrO_2, there is a strong chemical interaction with ·OH. ·OH is easily converted into O_{ads} to form M·O, which is considered more selective for lignin oxidation. On the contrary, for non-active electrodes like Ti/Sb–SnO_2, free ·OH at the electrode finds it more easy to non-selectively oxidize the lignin into CO_2 [13]. Cyclic voltammetry can reveal the active site of lignin oxidation since surface catalysis of lignin would cause the variation of the cyclic voltammetry curve due to the active site occupancy of OER. Conversely, the cyclic voltammetry curve remains unchanged when the lignin was oxidised in the electrolyte [32].

$$Lignin + M· \rightleftharpoons M·Lignin \tag{10}$$

$$M·Lignin + M·O \rightleftharpoons Lignin·O + 2M· \tag{11}$$
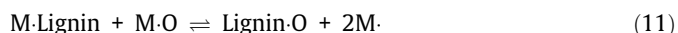
Another indirect oxidation reaction of lignin mediated by ROS occurs via oxygen reduction reaction (ORR) at the cathode. Oxygen generated at the anode acquire electrons at the cathode to produce $O_2^{-·}$, ·OOH, and H_2O_2 as well as its derivative ROS such as ·OH. ORR can be divided into two-electron and four-electron pathways, in which the product of the former is H_2O_2 while H_2O is the product of the latter [33]. Compared with a four-electron pathway (1.23 V vs reversible hydrogen electrode (RHE)), the two-electron pathway of ORR is conducted at a lower potential (0.70 V vs RHE). This indicates that lignin depolymerizes mediated by ROS from ORR and is advantageous to reduce the energy requirement of the overall process. In term of the ORR mechanism, it can be categorized as dissociative mechanism, associative mechanism, and peroxo mechanism [33]. Reaction mechanism and electron/proton transfer were delineated in Figs. 3(a) and (b) [33]. Notably, intermediate HOO* can be converted into OH* in associative mechanism. Additionally, in the peroxo mechanism, HOOH* can also be formed by

continuous addition of electron/proton pair towards HOO*. Furthermore, HOOH* can also be converted into OH*. For ORR reaction, common Pt-based catalyst exhibits strong interaction between molecular oxygen and catalyst. As a result, O_2 adsorption is not considered as rate-determining step. On the contrary, the theoretical overpotential is considered a function of binding energy of these intermediates, thus intermediates adsorption was considered as the rate-determining step [33].

Based on the Sabatier principle, the design of the catalyst should be considered from the perspective of binding energy. Briefly, the binding ability can neither be too strong nor too weak, a volcano-type relationship (Fig. 3(c)). It was reported that overpotential also significantly affected the binding energy, indicating that binding energy can be manipulated via the catalyst and by overpotential. Ideally, lignin depolymerization mediated by ROS from ORR should be conducted with fast kinetics and high current density, with relatively low overpotential. Without the presence of a membrane, anodic oxidation and cathodic hydrogen peroxide oxidation jointly participate in lignin depolymerization [13,34].

To sum up, relating to the synchronous occurrence of OER and lignin oxidation, it is crucial for anodic selective oxygenation of lignin to employ an electrode material that retains O_{ads} for as long as possible instead of oxygen generation. On the other hand, for ROS formation reaction from ORR, the competition reaction between H_2O and H_2O_2 production should be carefully regulated. Additionally, the strong chemical interaction between reactants and electrodes is also essential in an interface reaction. Overall, lignin solubility, properties of the catalytic layer, corrosion behavior of anode and species transport in solution are crucial limitations for the surface catalysis of lignin.

3.1.2. Indirect reaction pathway mediated by small molecules

Indirect oxidation reaction pathways of lignin mediated by redox species are divided into two types: small molecules-mediated lignin oxidation and enzyme-mediated lignin oxidation, both of which occur in the electrolyte. In small molecule-mediated
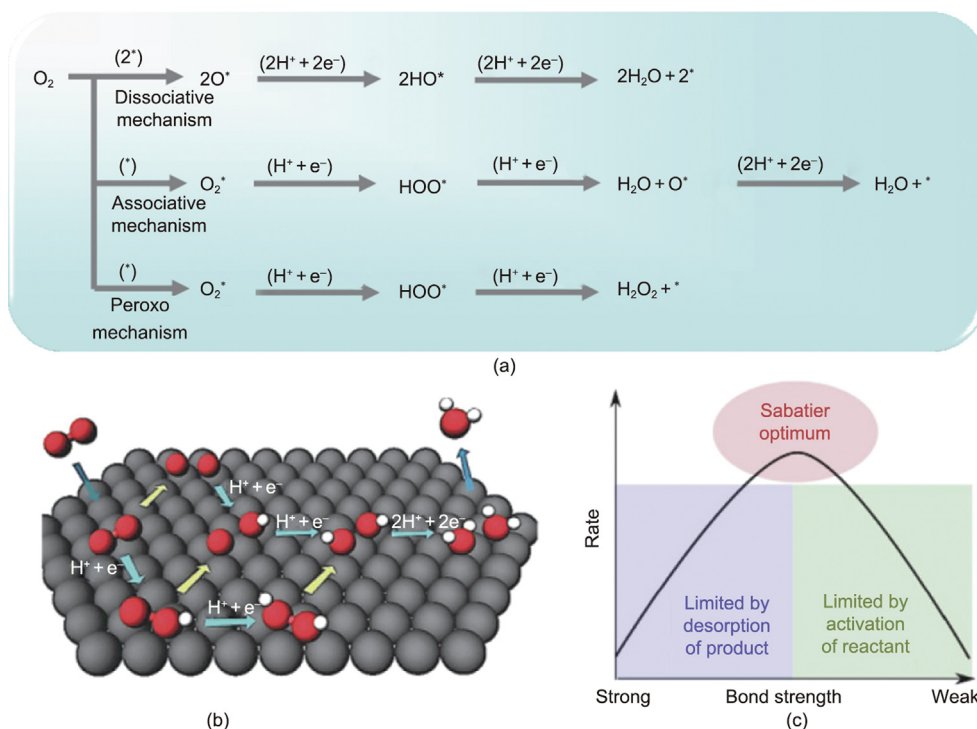

Fig. 3. (a) Pathway of ORR, (b) electron and proton transfer on catalyst (black sphere denotes catalyst atom, red sphere denotes oxygen atom, and yellow sphere denotes hydrogen atom), and (c) schematic representation of the qualitative Sabatier principle. Reproduced from Ref. [33] with permission.

lignin depolymerization, widely studied redox species mainly contain polyoxometalate (POM), Fe^{3+}/Fe^{2+}, 2,2,6,6-tetramethylpiperidine-*N*-oxyl (TEMPO), phthalimide-*N*-oxyl (PINO), nitroaromatics, and NaI [35–41]. POM, as a type of water-soluble molecular metal–oxide clusters, has been extensively used for decoupling of hydrogen and oxygen evolution in H_2O electrolysis by acting as electron-coupled-proton buffer. In term of POM-mediated lignin oxidation process, POM with high redox potential (0.8–1.0 V versus normal hydrogen electrode (NHE)) has the ability to oxidize the lignin. Firstly, lignin depolymerization is achieved by the hydrogen abstraction ability of POM under heating, simultaneously forming reduced $H-POM_{red}$ complex. Then, $H-POM_{red}$ complex is converted to POM at the anode. Also, the protons and electrons are simultaneously released [37,42]. A prominent advantage for this process is that a noble metal catalyst is not required. In the Fe^{3+}/Fe^{2+} ion pair-mediated lignin oxidation process, Fe^{3+} acts as a strong oxidant to depolymerize lignin under heating while Fe^{3+} is regenerated by oxidation of Fe^{2+} at the anode [35].

Two redox cycles with a potential range from -2 to $+ 2$ V versus saturated calomel electrode (SCE) are proposed in the TEMPO-mediated lignin oxidation process (Fig. 4) [29,43]. Analogous to POM, TEMPO can act as H atom abstractor to depolymerize lignin. Then, the TEMPO was regenerated by the anodic oxidation of produced hydroxylamine (TEMPOH). Also, protons and electrons were simultaneously released at the anode. Nonetheless, this model was limited by the weak hydrogen abstraction ability of TEMPO [44]. On the other hand, TEMPO can be oxidized to form active oxidizing species (oxoammonium ion), which easily react with the alcohols to generate aldehydes and carboxylic acids. TEMPO is regenerated at the anode [45]. As another hydrogen atom transfer (HAT) abstractor, PINO can be generated by the oxidation of *N*-hydroxyphthalimide (NHPI) under alkaline conditions [46,47]. But PINO is short-lived. Based on the high BDE (88 kcal·mol^{-1}, 1 kcal = 4.19002×10^3 J) for NHPI, PINO was considered as a potent HAT electrocatalyst [29]. Generally, PINO can efficiently react with C–H bonds, and allylic and benzylic units in lignin [44,48].

Additionally, nitroaromatics and NaI are also used as redox mediators for lignin depolymerization. Typically, tris(4-bromophenyl) amine (Ar_3N) can be as redox mediator (Ar_3N/Ar_3N^+) to oxidize lignin via single-electron transfer reaction under alkaline condition. In such process, the $C_\alpha-C_\beta$ bond is first broken. Then, aldehyde products like vanillin are generated via further electron transfer and deprotonation. Also, ketonic products are also generated due to the deprotonation at C_α competing with the $C_\alpha-C_\beta$ bond cleavage. Finally, Ar_3N was regenerated at the anode [40]. Analogously, in NaI-mediated electrochemical oxidation, iodide ion was oxidized into oxidation state ($I^\oplus$) by anodic oxidation. Meanwhile, the solvent methanol was reduced into MeO^- driven by cathodic reduction. After a series of reactions, the $C_\beta-O$ bond was selectively cleaved while MeO^- was incorporated into the products [41].

3.1.3. Indirect reaction pathway mediated by enzyme

Several microorganisms that can effectively degrade lignin have evolved in nature even though lignin is recalcitrant and resistant to chemical degradation. These microorganisms with lignin depolymerization ability are collectively called as white-rot fungi. Rot fungi degradation of lignin mainly depends on its secreted extracellular enzymes. The enzymes that have been extensively identified for lignin depolymerization include lignin peroxidase (LiP), manganese peroxidase (MnP), and laccase (Lac) [49–51]. At present, enzyme-mediated lignin electrochemical oxidation has been successfully applied. In this section, enzyme property and electrochemically activated enzymatic depolymerization pathways are highlighted.

Electrolysis produces O_2 and H_2O_2, which are vital activators for the enzymatic depolymerization of lignin. O_2 is necessary for Lac-mediated lignin depolymerization while LiP and MnP-mediated lignin depolymerization require H_2O_2 as an activator [49]. Lac, which weighs 50–70 kDa, consists of three cupredoxin domains with β-barrel symmetry. The reaction mechanism of Lac catalysis is shown in Fig. 5 [44–51]. In general, Lac contains four copper atoms, which make up three active sites (T1, T2, and T3) responsible for the catalytic depolymerization of lignin. In detail, T1 is the reaction's starting point to directly react with lignin, while T2 and T3 tend to form trinuclear copper clusters. During lignin depolymerization, T1 copper oxidizes lignin into a lignin radical. Then, the electron was transferred to T2/T3 copper clusters. In this way, four electrons from lignin are accepted by O_2 to form two molecules of H_2O. Additionally, Lac is regenerated to perform the subsequent lignin oxidation [49]. Conversely, the lignin depolymerization by LiP and MnP is accomplished in the presence of H_2O_2 instead of O_2 [50–52]. In addition, the active site of LiP and MnP contains Fe. Fig. 5 shows the detailed reaction mechanism. For LiP, the catalytic process can be divided into three steps: ① Fe(III) in ferric enzyme [LiP]–Fe(III) was oxidized to Fe(IV) ([LiP–Fe(IV)]$^+$), ② [LiP–Fe(IV)]$^+$ was reduced to [LiP–Fe(IV)] by capturing the electron in first lignin substrate, and ③ [LiP–Fe(IV)] was reduced to the initial status by further capturing the electron in second lignin substrate [50]. The reaction of the MnP catalysis process is similar to the LiP catalytic process.

3.2. Reduction reaction pathway in lignin electrochemical conversion

Lignin electrochemical reduction involves two mechanisms: direct reduction caused by electronation–protonation (electron acquirement not involving adsorbed hydrogen (H_{ads})) and indirect reduction resulted from H_{ads} (electrochemical hydrogenation or hydrogenolysis (ECH) involving H_{ads}) [53,54]. Direct reduction is considered to require a higher cathodic potential versus indirect reduction [54]. Regardless of direct reduction or indirect reduction mechanism, competing reactions would occur during lignin reduction depolymerization: for example, hydrogen evolution reaction (HER). HER is identified as a side reaction in lignin ECH [55]. During the reaction process [18], $M \cdot H_{ads}$ are formed on the cathode surface via the Volmer reactions (Eqs. (12) and (13)). Meanwhile, the lignin substrate is adsorbed on the catalytic active site on the cathode surface (Eq. (14)). Furthermore, ECH is accomplished, and the hydrogenated product was desorbed (Eqs. (15) and (16)). Nonetheless, the HER also occurs at the same time (Eqs. (17)–(19)). This is not conducive to the ECH of substrates since the H_{ads} is a vital active intermediate for ECH reactions [56]. H_{ads} production can be adjusted by altering the electrode potential or current density, which provides a feasible strategy to reduce the HER for the improvement of ECH [18]. It is worthy mentioned that regulation
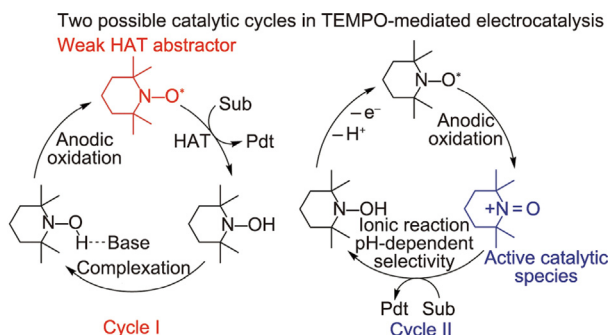

Two possible catalytic cycles in TEMPO-mediated electrocatalysis

Fig. 4. Schematic of possible catalytic cycles in TEMPO-mediated electrocatalysis. HAT: hydrogen atom transfer. Reproduced from Ref. [29] with permission.
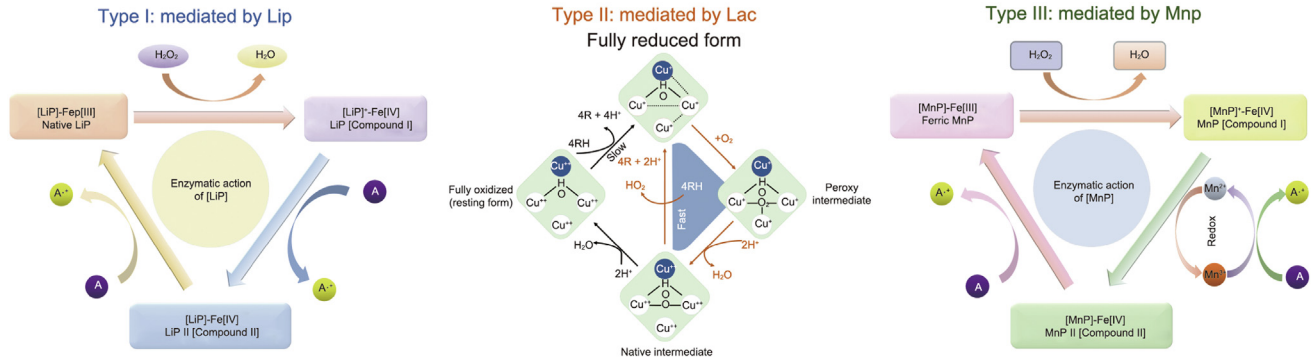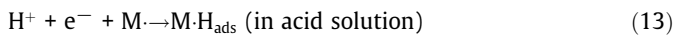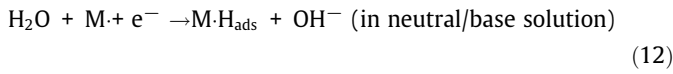
Fig. 5. Reaction pathway of lignin ECO mediated by enzyme. Reproduced from Refs. [49–51] with permission.

of the H_{ads} coverage by cathodic potential in electrocatalysis is equivalent to the alteration of hydrogen pressure in thermocatalytic hydrogenation–hydrogenolysis [18].

Volmer reactions:

$$H_2O + M\cdot + e^- \rightarrow M\cdot H_{ads} + OH^- \text{ (in neutral/base solution)} \tag{12}$$

$$H^+ + e^- + M\cdot \rightarrow M\cdot H_{ads} \text{ (in acid solution)} \tag{13}$$

Substrate adsorption on the catalytic active site:

$$R + M\cdot \rightarrow R_{ads}\cdot M \tag{14}$$

where R is the reactant during reaction.

Reaction between substrates and H_{ads}:

$$M\cdot H_{ads} + R_{ads}\cdot M \rightarrow (RH)_{ads}\cdot M \tag{15}$$

Desorption of the hydrogenated product:

$$(RH)_{ads}\cdot M \rightarrow RH + M\cdot \tag{16}$$

Heyrovsky reaction:

$$M\cdot H_{ads} + H_2O + e^- \rightarrow H_2 + M\cdot + OH^- \text{ (in neutral/base solution)} \tag{17}$$

$$M\cdot H_{ads} + e^- + (H^+)_{aq} \rightarrow H_2 + M\cdot \text{ (in neutral/base solution)} \tag{18}$$

Tafel reactions:

$$2\ M\cdot H_{ads} \rightarrow H_2 + 2M\cdot \tag{19}$$
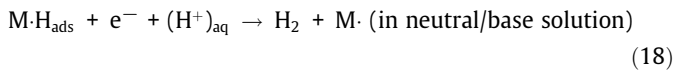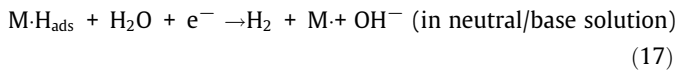
4. Kinetics/thermodynamics and electron transfer mechanism in electrochemistry

The cleavage of C–C bonds and C–O bonds in electrochemistry have been extensively studied in chemicals synthesis. They can be regulated by potential, current density, and mediators [57,58]. The reaction mechanism of bond cleavage can be explained by the Arrhenius law and Nernst equation, which described the kinetics and thermodynamics in electrochemical reaction [59]. The Nernst equation has provided an explanation for the occurrence of endothermic reaction under standard conditions driven by electrochemical potential. Conversely, the kinetics of electrochemical reaction is quite complicated, electrocatalysts can enhance the reaction rate by improving the electron transfer, and then further promote the cleavage or formation of chemical bond [60]. Also, the overpotential greatly affects the reaction kinetics [60]. Kinetics can be categorized by two situations, inner-sphere and outer-sphere electron transfer mechanisms [59–61]. Detailed

information about electron transfer mechanism and kinetics are illustrated in Appendix A Sections S2 and S3. Here, some vital reaction equation like reaction rate of lignin ECH upgrading relating to electrochemical reduction process are described, as shown in Eqs. (20)–(24) [54].

$$R_{ECH} = \frac{C_{rECH}}{T \times M_{cat} \times M_{loading}} \tag{20}$$

$$R_{HER} = \frac{G_{HER}}{T \times M_{cat} \times M_{loading}} \tag{21}$$

$$TOF(s^{-1}) = \frac{C_r}{T \times I \times M_m} \tag{22}$$

$$FE = \frac{E_h}{E_{h,total}} \tag{23}$$

$$Conversion = \frac{C_r}{M_{initial}} \times 100\% \tag{24}$$

where R_{ECH} (mol·s^{-1}·g^{-1}) and R_{HER} (mol·s^{-1}·g^{-1}) denote the specific ECH rate and specefic HER rate; C_{rECH} denote the moles of reactant consumed via ECH; G_{HER} denotes the moles of hydrogen gas generation; T denotes reaction time; M_{cat} and $M_{loading}$ denote the mass of catalyst and metal loading; TOF denotes turn over frequency; C_r denotes the moles of reactant consumed; FE denotes Faradaic efficiency; I and M_m denote the dispersion of metal and moles of metal in the catalyst. E_h and $E_{h,total}$ denotes the electrons consumed by hydrogenation/hydrogenolysis of organic compounds and total electrons passed; $M_{initial}$ denotes the initial moles of reactant.

Based on these equations related to electrochemical reduction process reported by Akhade et al. [54], the relevant equations involved in ECO of lignin into chemicals are proposed in this review, as depicted in Eqs. (25)–(27). Notably, the prerequisite of Eq. (25) applied for lignin electrochemical oxidative valorization into useful chemicals is that there is no the occurrence of overoxidation (i.e., without generating CO_2). When considering the presence of CO_2 production reaction, specific ECO rate of lignin valorization can be obtained by Eq. (26).

$$R_{ECO} = \frac{C_{rECO}}{T \times M_{cat} \times M_{loading}} \tag{25}$$

$$R_{ECO} = \frac{C_{rWhole} - C_{rCO_2}}{T \times M_{cat} \times M_{loading}} \tag{26}$$

$$R_{OER} = \frac{G_{OER}}{T \times M_{cat} \times M_{loading}} \tag{27}$$

$$FE = \frac{E_o}{E_{o,total}} \quad (28)$$

where R_{ECO} (mol·s^{-1}·g^{-1}) and R_{OER} (mol·s^{-1}·g^{-1}) denote the specefic ECO rate and specefic OER rate; C_{rECO} denote the moles of reactant consumed via ECO; G_{OER} denotes the moles of oxygen gas generation; C_{rWhole} denotes the moles of reactant consumed by whole process; C_{rCO_2} denotes the moles of reactant consumed by CO_2 generation; M_{cat} and $M_{loading}$ denote the mass of catalyst and metal loading; E_o and $E_{o,total}$ denote the electrons consumed by oxygenation of organic compounds and total electrons passed.

Notably, comparing with model compounds, these formulae mentioned above such Eqs. (20) and (25) are inapplicable to actual lignin because it is difficult to determine a real mole of actual lignin at this current stage. Thus, the method of determining the real mole of actual lignin should be established in further work to promote the universality of these formulas.

5. Electrochemical conversion of lignin

Presently, large amounts of works have been carried out to achieve the lignin depolymerization and upgrading of lignin derivative via ECO and ECR technique. In this section, typical cases of lignin ECO and ECR are discussed. More points about lignin ECO and ECR are summarized in Table S3 and S4 in Appendix A, respectively. Also, the application of electrochemical techniques to the upstream and downstream process of lignin biorefinery were elucidated in Appendix A Section S4.

5.1. Electrochemical oxidative conversion of lignin

In this section, typical features and relevant mechanisms in lignin ECO are introduced rather than tedious elaboration involving different lignin substrates, including the application of various types of electrodes on lignin ECO, lignin ECO mediated by ROS, small molecules and enzyme, lignin ECO in ionic liquids (ILs), deep eutectic solvent (DES) and in *in situ* separation system, and the hybrid conversion of integrating lignin ECO and other processes (Fig. 6) [62].

5.1.1. Application of various types of electrodes

Currently, reported electrodes in lignin oxidation mainly involve metals (Pt, Au, Ni, Cu, and Co), metal oxides (Pb/PbO$_2$-based and TiO$_2$-based) and doped systems (Pt$_1$/N- carbon nano tubes (CNTs)). A Ni electrode is outstanding for lignin depolymerization due to the stability and high electrocatalytic activity [13]. Under alkaline conditions, catalytic activity of the electrode can be greatly increased due to the formation of NiOOH. Most impor-

Fig. 6. Lignin depolymerization methods and lignin ECO classification. Reproduced from Ref. [62] with permission.

tantly, overoxidation of the aromatic monomers can be avoided [63]. By applying nickel foam as electrocatalyst for ECO of organosolv lignin isolated from sweetgum, a maximum yield of 17.5% for aromatic monomer was achieved. Nonetheless, it is worthy of mention that the application of single metal electrode on lignin depolymerization poses the risk of electrode passivation.

Parpot et al. [64] comprehensively evaluated the ECO of kraft lignin in batch and flow cells using Pt, Au, Ni, and Cu as the anode. Kinetic analysis revealed that the conversion and yield of vanillin relied on loaded current density. Conversely, the reaction rate was determined by anodic material. Although kraft lignin depolymerization was successfully achieved, the required potential is higher than OER to avoid electrode passivation. In such a case, the competition reaction between lignin oxidation and OER was intensified. Also, the high cost for precious metal electrodes also should be considered. In order to achieve the lignin depolymerization without the occurrence of OER, alloy electrode provided a viable option, which attributed to the advantages of low cost, higher catalytic activity and corrosion resistance caused by the synergistic effects of various metals. This statement has been verified by Movil et al [65]. Although Co–C electrodes displayed a relatively high reactive rate for lignin oxidation than alloy electrode NiCo–C at the beginning, activities of Co–C electrode was rapidly reduced because of the decrease in active sites resulted from lignin and oxidized products adsorption. In the lignin depolymerization mediated by alloy electrode, electrode potential might cause the difference in some oxidation mechanisms and products distribution, indicating that homogeneous chemical and heterogeneous electrochemical reactions simultaneously occurred [14].

Considering the further optimization of the catalytic efficiency and corrosion resistance, Wang et al. [66] used metal oxide electrode Pb/PbO$_2$ as the anode to oxidize aspen lignin, acquiring a maximum yield of 4-methylanisole (343.3 g·kg^{-1} lignin) under optimal operating conditions. Likewise, Cai et al. [56] used Pb/PbO$_2$ as anode and Cu/Ni–Mo–Co as cathode to study the ECO depolymerization of corn stover lignin in alkaline solution, obtaining large amounts of valuable chemicals. A common point for these works is that products were formed by firstly lignin oxidation into intermediates at the anode following by hydrogenation. However, it is well-known that Pb poses toxicity problems, limiting its further development [12]. In contrast, due to their stability, ideal electrocatalytic activity and environmental friendliness, TiO$_2$-based and IrO$_2$-based electrodes were extensively employed for lignin depolymerization. Tolba et al. [67] prepared four IrO$_2$-based electrodes (Ti/RuO$_2$–IrO$_2$, Ti/SnO$_2$–IrO$_2$, Ti/Ta$_2$O$_5$–IrO$_2$, and Ti/TiO$_2$–IrO$_2$) via thermal decomposition approach to explore the ECO of lignin. Pseudo-first-order kinetics was followed for both four electrodes in lignin oxidation. Among the four electrodes, Ti/TiO$_2$–IrO$_2$ electrode exhibited the optimal reactive activity towards lignin oxidation. While, Ti/Ta$_2$O$_5$–IrO$_2$ electrode can be used as the ideal material of OER. Recently, Chang et al. [68] explored the performance of using TiO$_2$ nanotube as anode for lignin oxidation. The rate constant of lignin oxidation with electrochemically reduced TiO$_2$ nanotubes as the anode is 11 times than Pt. Also, the stability of electrochemically reduced TiO$_2$ nanotubes was confirmed.

Another challenge in lignin depolymerization is the regulation of selectivity. To enhance the depolymerization product selectivity and yield in ECO, Zhou et al. [69] designed Mn-doped cobalt oxyhydroxide (MnCoOOH) catalyst via an electrodeposition method as the anode to selectively cleave the C(OH)–C and C(O)–C bond of lignin into carboxylic acid product, with the high yields for benzoate (91.5%) and adipate (64.2%). The reaction selectivity can be explained by tandem nucleophilic oxidation reactions (NOR) (Fig. 7) [69]. Under alkaline conditions, ketones and alcohols were derivatized as reactive nucleophiles by deprotonation. Then, these reactive nucleophiles were oxidized via electrophilic oxygen
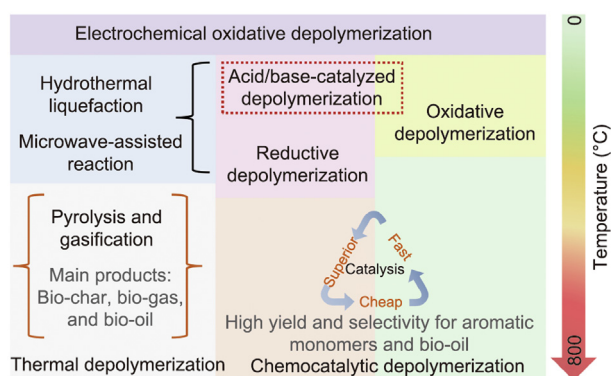
species on MnCoOOH before the oxygen evolution reaction (OER) occurs (Fig. 7).

Similarly, Cui et al. [70] successfully constructed a single-atom Pt catalyst anchored on Pt_1/N-CNTs catalyst via a stepwise polymerization–carbonization–electrostatic adsorption strategy to selectively convert lignin into benzaldehyde [70]. Investigations indicated that atomically dispersed $Pt-N_3C_1$ sites on nitrogen-doped carbon nanotubes pose intense activity and selectivity for $C_\alpha-C_\beta$ in β-O-4 dimeric model compounds. As such, 99 % of the substrate was converted and the benzaldehyde yield was up to 80%. In addition, the performance between Pt_1/N-CNTs and bulk Pt electrodes or commercial Pt/C catalysts was further compared by researchers. In contrast, Pt_1/N-CNTs (0.41 wt%) showed a better yield of benzaldehyde. By combing experimental studies and density functional theory calculations, it was shown that the superior performance of Pt_1/N-CNTs is caused by that atomically dispersed $Pt-N_3C_1$ sites promoting the formation of crucial C_β radical intermediates, further inducing free radical/radical coupling. Subsequently, the cleavage of $C_\alpha-C_\beta$ bonds was achieved (Fig. 8) [70].

Overall, the major challenges in the surface electrocatalysis mainly include catalytic activity, electrode corrosion resistance and products selectivity. Although various types of electrocatalyst have been designed, the electrocatalyst that integrates multiple advantageous features is still scarce. Especially, the application of these developed electrocatalysts or electrodes should be further explored in real lignin electrochemical depolymerization. Continued work in superior electrocatalyst design is still very important. Also, the applicability of novel electrocatalyst should be concentrated on real lignin rather than model compound to promote the industrial application of lignin valorization via electrochemical conversion.

5.1.2. Mediated by ROS

Lignin depolymerization mediated by ROS is a non-selective pathway, which is achieved by the ORR. ROS (*in situ* generated H_2O_2 and its decomposition products), as a type of environment-friendly and strong oxidizing agent, can achieve lignin depolymerization by cleaving the ether bond and alkyl–O–aryl bond of lignin (Fig. 9) [5,71,72]. High ROS concentration is more conducive to acquiring low molecular weight products. In the work reported by Zhu et al. [71], large amounts of products such as phenol, vanillin, and phenylacetic acid etc., are acquired by ROS-mediated ECO including anodic electrooxidation and cathodic chemical oxidation mediated by H_2O_2 from ORR. Additionally, the average molecular weight of the solid product was reduced to 1000. Temperature and current density are vital parameters for controlling
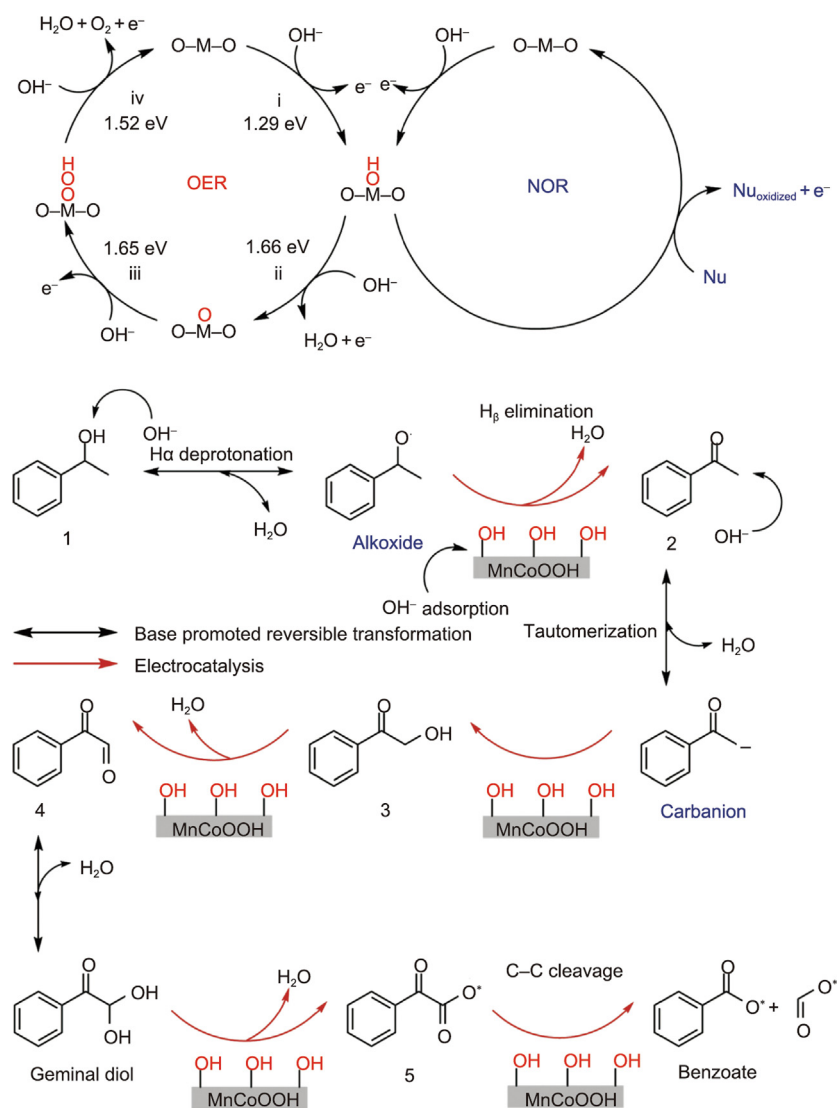

Fig. 7. Schematic of the formation of OER electrophiles and NOR mechanism. Reproduced from Ref. [69] with permission.
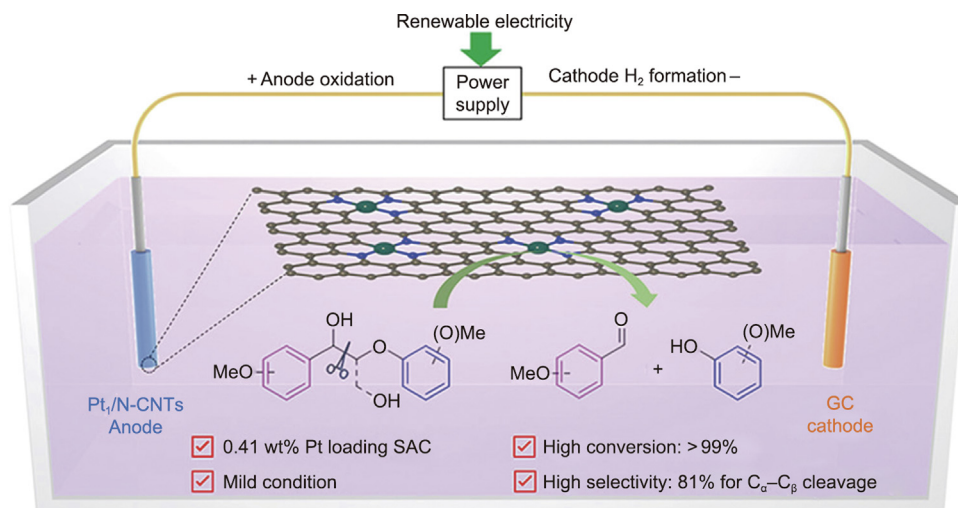
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Fig. 8. Pt$_1$/N-CNTs-catalyzed conversion mechanism of lignin β-O-4 dimeric model compounds into benzaldehyde. Reproduced from Ref. [70] with permission.
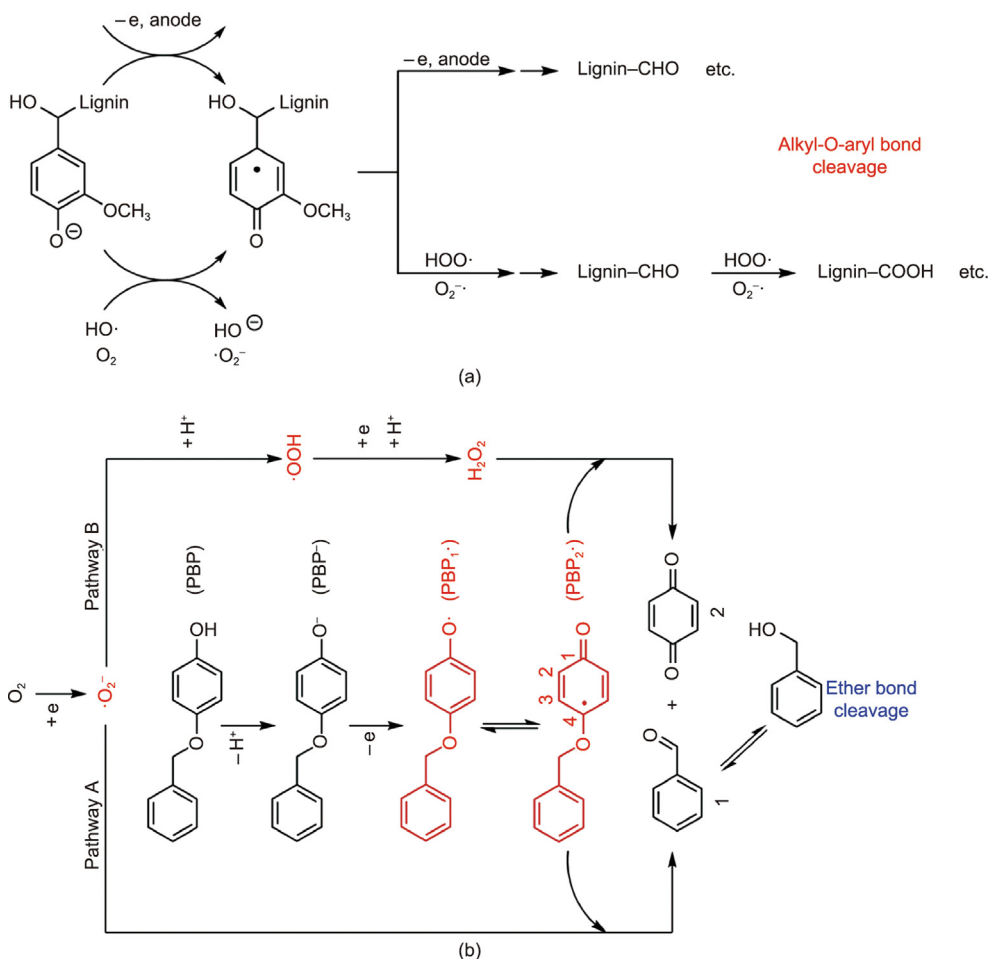

Fig. 9. Reaction pathway of ROS-mediated electrochemical oxidation of lignin. (a) ROS-mediated electrochemical oxidation of crude lignin. Reproduced from Ref. [71] with permission. (b) ROS-mediated electrochemical oxidation of lignin model. Reproduced from Ref. [72] with permission.

products composition. Elevated temperature led to more hydrophilic functional group products like phenols and acids. This is because that the higher temperature accelerated ROS formation. On the other hand, enhancing the current density promotes the cleavage of C–C bonds, thus facilitating formation of the aldehydes or

ketones [71]. Wang et al. [72] adopted ORR to degrade lignin model p-benzyloxyl phenol and identify the ROS. By electrochemical analysis, $O_2^{-\cdot}$ generated by the single-electron reductive reaction of dioxygen was proved to be the main product. Then, $O_2^{-\cdot}$ was further converted into ·OOH using protons from p-benzyloxyl phenol.

Lastly, ·OOH received a mole electron to form H_2O_2, which responds to the cleavage of the ether bonds in *p*-benzyloxyl phenol.

Recently, Ma et al. [73] first reported the case of *tert*-butyl hydroperoxides (*t*-BuOOH)-mediated lignin model substrate ECO at room temperature. *t*-BuOOH was used as the sacrificial oxidants to promote the electrocatalytic depolymerization of the lignin model substrate. The reaction mechanism was delineated in Fig. 10 [73]. During electrocatalytic conversion, *tert*-butylperoxy radical and radical A with C_β–H were formed. Further, the peroxide intermediate was created by the radical/radical cross-coupling between radical A with C_β–H and radical A with active C_β-centered radical A, then bring about the cleavage of the C_α–C_β in lignin model substrate. High yields of aromatic monomers were acquired. Also, the workers extended the substrate to a more complex polymeric model substrate with β-O-4 bonds. Excitingly, the proposed electrocatalytic system still gave a superior selectivity for C_α–C_β cleavage, and the substrate was converted to p-hydroxyl acetophenone in a 5.1% yield.

Compared with the exogenous oxidant, the endogenous oxidant generated by ORR is more economically viable. Notably, mixed reactions (oxidation and reduction reactions) may occur since the endogenous ROS generation is accomplished by the produced oxygen from anodic region, indicating that the products selectivity is difficult to regulate. A feasible solution is to design the specific reactor to transfer the oxygen from the outside to the cathode region. Additionally, due to the non-selective feature of ROS, it seems to be more advantageous using ROS as an auxiliary tool to reduce the molecular weight of lignin rather than product generation. Then, low molecular weight lignin fragments are selectively converted into target products via other strategy.

5.1.3. Mediated by small molecules

The reported small molecules for assisting lignin ECO conversion mainly includes NaI, TEMPO, and NHPI/PINO. This section discusses some typical cases of lignin ECO mediated by small molecules. Gao et al. [41] reported the case of iodide ion-mediated ECO of β-O-4 lignin model substrates using methanol as electrolyte in a single chamber reactor. They observed that electrolytic conditions significantly affected the distribution of cracking products. In the presence of 60 mol% of NaI as the redox mediator and 6 mA·cm^{-2} of current density, the C_β–O bond was selectively cleaved. Lignin model compounds were converted to 2,2-dimethoxy-2-phenylacetaldehyde in a 68% of yield.

Sannami et al. [74] explored the ECO conversion of lignin model substrate with β-O-4 containing non-phenolic subunits using TEMPO and 4-acetoamido-TEMPO as redox mediators. They noted that the selectivity between C_α-carbonylation and C_γ-carboxylation of substrate strongly depended on electrolytes. In the system consisting of CH_3CN–H_2O and $LiClO_4$, carbonylation

(benzylic oxidation) was preferred. At the same time, a low products yield was observed (1.9%–11.1%). In the dioxane/phosphate buffer, carbonylation (aliphatic oxidation) was favoured. A high products yield (72.0%–93.2%) was achieved. The workers further verified the reason for reaction selectivity by using 4-acetoamido-TEMPO as redox mediators. As with the case in the dioxane/phosphate buffer, the same selectivity was observed but with a higher product yield versus TEMPO. Lately, the 4-acetamido-TEMPO-mediated electrocatalytic conversion of primary alcohols in lignin has been investigated [38]. High selectivity of alcohols to carboxylic acids was observed. By using oxidized lignin under acidic conditions as substrate, about 30% of aromatic monomers was obtained in this electrocatalytic system.

Shiraishi et al. [75] studied the NHPI-mediated ECO conversion of non-phenolic lignin substrate. 2,6-lutidine significantly enhances the selectivity of C_α-carbonylation of lignin substrate. Lignin substrates were converted to C_α-carbonyl compounds in a high yield (85%–97%). Meanwhile, the ECO conversion of dimeric lignin mediated by NHPI also acquired 88%–92% yield of C_α-carbonyl compounds. Also, the 2,2'-azino-bis(3-ethylbenzothiazoline-6-sulfonate) (ABST)-mediated dimeric lignin oxidation was studied, which gave a low yield (5%–40%) for the C_α–C_β cleavage product. In contrast, NHPI provided a high selectivity for converting non-phenolic β-O-4 to C_α-carbonyl compounds.

Electrochemical depolymerization of lignin mediated by various types of small molecules has been successfully performed, which is conducive to reduce the reaction potential and further avoid the occurrence of OER. Nonetheless, it is worth mentioning that the economic cost, molecular recyclability and reuse should be explored in future work, and especially for the application of real lignin.

5.1.4. Mediated by enzyme

Lignin depolymerization mediated by enzymes provides a promising pathway in term of product purity. In general, Lac can oxidize phenolic subunits such as polyphenols and methoxy-substituted phenols. Lac itself contains non-phenolic subunits, and thus non-phenolic subunits cannot be oxidized by Lac [50]. The fundamental reason is that the redox potential required by non-phenolic subunits oxidation is higher than the value provided by the T1 active site [13,49]. It was reported that the maximum redox potential of Lac depends on T1, which determined the application range of Lac-mediated lignin oxidation [49]. Although the study on Lac-mediated ECO conversion of lignin is rare, it presents promising potential. In Lac-mediated lignin oxidation, two reaction mechanisms were proposed: that is, e$^-$ transfer and H atom transfer mechanism [76,77]. For the former, the electron was captured from lignin substrate, forming a radical cation. Conversely, a hydrogen atom and an electron are simultaneously captured to create a radical in H atom transfer mechanism. This provides the
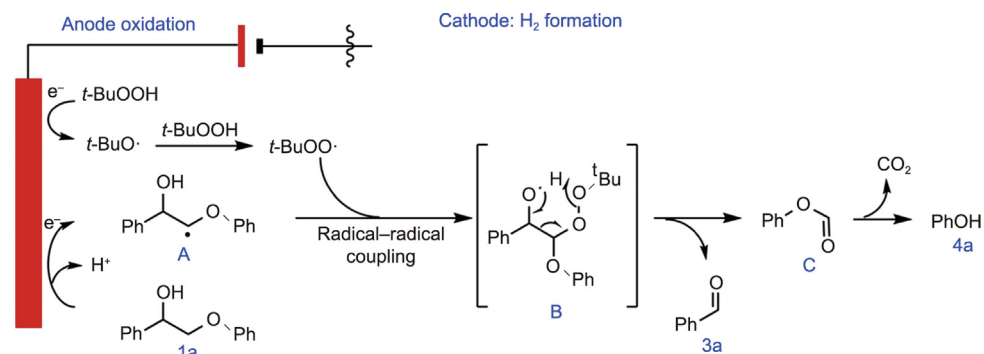

Fig. 10. Mechanism of the C_α–C_β cleavage in *t*-BuOOH-mediated electrochemical oxidation of lignin model. Reproduced from Ref. [73] with permission.

opportunity to integrate electrocatalysis and Lac oxidation. Overall, two advantages for Lac-mediated electrocatalysis process are presented: ① broadening the operating condition window like pH and temperature, and ② increasing redox potential of the system by introducing other mediators. At present, smaller mediator molecules such as hydroxybenzotriazole, TEMPO and violuric acid have been adopted for electrocatalytic conversion of non-phenolic lignin dimers using Las as a mediator [78,79]. Although the C_α=O bond is enhanced and the C_α–C_β bond was cleaved, the products are still dimers [80].

It has been convincingly shown that LiP can oxidize phenolic subunits (β-O-4 bond), non-phenolic subunits, and organic matter with oxidation potential less than 1.4 V [51]. However, the LiP-mediated lignin oxidation requires the addition of H_2O_2, barring the development of this technique. Lee et al. [81] conducted the oxidation depolymerization of lignin model substrate veratryl alcohol in the LiP-mediated electrocatalytic system consisting of a two-chamber electrochemical reactor separated by a proton exchange membrane, avoiding any crossover from the anodic reaction and the cathodic reaction. LiP was activated by the *in situ* generated H_2O_2 at the cathode, which converted veratryl alcohol to veratryl aldehyde. Likewise, Ko et al. [82] developed a three-chamber LiP-mediated photo-electrocatalytic system using a Co-based electrocatalyst and Co–N/CNT catalyst as anode and cathode. The anode and cathode unit are separated via a nanofiltration membrane. Furthermore, the cathode chamber and broth containing LiP and lignin dimer are separated by a cellulose membrane. The *in situ* generated H_2O_2 at the cathode goes across the cellulose membrane to activate LiP, achieving 94% of substrate conversion. MnP can break both the β-O-4 bond in phenolic subunits, C_α–C_β and β-aryl ether bonds in non-phenolic subunits of the substrate [50]. This is conducive to broadening the window on lignin substrates. However, studies on MnP-mediated electrocatalytic conversion of lignin are quite rare and more relevant work is urgently needed.

It is worth mentioning that the repolymerization caused by phenoxy radicals should be taken seriously when building the peroxidases-mediated electrocatalytic system. Additionally, operating conditions like pH and H_2O_2 concentration need to be strictly controlled for precise catalytic conversion of lignin. There are still huge gaps to be filled in term of enzyme-mediated lignin ECO conversion, especially the in-depth mechanism on lignin depolymerization.

5.1.5. ECO conversion of lignin in ILs and DES

The ECO depolymerization of lignin in ILs has several advantages [5]: ① ILs are directly used as electrolytes and solvents, avoiding the use of electrolyte and solvent mixtures; ② lignin solubility was enhanced; ③ adverse reaction during the process of ECO degradation of lignin was reduced because of the wide electrochemical window; ④ under the mild condition, specific products, higher selectivity and catalytic activity can be achieved by applying various voltages to the electrodes; ⑤ the current intensity generated from the electrocatalytic depolymerization reaction is proportionate to the yield of intermediate or the final product; and ⑥ energy consumption of lignin fractionation and recovery was significantly decreased. Therefore, the electrochemical degradation of lignin in ILs has attracted wide attention.

Dier et al. [83] explored the lignin depolymerization in protic ILs (ammonium triethylmethanesulfonate (TMS)) and aprotic ILs (1-ethyl-3-methylimidazolium trifluoromethanesulfonic acid [Emim][OTf]) with two parallel meshed glassy carbon electrodes. Investigations indicate that water strongly affects the lignin depolymerization and protic ILs are more conducive to the generation of H_2O_2. In another work reported by Jiang et al. [84], the authors also demonstrated that H_2O_2 is generated by the

two-electron reduction reaction of O_2 at the cathode. H_2O_2 is used as an oxidant to break the α-O-4 bond of the lignin model compound, resulting in 48.2% of the substrate degradation. Further, Wang et al. [72] performed the lignin model depolymerization experiment in aprotic ILs1-butyl-3-methylimidazolium tetrafluoroborate ([Bmim]BF_4) with RuO_2–IrO_2/Ti meshes and porous C-polytetrafluoroethylene (PTFE) as electrodes. In such a system, *in situ* generated ROS (O_2^-, H_2O_2) attacks the ether bond in lignin and causes lignin depolymerization. Recently, Liu et al. [5] explored the ECO depolymerization of lignin phenolic model compounds in an acidic protic ionic liquid 1-sulfobutyl-3-methylimidazolium trifluoroMethansulfonate [BSO$_3$Hmim][OTf]. ROS were identified by analyzing the redox potential. During electrocatalytic conversion, two depolymerization pathways are verified by altering the ambient atmosphere (Fig. 11) [5]. Under a N_2 atmosphere, the model substrate was directly oxidized on the RuO_2–IrO_2/Ti mesh electrode to form quinones and carbocations by breaking the C_{aryl}–O bond, while under an O_2 atmosphere, in addition to direct oxidation, the lignin substrate was indirectly oxidized on electrodes via *in situ* generation of H_2O_2. The constructed proton-type ionic liquid–water electrolyte system achieves mild transformation of aryl ether bonds in lignin. DES was also employed for lignin catalytic depolymerization. Di Marino et al. [85] explored the ECO depolymerization of kraft lignin in DES and determined the optimal ratio of lignin dissolution required ethylene glycol-choline chloride mixture (molar ration: 1/2). DES does not react with water, and lignin was oxidized in the form of an emulsion. That is to say, the product can be separated *in situ*. After 24 h of treatment, the molecular weight of soluble lignin was decreased to 30% of raw lignin. Significant quantities of products are detected: vanillin (34%–37%), guaiacol (30%–38%) and syringaldehyde (12%).

In fact, ILs and DES are ideal solvents for lignin in term of solubility, conductivity, product recovery and energy consumption. ILs and DES have the capacity to extract lignin from biomass driven by hydrogen bonds and π–π or n–π interactions [86,87]. Obviously, this provides a viable pathway to integrate the lignin fractionation and ECO depolymerization by a one-pot method. However, the cost, toxicity, and viscosity issues for ILs and DES need to be addressed.

5.1.6. ECO conversion of lignin in in situ separation system

A significant limitation in ECO conversion of lignin is the overoxidation of products. To overcome this obstacle, numerous *in situ* products separation systems were designed to minimize product overoxidation, such as *in situ* extraction and in-line membrane separation [85,88,89]. Di Marino et al. [85] designed an *in situ* products extraction system to offset the product's overoxidation of kraft lignin depolymerization. In this process, a deep eutectic solvent was used to dissolve lignin while methyl isobutyl ketone was employed for extraction. The lignin was oxidized in the form of an emulsion and the lignin depolymerization and product separation were simultaneously achieved. However, consumption of chemical agents significantly increases the economic costs of the process.

An electrochemical membrane reactor is a tempting since there is no requirement for extra solvent investment like *in situ* extraction. This has been widely employed for various applications like metal wastewater disposal and substance separation in pulping wastewater [90,91]. Stiefel et al. [88] adopted a nanofiltration membrane to construct an electrochemical membrane reactor for continuous products separation from the reaction environment (Fig. 12) [88]. The product's yield was increased by one time. To reduce the membrane pollution and polarization phenomena, electrode rods are embedded into a turbulence-enhancing mixer printed by three dimension (3D). Recently, Bawareth et al. [89] also
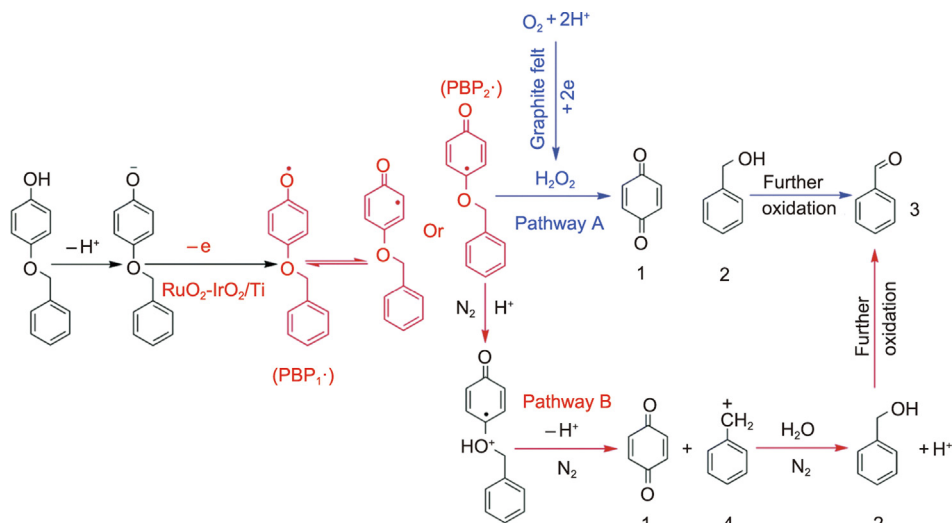
Fig. 11. The mechanism of electrochemical degradation of lignin by direct oxidation (pathway A) and indirect oxidation (pathway B). Reproduced from Ref. [5] with permission.
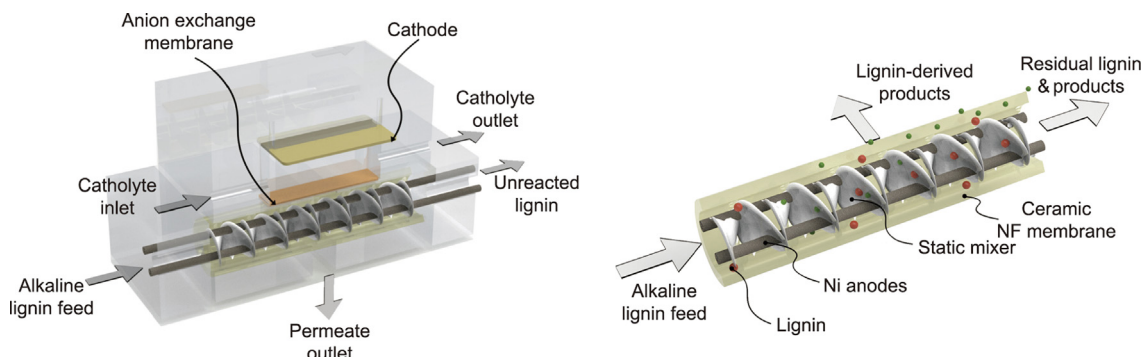

Fig. 12. Scheme of the electrocatalytic membrane reactor. Reproduced from Ref. [88] with permission.

developed an electrochemical membrane reactor and optimized operating parameters to improve the aromatic chemicals yield. Investigations indicated that a nanofiltration membrane with a pore diameter of 1.0 nm allows products with molecular weights below 750 Da to be recovered across the membrane. The aromatic product yields in the membrane reactor increased by 1100 times versus that in the batch reactor. It is worth noting that membrane fouling and high cost are still a major problem that needs to be addressed, especially application of raw lignin. Further focus of work should turn to the development of inexpensive and strong anti-pollution membrane materials. Also, continued work in this field should be conducted to design novel membrane bioreactors.

5.1.7. Hybrid conversion of integrating ECO and other process

Lately, the ECO of lignin model molecule dimers was performed in a sequential two-step one-pot process (firstly ECO followed by photocatalysis) at ambient temperature [39]. The researchers observed that using NHPI as a redox catalyst can significantly reduce the oxidation potential of the ECO process and provide a strong selectivity for the oxidation of benzylic alcohol. The bond dissociation energy of β-O-4 was decreased due to the conversion of the C–OH to the C=C bond. In such a one-pot process, 75 % of 4-methoxyacetophenone was obtained. Two reaction mechanisms involving anodic oxidation and superoxide oxidation were proposed (Fig. 13) [39]. Anodic oxidation was induced by PINO generated from NHPI. In the presence of 2,6-lutidine, the reaction was

further accelerated by proton coupled electron transfer (PCET). Afterwards, NHPI was regenerated by accepting the H atom from the substrate driven by the HAT reagent. In addition, an α-hydroxy radical was generated. But the route of ketyl radical anion to ketone 2 was not observed. Conversely, ketone 2 and superoxide can be directly provided by using O_2 as the oxidant (another mechanism). Under the same conditions, O_2 significantly enhanced the catalytic activity. Two mole electrons for per mole substrate is required under the anaerobic condition while only 1 mole electron is needed for aerobic condition. The rate constant in an oxygen atmosphere is higher than that in a nitrogen atmosphere. Also, the H_2O_2 generated in the oxygen atmosphere is conducive to the C–OH oxidation. Although the superiority of the ECO-photocatalytic process was demonstrated, the applicability of this technique should be carefully considered since the lignin solution is strongly coloured.

It is recognized that product formation strongly relies on temperature [92]. However, most works about lignin were performed below 100 °C, indicating that such temperature conditions are not conducive to product maximization. Zirbes et al. [92] found that the yield of vanillin in the electrochemical conversion of Kraft lignin is positively correlated with temperature. Limited to the experimental device, the optimal temperature was not observed. Subsequently, the authors designed a steel electrolysis cell (unindividual cell) to perform the ECO depolymerization of kraft lignin at high temperature (160 °C). By applying such a device in common
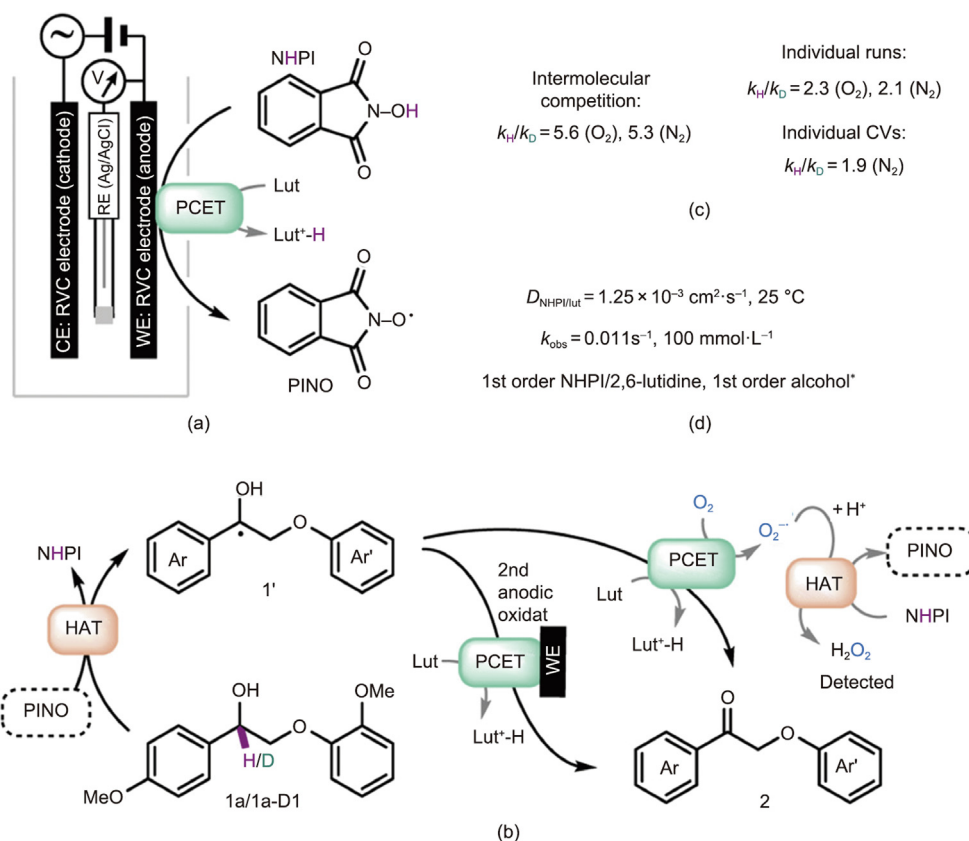
Fig. 13. The mechanism of NHPI/2,6-lutidine-mediated lignin ECO under anaerobic and aerobic conditions. (a) Initiation; (b) propagation and termination; (c) kinetic isotope effect (KIE) experiments for 1a/1a-D1; (d) NHPI/2,6-lutidine performance. Lut: lutidine. Reproduced from Ref. [39] with permission.

nitrobenzene oxidation of lignin, a maximum yield of 4.2% for vanillin was obtained. Compared with common nitrobenzene oxidation, the selectivity was enhanced, with 67% of efficiency. This work provides a viable pathway to integrate electrocatalysis and thermocatalysis, which is crucial for temperature-sensitive aromatical product generation in ECO depolymerization of lignin.

5.1.8. Co-production of chemicals and hydrogen

Considering the slow kinetic feature arising from complex four-electron procesess of OER [93,94], utilizing thermodynamically favorable lignin electrooxidation reaction to substitute the OER is more conducive to enhance energy efficiency of the whole process for co-production of chemicals and hydrogen [69,95]. Recently, the feasibility of relevant case has been verified. By using lignin derivate as a anodic oxidation in the dual-chamber electrocatalytic system using MnCoOOH as anodic electrocatalyst, the cathodic H_2 generation rate was enhanced from 0.1 mmol·$(cm^2·h)^{-1}$ of traditional water splitting to 1.41 mmol·$(cm^2·h)^{-1}$ at a constant potential (1.5 V vs RHE) [69]. Nonetheless, the applied potential may need to be further reduced considering the optimization of energy efficiency. Phosphomolybdic acid (PMA) provide a promising option to extract electron from lignin and reduce the applied potential [95]. By applying PMA as electrocatalyst, the potential required by hydrogen generation was decreased from 1.5–1.6 V versus RHE in traditional water splitting with Ir- and Pt-based noble metal as electrocatalysts to 0.95 V versus RHE, significantly reducing the efficiency of OER and altering the temperature window of lignin valorization into chemicals from refractory decomposition of lignin at high temperature to easy conversion of lignin at low temperature [95]. As such, reasonable strategy development is important in co-production system of chemicals

and hydrogen in term of the energy efficiency variation caused by potential and temperature.

Notably, most studies on cathodic half reactions were focused on the hydrogenation or hydrogenolysis of lignin derivatives by the H_{ads} rather than the hydrogen energy generation. A vital reason is that ECH is favored thermodynamically versus HER since the reduction potential required by ECH is more positive than that of HER [54]. This is beneficial to improve the energy efficiency of whole process. Also, ECH is more advantageous on operation due to that the *in situ* generated H_{ads} was directly utilized for the upgrading of lignin derivatives while hydrogen need to be further transferred and stored. Whereas, HER may be faster than ECH in term of kinetics, indicating that a higher potential is needed to enhance the amount of H_{ads} or achieve the direct reduction of lignin for maximizing reaction rate. Explicitly, the applied potential value that exceeds the thermodynamics redox potential is called the overpotential, which varies with electrode material on achieving a given current density for specific reaction [54]. More detailed information about these aspects is seen in Section 4.

5.2. Electrochemical reductive conversion of lignin

In general, bio-oil derived from lignin features high corrosiveness, chemical instability, low energy value, easy polymerization and elevated viscosity attributing to the existence of reactive oxygenated moieties C=O from aldehydes, ketone, carboxylic acids, and so forth [96,97]. This limits the direct use of bio-oil derived from lignin as biofuel. Consequently, upgrading of bio-oil is necessary to enhance the oil quality. Traditional upgrading strategies are usually conducted under high H_2 pressure (7–20 bar, 1 bar = 10^5 Pa) and temperature (150–500 °C) (Fig. 14) [98,99]. In contrast,
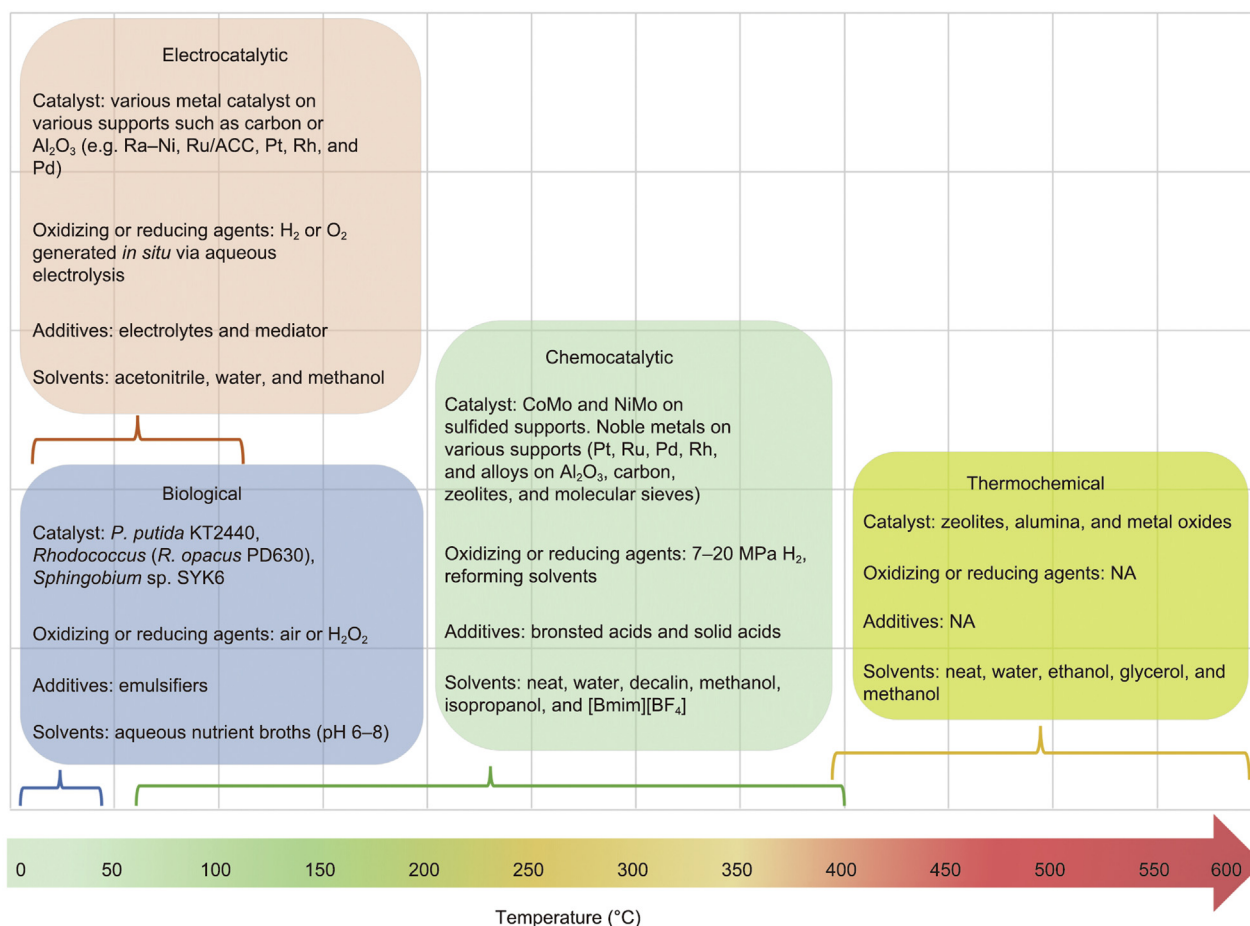
Fig. 14. Comparison of various techniques for lignin upgrading processes. ACC: activated carbon cloth; NA: not available. Reproduced from Ref. [99] with permission.

green H can be produced *in situ* via electrocatalytic reduction. This provides the feasibility to upgrade the bio-oil under mild conditions. It should be emphasized that we have concentrated on the typical characteristics including parameter influence and the selective cleavage of C=C and C–O(CH$_3$) bonds in lignin electrochemical reductive conversion rather than tedious elaboration involving different lignin substrates.

5.2.1. Upgrading of lignin model molecules

A variety of lignin model molecules have been adopted to investigate the ECH of lignin. These model compounds include phenol, guaiacol, syringol, and some alkyl compounds. Li et al. [100] studied the ECH of phenol, guaiacol and syringol using Ru supported on an activated carbon cloth (Ru-ACC) electrode. The performance of electrocatalysts prepared by incipient wetness impregnation and cation exchange methods with Ru as precursors were compared. Ru-ACC prepared by cation exchange methods exhibited a higher electrocatalytic activity versus the case of incipient wetness impregnation, which might ascribe to the functionalization of ACC surface from HNO$_3$ oxidation pretreatment, like the formation of carboxylic acid and lactone. The reaction pathway for ECH of guaiacol related to the saturation of C=C and C–O(CH$_3$) bonds cleavage (Fig. 15) [100]. Besides, temperature and solution pH significantly affect electrocatalytic efficiency and product selectivity. The optimal product yield was achieved at 50 °C. Compared to the alkaline condition, the acidic condition is more conducive to guaiacol conversion and cyclohexanol selectivity.

The electrocatalyst, electrolyte, and the alkyl chain length of lignin substrate also significantly affect the yield and selectivity of the
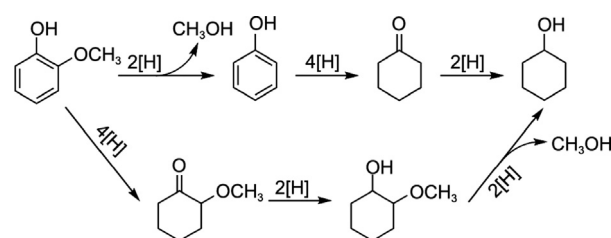

Fig. 15. Reaction pathway for guaiacol ECH. Reproduced from Ref. [100] with permission.

target product. Wijaya et al. [101] investigated the synergistic influences between electrocatalyst and electrolyte for the ECH of lignin model compound including guaiacol and phenol in dual chamber electrocatalytic reactor. Three catalysts (Pt/C, Ru/C, and Pd/C) were selected and tested by using acid electrolyte (H$_2$SO$_4$) and neutral electrolyte (NaCl) respectively at the cathode. All catalysts displayed the superior catalytic ability for ECH of guaiacol and phenol, with the order of Pt/C > Pd/C > Ru/C for phenol ECH. For Pt/C catalyst, the acidic electrolyte more favored the ECH of guaiacol. Conversely, the neutral electrolyte is more conducive to ECH of guaiacol on Ru/C and Pd/C catalyst attributing to the formation of OH$^-$. This suggests that high pH reduced the catalytic activity of Pt/C on the ECH of guaiacol while the catalytic activity of Pd/C and Ru/C was enhanced. The catalytic activity of guaiacol ECH increases as follows: Pd/C < Ru/C < Pt/C. The ECH reaction pathway of guaiacol and phenol was delineated in Fig. 16 [101]. Regardless of catalyst,
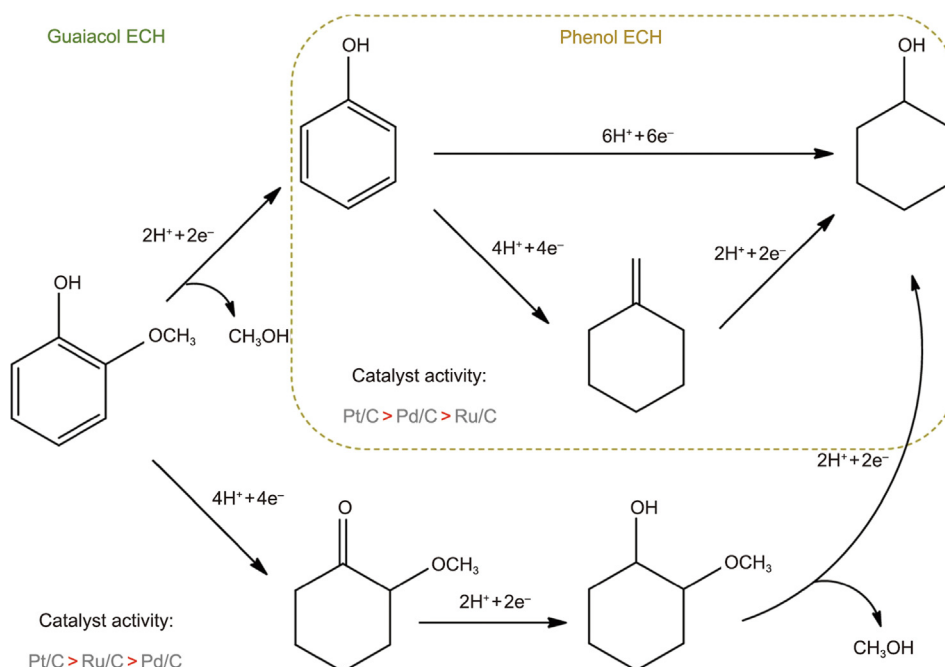
Fig. 16. Schematic of the reaction pathways for ECH of guaiacol and phenol. Reproduced from Ref. [101] with permission.

phenol conversion took precedence over guaiacol. ECH of phenol mainly involved the saturation of C=C bond via a series of reaction while the demethoxylation and C=C bond saturation reaction simultaneously occurred in the ECH of guaiacol.

In a recent work, the effect of alkyl chain length on ECH conversion of lignin model compounds including phenol, ethers, guaiacol, and syringol was explored via ECH using Ru-ACC [102]. Likewise, the simultaneous occurrence of saturation of C=C and the C–O(CH$_3$) cleavage reaction was observed. But alkyl chain length had a significant effect on products conversion rates and selectivity. Concretely, an increase in alkyl chain length is not conducive to the conversion of the products. Also, the products selectivity was altered. Long alkyl chains favored the generation of 2-methoxycyclohexanols rather than the demethoxylated products. Additionally, the products yield and selectivity were also affected by the relative position of methoxy and hydroxyl groups on the aromatic rings.

A great challenge for lignin electrocatalytic reduction is to selectively produce the high value-added chemicals containing C–O(CH$_3$) instead of simultaneous occurrence of hydrogenation and hydrogenolysis because demethoxylation is thermodynamically more favorable [103]. In the ECH of the lignin monomer guaiacol in the flow-cell system with a bipolar membrane separator, Peng et al. [103] designed novel ternary alloys electrocatalysts (PtRhAu) to selectively hydrogenate aromatic rings and inhibit demethoxylation (Fig. 17) [103]. Attributing this to the high adsorption energy of Pt (2.12 eV, 1 eV = 1.602176 × 10^{-19} J) and Rh (2.67 eV) towards guaiacol, they considered preparing an electrocatalyst. Further verification indicated that binary alloy PtRh has higher adsorption energy, which was beneficial for the hydrogenation of guaiacol (Fig. 17(c)). Subsequently, Au was adopted to modulate PtRh and inhibit the demethoxylation by altering the adsorbed guaiacol C–OCH$_3$ bond length. Au can kinetically inhibit demethoxylation since the bond length for Au (1.360 Å, 1 Å = 10^{-10} m) is shorter than Pt (1.365 Å) and Rh (1.378 Å). Compared with Pt and PtRh, PtRhAu catalyst exhibited higher FE under various current density (Fig. 17(b)). As such, guaiacol was selectively converted to methoxylated cyclohexanes without the occurrence of an

hydrogenolysis reaction under low current density accompanied by high FE (58%). Additionally, the catalyst exhibited an outstanding stability. After 50 h of running, FE conversion to the target product was maintained above 50% (Fig. 17(d)). Further, the ECH of 4-propylguaiaco derived from wood was investigated. High selectivity (90%) toward the 2-methoxy-4-propylcyclohexanol and FE (56%) were observed. Perhaps, future works should concentrate on the selective cleavage of C=C or C–O(CH$_3$) instead of simultaneous occurrence of hydrogenation and hydrogenolysis. This was significantly affected by temperature, pH, catalyst synthesis method, substrate structure, and catalyst surface electron structure. More work should be conducted to elucidate the interaction between these factors.

In conclusion, the ECH of lignin is the multifactorial process that relies on the solution pH, temperature, electrocatalyst, electrolyte, and lignin substrate structure, etc. Attributed to the coupling effect of these parameters, the relationship between these processes becomes particularly complex. To maximize the product yield, further work needs to be performed in a systematic fashion to reveal these complex relationships more clearly. In addition, information on kinetics and thermodynamics should be elucidated, which is conducive to tailor a superior strategy for achieving selective conversion of lignin (C=C and the C–O(CH$_3$) cleavage reaction occurs independently).

5.2.2. Upgrading of bio-oil

A typical case about the ECH of real bio-oil rather than model compounds is introduced here. Recently, simultaneous lignin ECO and bio-oil ECH via the dual cell was proposed for the first time (Fig. 18) [97]. As the OER requires higher potential, they adopted Fe(III)/Fe(II) (0.77 V vs NHE) as a redox mediator for lignin oxidation to substitute OER at the anode. Ruthenium anchored in ordered mesoporous carbon was used as an electrocatalyst at the cathode. They observed carbon distribution after 3 h of ECH: 89.7% in the cathodic electrolyte (e.g., upgraded water-soluble bio-oil (WSBO)), 7.2% on the cathode, 0.4% on the membrane, and 1.2% for volatilization. Elemental analysis of WSBO demonstrated the increase of H content and decrease of O content. Additionally,
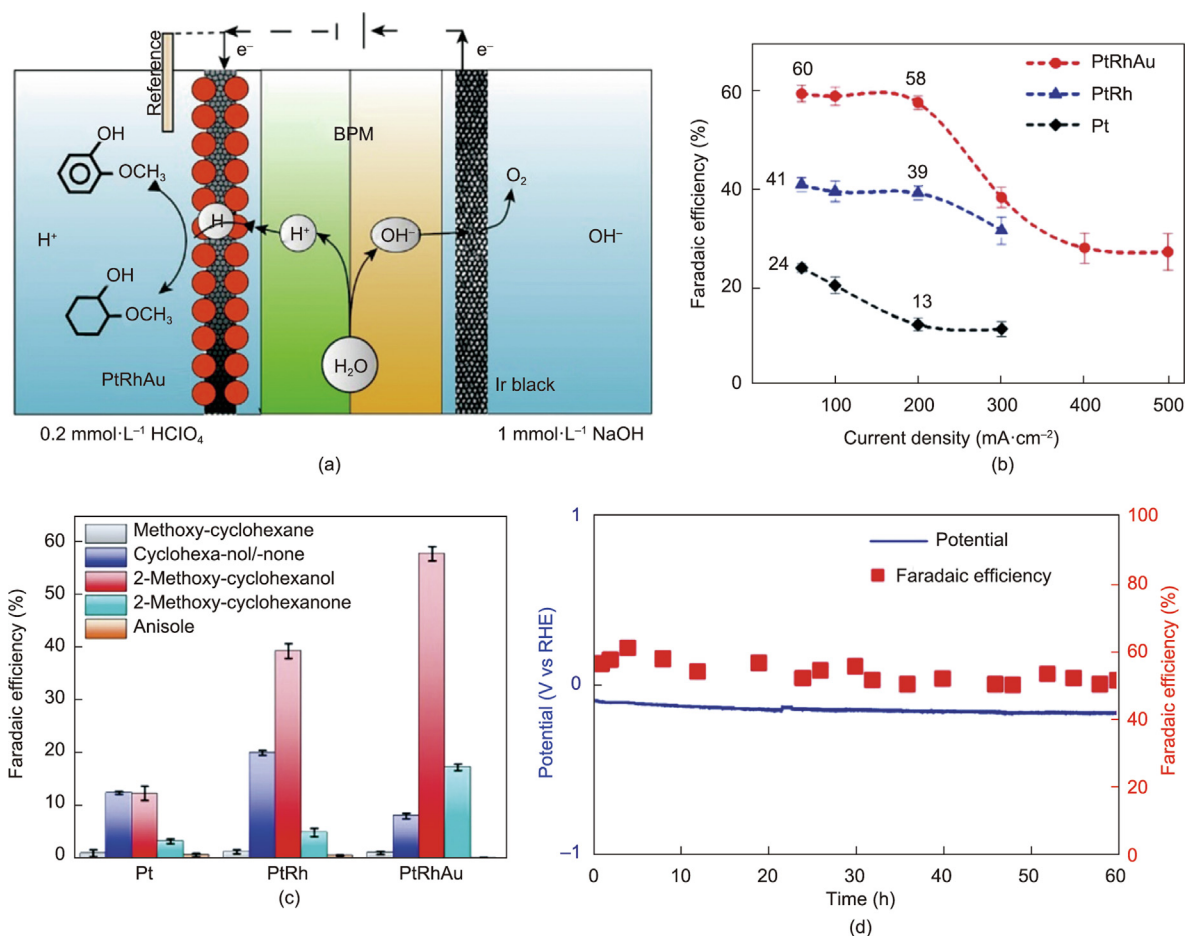
Fig. 17. (a) Schematic of ECH reactor, (b) FE of Pt, PtRh, and PtRhAu catalyst under virous current density, (c) FE towards various products on Pt, PtRh, and PtRhAu catalyst (current density: 200 mA·cm^{-2}; time: 1 h); (d) table chronoamperometric operation of PtRhAu under optimal conditions (current density: 200 mA·cm^{-2}; time: 60 h). BMP: bipolar membrane. Reproduced from Ref. [103] with permission.
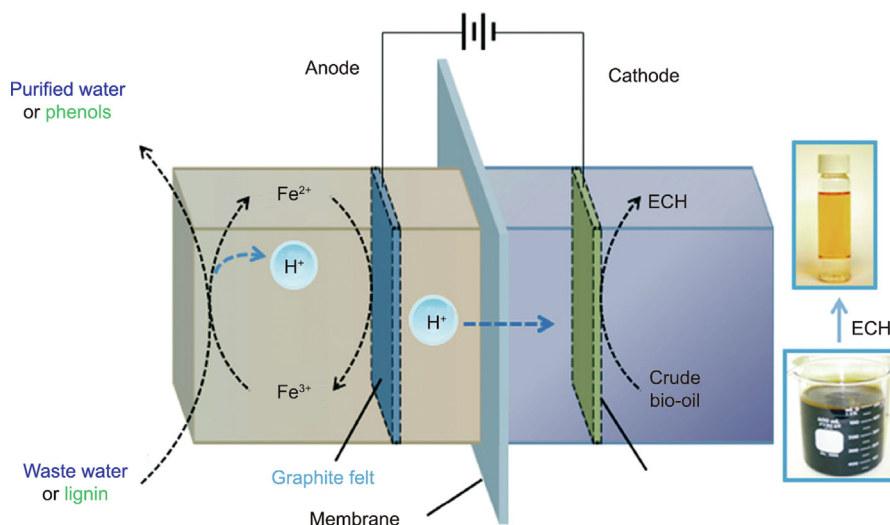
Fig. 18. Schematic of low-energy ECO of lignin and ECH of bio-oil. Reproduced from Ref. [97] with permission.

number-average molecular weight (M_n) and weight-average molecular weight (M_w) were significantly increased compared to the original bio-oil, suggesting that hydrogenation is dominant instead of hydrodeoxygenation. The statement was further verified by the variation in alcohol carbon content before and after electro-catalysis (3.5 times higher than the original content). Using Fe(III)/ Fe(II) as a redox mediator to substitute OER at the anode greatly enhanced the FE during ECH. Additionally, ECO depolymerization

of lignin via Fe(III) was also investigated. 11.87% of aromatic products were produced. This design provides a promising direction in simultaneous lignin depolymerization and upgrading of bio-oil.

5.2.3. ECH of lignin

Only a few publications on lignin ECH have been reported. Most studies on ECH depolymerization of lignin were conducted on lignin model compounds. Mahdavi et al. [104] investigated the ECH of lignin model dimers using Raney nickel electrodes in ethano–water. In order to achieve lignin depolymerization, the hydrogenolysis of ether bonds must occur in preference to the hydrogenation of aromatic rings. In addition, HER accompanied by ECH needs to be minimized. During the ECH, 2 mol of electron is required for the cleavage of the benzyl–O–aryl bond per mole of substrate. For high-efficient selectivity and acceptable current efficiencies, the effect of substrates concentration, current density and temperature on the ECH of C–O in the benzyl phenyl ether were evaluated under constant current conditions. They observed that current density does not influence product selectivity, suggesting that hydrogenolysis of ether bonds takes precedence over the hydrogenation of aromatic rings. With decreasing current density, HER was inhibited. 100% of current efficiency and selectivity were acquired in the 26 mmol·L^{-1} of substrate concentration, 20 mA·dm^{-2} of current density and 40 °C of operating temperature. Under the same conditions, the authors further investigated the ECH of α-phenoxyacetophenone and β-phenoxyethylbenzene, representing the other two C–O bond types. Results indicated that the ECH of C$_\beta$–O is less efficient than C$_\alpha$–O due to the higher BDE for C$_\beta$–O.

In another work, the ECH of the β-O-4 model compound in an aqueous sodium hydroxide solution was carried out under the constant current density using Raney nickel and palladium-based cathodes, within the temperature range 25 to 75 °C [105]. For both electrodes, they observed that the β-O-4 bond in phenolic β-arylethyl-aryl ethers was effectively ECH to acquire the corresponding phenolic compounds. Nonetheless, ECH did not occur when the phenolic group was alkylated, indicating that ECH would take place on intermediates in which C–O aryl bonds conjugated with π electron array. Compared with electron-less O-alkylated derivatives, these intermediates were formed more quickly by an electron-rich phenolate anion. Additionally, the conversion of 4-phenoxyphenol to phenol demonstrated the feasibility of 4-O-5 linkage cleavage at the Raney nickel electrode. ECH of 4-O-5 occurs on intermediates on the cyclohexadienone tautomer of the phenol in which C–O aryl bonds is again conjugated to a π electron array. This provides the opportunity for Kraft lignin depolymerization since kraft lignin is abundant in the 4-O-5 type of linkage.

Recently, Fang et al. [106] conducted the cleavage of the β-O-4 model compound in an H-type electrocatalytic cell using reticulated vitreous carbon as cathode via a thiol-assisted electrocatalytic reduction strategy. Additionally, they further expanded the substrate scope to poplar lignin oxidized by 2,3-dichloro-5,6-dicyano-1,4-benzoquinone. In such a system, thiol and disulfide were used as a redox couple to achieve the lignin depolymerization. In the presence of disulfide and radical inhibitor, nonphenolic β-O-4 dimers were effectively reduced under the current density of 2.5 mA·cm^{-2}, with 90% of yield for phenolic and keto monomers. Applying the strategy to oxidize lignin, surprising depolymerization performance was observed after 6 h treatment under room temperature. The products mainly contained ethyl acetate soluble fragments (36%) and aqueous soluble fragments (26%). Only 38% of insoluble residue were observed. Two reaction mechanisms in this work were involved (Fig. 19) [106]. One mechanism for the C–O ether bond cleavage was considered as a one-electron reduction. In this case, the disulfide radical anion (RSSR$^-$) was used as the electron vector. Another reaction mechanism relied on oxygen: Oxygen extracts the electron from the electron transfer agent and thus diverts the reaction. This reduced the cleavage rate of 2-phenoxyacetophenone. Therefore, the reaction conditions need to be strictly controlled.

Significantly, the ECH of lignin is not as prevalent as the ECH of lignin derivatives. One reason is that the pH required by lignin dissolution and high-efficiency production of H$_{ads}$ is not compatible. In detail, real lignin dissolution strongly depends on alkalinity while acidity is more conducive to enhance the rate of active hydrogen generation. The kinetic of HER in acidic medium is about to 2–3 orders of magnitude higher than that in alkaline medium [107]. In alkaline medium, the production of H$_{ads}$ in ECH is seriously limited by the O–H bonds cleavage in H$_2$O, thus causing poor efficiency in real lignin cleavage via ECH. Consequently, such bottlenecks severely hinder the application of ECH to real lignin depolymerization. One strategy to overcome this is to modify some functional groups of lignin to alter lignin solubility. Alternatively, electrocatalysts with efficient H$_{ads}$ adsorption and storage capacity under alkaline conditions should be further developed.

6. Challenge and perspective

Despite electrochemical conversion technique offering a viable and alternative method to promote lignin biorefinery development toward sustainability and carbon neutralization, many challenges still need to be overcome prior to being commercialized. Presently, most works about lignin electrochemical conversion are carried out using lignin model compounds in H-type cell to reveal the reaction pathway and guide the development of real lignin depolymerization. The efficiency in real lignin depolymerization was poor. A benefit of studies of model compounds is to acquire the reaction pathway by simulating various type of linkage cleavage in real lignin under extensive operating conditions. However, the applicability of these results on the guidance of real lignin depolymerization needs to be carefully considered due to the difference of dissolution property. Adopted model compounds are usually non-water-soluble substances (dissolution with the assistance of
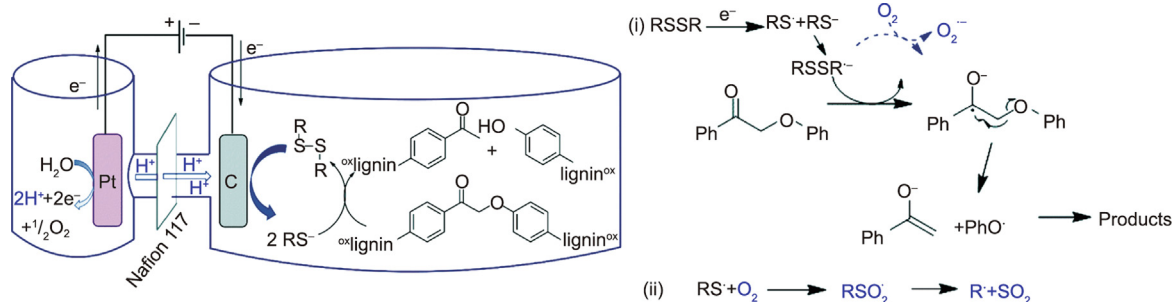

Fig. 19. Schematic of lignin depolymerization mechanism in a thiol-assisted electrolytic reduction system. ox: oxidation. Reproduced from Ref. [106] with permission.

organic solvents like alcohol) while lignin or bio-oil with high molecular weight is relatively insoluble in pure water (dissolution with the assistance of pH regulation) because of hydrophobic groups. Also, there is a great difference on shock load (e.g., electrode corrosion) caused by model compounds and real lignin. This difference may cause the failure of large-scale applications of a lignin electrochemical biorefinery when basing them on the results from model compounds. More works in the future should be conducted towards enhancing depolymerization efficiency of real lignin and on large scale application.

In terms of the reactor, the long electrode spacing and membrane barrier in H-cell increases the voltage losses, greatly aggravating the economic burden for large-scale applications. In order to further promote the development of electrochemical technique in lignin valorization, more work should be conducted toward the real lignin depolymerization and reactor design. One of the most basic considerations for lignin depolymerization is to select a proper solvent, which determines the lignin solubility ability and conductivity (further affecting FE of the whole electrochemical reaction). ILs and DES are ideal solvents for lignin in term of solubility, product recovery and energy consumption. Also, their outstanding fractionation ability for biomass provides a viable pathway to integrate the lignin electrochemical fractionation and depolymerization by one-pot method. However, the viscosity issues for ILs and DES need to be effectively addressed. In term of downstream processing in lignin valorization, membrane-based electrolysis cell provides the opportunity to separate the products. Electrochemical technique builds a bridge between fractionation, depolymerization, upgrading and product separation. More efforts should be conducted toward these aspects to simultaneously perform multi-steps in lignin electrochemical biorefinery network in a single operating unit.

For target chemicals, ECO is conducive to elevate the oxygen content in products while hydrogen content in products can be increased by ECH [34]. As such, ECO is often adopted for lignin depolymerization. Conversely, ECH is frequently used for the upgrading of lignin derivative. Undeniably, no matter whether ECO or ECH, it is a multifactorial process that relies on the solution pH, temperature, electrocatalyst, electrolyte, and lignin substrate structure, etc. For example, Low current density may result in a poor depolymerization efficiency. Conversely, exorbitant current density accompanies with overoxidation of products and the occurrence of OER and HER. This causes the decreased FE and increased CO_2 emissions. Likewise, temperature strongly affect the products selectivity (e.g., hydrodeoxygenation) and yield of temperature-sensitive aromatical products. Furthermore, electrocatalysts significantly affect reaction rate. Overall, to maximize the target product yield, the interactive influence of these factors on product yield should be fully elucidated.

In order to achieve an in-depth understanding of the reaction mechanism of lignin electrochemical reaction at an atomic level, a clear understanding on kinetics is necessary to guide the lignin electrochemical conversion. Also, thermodynamics important for the successful implementation of organic synthesis like hydrodeoxygenation reactions. However, these studies in lignin electrochemical biorefinery field are scarce. Thermal catalytic depolymerization of lignin is a widely studied method to produce chemicals and bio-oil, but the operating harsh conditions and further upgrading of bio-oil are still the main limitations. By contrast, electrocatalysis can achieve the lignin depolymerization and bio-oil upgrading under milder condition. Most importantly, electrocatalysis promises to conduct multiple steps of lignin valorization network in a single operating unit. Recent research has tried to build a connection between thermal catalysis and electrocatalysis. For example, Ryu et al. [108] found that thermochemical oxidation can be divided into two coupled electrochemical half-reactions of

oxygen reduction and substrate oxidation for analysis. By analyzing the polarization curves of the two half-reactions, mixed potential of the catalyst during thermochemical catalysis can be predicted. Such cases provide a reference for lignin electrochemical conversion. This may also provide valuable information about how to apply catalysts from traditional thermal catalytic process to electrocatalytic process.

The development of catalyst should consider the CO_2 emission. Ru and Pt have been extensively studied, and the emissions of greenhouse gases accompanied by the mining and purification for these elements is of significant environmental risk, like Pt (12.5 $t_{CO_2} \cdot kg^{-1}$). By comparison, less than 10 $kg_{CO_2} \cdot kg^{-1}$ was released for no-noble metal [8]. Transition metals like Fe and Co are promising in terms of greenhouse gas emission reduction and economic feasibility. Thus, catalyst development should be directed toward lower cost transition metals-based material. In addition to material cost, catalyst stability is vital in lignin electrochemical conversion since it has a profound impact on catalytic activity. The fluctuation of catalyst stability in electrochemical reactions relates to six aspects [13,109]: ① loss of active components because of harsh environments like strong acid and base; ② catalyst active components agglomeration or dissolution under high temperature and high current density, ③ catalyst deactivation caused by the polymerization of substrate or intermediate; ④ transient dissolution and steady state dissolution due to surface reconstruction of catalyst (like lattice oxygen exchange) under high potential; ⑤ interfacial supersaturation, active site coverage, structural oscillation, and larger ohmic resistance resulted from the gas bubbles evolving from OER and HER under high current density; and ⑥ blocking of the catalytic sites arisen from impurity deposition on catalyst. A deeper understanding about catalyst stability can provide vital hints for the development strategies for stable catalysts in a lignin electrochemical biorefinery. Future work should establish close connection between cost, catalytic activity and stability of the electrocatalyst.

Also, the identification of active sites on the electrocatalyst is crucial since the surface atoms at active sites offers the highest catalytic activity to drive the occurrence of specific chemical reactions compared to other sites [110]. Common electrocatalysts includes metal-based catalysts, carbon-based catalysts and single-atom catalysts (SACs). The active sites have been well-revealed in electrochemistry, such as terraces, steps, kinks, and edge and corner sites in metal-based catalyst, doped heteroatoms or carbon atom activated by doped heteroatoms in carbon-based catalyst and metal atoms in SACs [110–113]. Still, in term of the electrochemical lignin biorefinery field, the relationship between the role of active sites and reaction mechanism should be further elucidated, which would be conducive to guild the design of high-performance electrocatalysts in a lignin electrochemical biorefinery.

Although electrochemical conversion of lignin has been widely studied, considerable effort is still needed prior to commercial application. In term of a lignin biorefinery, the processes are categorized as extraction, separation, depolymerization, upgrading, and products separation. Thus, the economic feasibility of chemicals production can be considered by theses aspects. Ideally, the by-product lignin produced by pulp and paper industry can be directly used as raw material for chemicals production. However, separation and purification steps are required since the various impurities in mixture contains will accelerate the electrode corrosion in depolymerization process and cause reduced lignin depolymerization efficiency, indicating that the additional cost is not negligible. Depolymerization and upgrading can be simultaneously achieved by electrochemical technique. Despite large amounts of work claiming that renewable energy like wind energy and solar energy can be used as the electricity supply to reduce the input cost, the renewable energy cannot be directly incorporated into

the power grid since the nature of renewable energy is variable and intermittent [16,17]. Also, the use of energy storage systems with mitigating intermittency further increases cost. Various power generation technologies still present relatively higher power generation cost, like 0.258–0.602 USD·(kW·h)$^{-1}$ for PV, 0.166 USD·(kW·h)$^{-1}$ for wind energy and 0.510 USD·(kW·h)$^{-1}$ for solar energy [15]. In terms of the products, vanillin has the capacity to compete with petrochemical-derived vanillin on a commercial scale [114]. It has been reported that the average net profit of vanillin is 0.44 USD·kg^{-1} lignin and the maximum net profit even reaches 3.39 USD·kg^{-1} [114]. Ideally, the optimal economic benefit of vanillin generation could be acquired in a 22.63% internal rate of return (payback period of 6.19 years) [115]. Additionally, other high value-added products can further increase the overall revenue of lignin valorization. For example, the net profit of succinic acid and cyclohexylamine are 0.54 and 0.71 USD·kg^{-1} lignin, respectively [114]. Attributing to the product diversity of lignin depolymerization, the separation of products is also a vital factor to increase the economic cost. Also, the products yield is still low for real lignin conversion. This means that the economic benefits of chemicals may be far less than the expensive costs caused by whole process. Overall, considerable efforts need to be conducted to reduce investment to achieve the economic feasibility of chemicals production by an electrochemical biorefinery.

7. Conclusions

This review provides a comprehensive overview of lignin electrochemical conversion. Results indicate that a huge gap needs to be filled in this field. For example, the kinetic and thermodynamic studies for lignin electrochemical are lacking. Also, more integrated techniques should be developed, such as multi-subprocess coupling of electrochemical biorefinery in a single operating unit. Most importantly, electrochemistry should be further developed in terms of the existing limitations, which can draw on experience from other fields such as organic synthesis. Overall, these technical hurdles need to be overcome prior to economic feasibility. Interdisciplinary collaboration will help provide the direction for future works.

Acknowledgments

Compliance with ethics guidelines

Rui Hu, Yuying Zhao, Chen Tang, Yan Shi, Gang Luo, Jiajun Fan, James H. Clark, and Shicheng Zhang declare that they have no conflict of interest or financial conflicts to disclose.

Appendix A. Supplementary material

Supplementary data to this article can be found online at https://doi.org/10.1016/j.eng.2022.10.013.

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