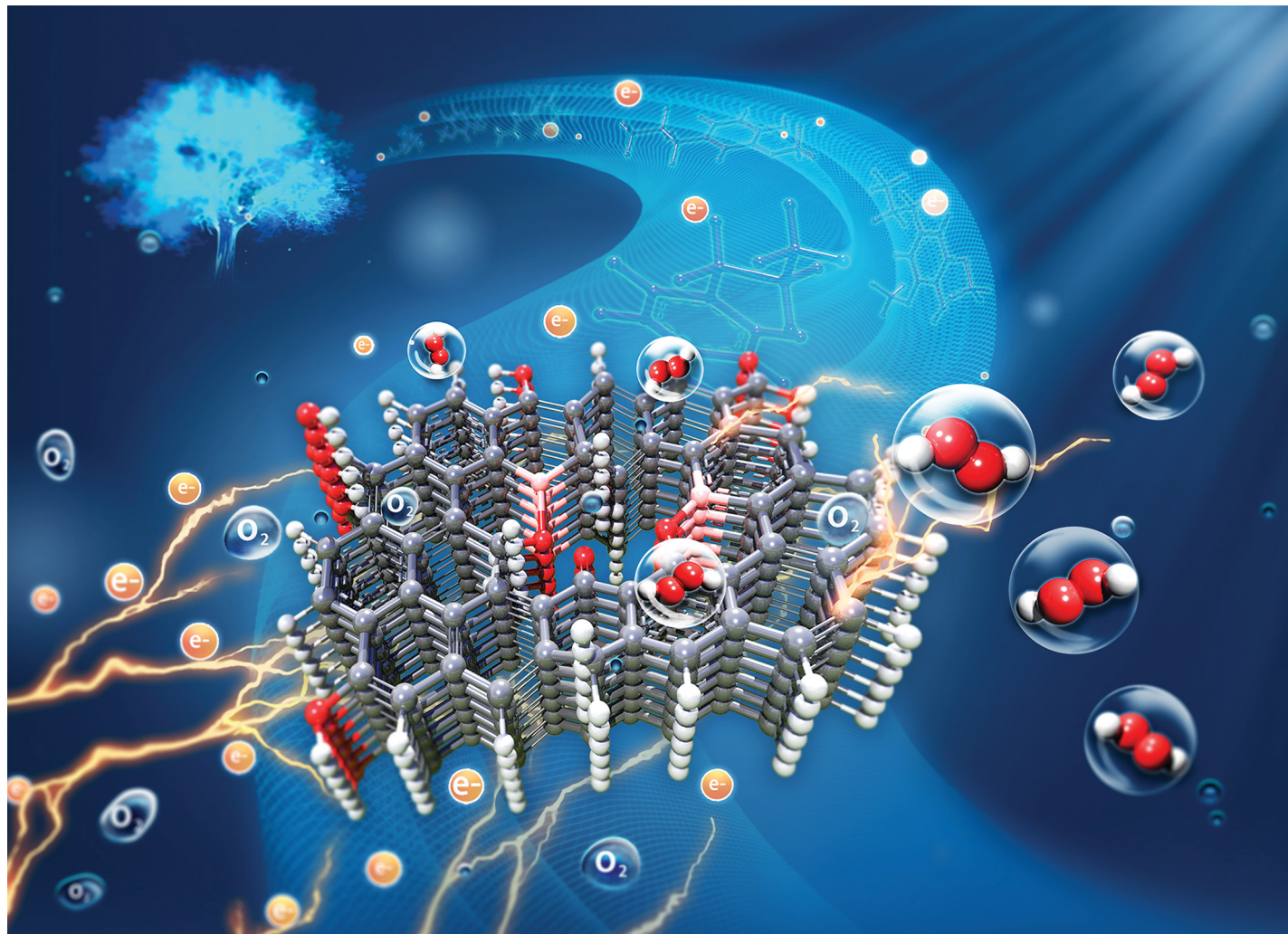




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Self-powered electrochemical synthesis of hydrogen peroxide from air and lignin

Lignin is a sustainable feedstock for production of carbon fuels and materials. Here, a novel coupled electrochemical system to achieve efficient production of H_2O_2 with air as the oxygen source and lignin as a carbon-based catalyst precursor and electron donor (fuel) has been developed. By using a direct lignin fuel cell to power a paired electrolytic cell, the endogenous electrons of lignin can be transferred to air. This novel self-powered system can achieve production of H_2O_2 without input of external electricity.

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Energy Environ. Sci., 2025, **18**, 3633.

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2025, 18, 3633

Self-powered electrochemical synthesis of hydrogen peroxide from air and lignin†

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Lignin, which is typically available as a by-product of the pulping process and biomass biorefinery, is a sustainable feedstock for production of carbon fuels and materials. Here, we report a novel coupled electrochemical system to achieve efficient production of H₂O₂ with air as the oxygen source and lignin as a carbon-based catalyst precursor and electron donor (fuel). By using a direct lignin fuel cell to power a paired electrolytic cell, the endogenous electrons of lignin can be transferred to air, resulting in the formation of H₂O₂ via a two-electron oxygen reduction reaction. A facile and efficient approach to synthesizing a B,O-doped carbonaceous catalyst was developed with lignin as a carbon precursor, achieving a H₂O₂ productivity of 11812 mmol g⁻¹ h⁻¹ and a faradaic efficiency of 95.7%. Moreover, by using the [Fe(CN)₆]³⁻/[Fe(CN)₆]⁴⁻ redox couple as the electron mediator for oxidation of lignin on the anode instead of the oxygen evolution reaction, the energy consumption of the electrolytic cell could be decreased by 11.4%. The self-powered system could obtain 93.7% of total electron transfer efficiency and avoid using external electricity. Therefore, this work provides a novel technical route for lignin utilization and production of H₂O₂ and biomass-based chemicals in a sustainable way.

Received 23rd December 2024,
Accepted 3rd March 2025

DOI: 10.1039/d4ee06106c

rsc.li/ees

Broader context

The use of biomass and application of renewable electricity to synthesize fuels and chemicals have attracted great interest in recent years for achieving carbon neutrality. As the most abundant aromatic polymer in nature, lignin is usually available as waste in pulping and papermaking industries, and lignocellulose biorefinery such as cellulosic ethanol production. Lignin has a relatively high content of carbon element, and thus it can be used as a good fuel for electricity generation and as a precursor for carbon materials. Electrochemical synthesis of H₂O₂ has been considered a promising alternative approach because of its mild conditions and flexible application scenarios. Herein, we demonstrate a novel coupled system for efficient production of H₂O₂ by electrochemical reduction of oxygen (air) with lignin as a carbon precursor and electron donor. By using a direct lignin fuel cell as a power source, the system can achieve transfer of the endogenous electrons of lignin to air, avoiding using external electricity. The driving force of this system is only the Gibbs energy change of the oxidation reaction of lignin by oxygen. This system can achieve utilization and treatment of lignin waste for the production of high value-added products in a sustainable way.

Introduction

Lignin is one of the three main components of lignocellulosic biomass, and the second most abundant organic substance in the natural world after cellulose.^{1,2} As a by-product in the pulping industry and biomass biorefinery, lignin is usually used as a fuel, and even discharged as waste causing environmental issues.³ Therefore, it is of great environmental significance to develop an effective high-value utilization strategy for lignin and meanwhile diminish the pollution of lignin waste. Lignin has been proven to be a promising candidate for nanoporous carbon precursors for application in electrochemistry.⁴ As one of the 100 most important chemicals in the world, hydrogen peroxide (H₂O₂) has very wide applications in various

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industries such as chemical synthesis, wastewater treatment, disinfection, and pulp bleaching for papermaking.^{5–7} At present, 95% of commercial H_2O_2 is produced by an indirect chemical process based on anthraquinone oxidation and reduction.⁸ However, the conventional process requires complex infrastructures, harsh reaction conditions (noble metal catalysts, high temperature and pressure) and fossil-based hydrogen.^{8,9} Electrochemical H_2O_2 production based on the two-electron (2e^-) oxygen reduction reaction (ORR) has become a promising alternative approach because of its mild conditions and flexible application scenarios without the need for sophisticated equipment.^{10,11} Moreover, by using green electricity, the net CO_2 emission of electrochemical synthesis of H_2O_2 could be significantly decreased compared with the conventional anthraquinone process.^{11,12}

Regulation of the interaction between the active centre and oxygen molecules is a key point for developing efficient ORR catalysts with high path selectivity. Moderate interaction is necessary to avoid the cleavage of the formed O–O bond and stabilize the *OOH intermediate.¹³ Noble metals and their alloys have already been proven to possess relatively high H_2O_2 molar selectivity and current efficiency.^{14–16} However, the high cost of the noble metals limits their large-scale industrial use. Carbon-based materials are promising candidates for the 2e^- -ORR in the industry due to their low cost, ease of modification, and wide availability.¹⁷ In recent years, many carbon-based materials with glorious 2e^- -ORR activity have been

synthesized, including ordered mesoporous carbon,¹⁸ defective carbon,^{10,19} and heteroatom doping carbon.²⁰ For example, Kim *et al.* confirmed that certain variants of the mildly reduced graphene oxide exhibited highly selective and stable H_2O_2 activity with low overpotentials.¹⁰ Xia *et al.* reported that B doped carbon with carbon black as a precursor exhibited excellent H_2O_2 selectivity (85–90%) under industrial-relevant current density.²⁰ Some methods to improve the performance of carbon-based catalysts for the 2e^- -ORR have also been explored like incorporation of Lewis acid sites²¹ and steering sp-carbon content,²² but the internal mechanisms remain unclear. Overall, it has been well confirmed that carbon-based catalysts with superior H_2O_2 production capacity can be obtained by appropriate pore structure regulation and heteroatom doping. However, it is worth noting that the carbon precursors mostly used are functional carbon-based materials, such as graphene, carbon nanotubes, and activated carbon, which are produced from coal or petrochemical products through energy-intensive or harsh synthetic processes.²³ It is highly desired to develop effective methods to prepare carbon-based catalysts from renewable resources and to produce H_2O_2 sustainably.

Herein, as illustrated in Fig. 1, we demonstrated a novel coupled system to achieve production of H_2O_2 from air and lignin. A scalable method was firstly developed to prepare highly active B and O doped carbon-based catalysts (B,O-C) to boost the 2e^- -ORR kinetics using sodium lignosulfonate (LS) as

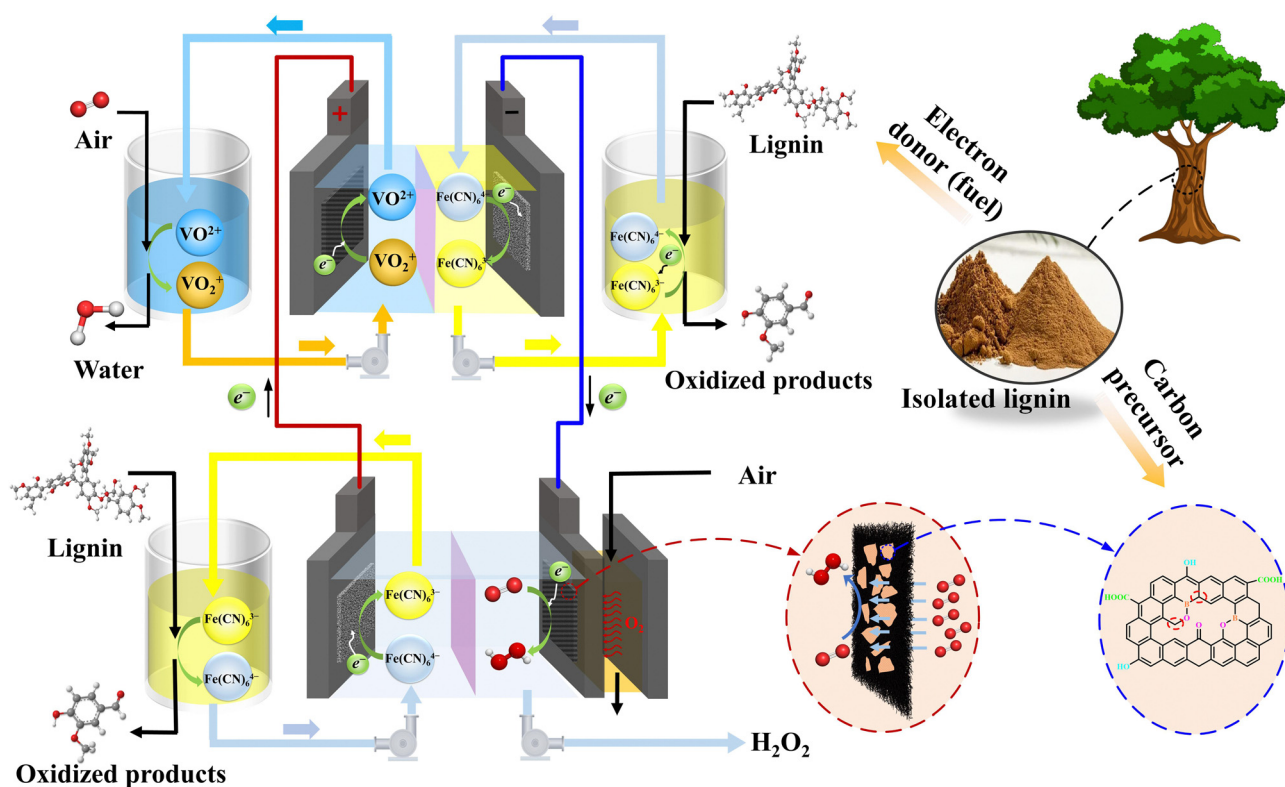


Fig. 1 The coupled system developed in this work for electrochemical production of H_2O_2 with air as the oxygen source and lignin as a sustainable carbon precursor and electron donor.

a carbon precursor. A novel paired electrolytic system was then developed for H_2O_2 production with lignin as an electron donor under the mediation of electron mediators on the anode to reduce the large overpotential generated by the sluggish kinetics of the conventional oxygen evolution reaction (OER). Furthermore, by using a direct lignin fuel cell (DLFC) as a power source, a sustainable system was established to transfer endogenous electrons from lignin to air thus achieving successful production of H_2O_2 without external electricity. The *in situ* use of H_2O_2 for oxidation of 5-hydroxymethylfurfural (HMF) under the catalysis of Ag_2O to obtain 5-hydroxymethylfuroic acid (HMFCA) was also demonstrated. This work can provide a novel route for sustainable production of H_2O_2 with lignin as both the catalyst precursor and electron donor, and *in situ* use of the formed H_2O_2 for the production of high value-added biomass-based chemicals.

Results and discussion

Preparation and characterization of the lignin-based B,O-C catalysts

The synthetic process of the B,O-C was described in Fig. 2(a). Nano-silica (SiO_2) was used as a hard template to increase the porosity of the obtained carbon materials after pyrolysis.²⁴ This process was facile but effective and easy to scale-up. Typical scanning electron microscopy (SEM) images (Fig. 2(b) and (c)) illustrated the surface morphology and microstructure of the catalysts obtained after pyrolysis at 900 °C (B,O-C-900), revealing that the catalysts had a clear lamellar structure with abundant pores. In general, a porous structure can provide more active sites and a larger gas-liquid contact interface, which in turn improves the rate of ORR.²⁵ The samples without using SiO_2 templates had a smooth surface without abundant pores (Fig. S1, ESI†). In the subsequent experiments on the catalyst performance, higher 2e-ORR activity was achieved by the catalysts with porous structures, indicating that pore structure played an important role in improving the 2e-ORR performance. The energy dispersive spectrometry (EDS) element mapping images confirmed the uniform distribution of B and O on the catalyst surface (Fig. 2(d)). No Si signal was detected, indicating that SiO_2 templates were completely removed during the post-treatment by KOH. The microstructure of B,O-C-900 was further analyzed in detail using transmission electron microscopy (TEM) images (Fig. 2(e)–(g)), and the pore structures were clearly visible. A disordered carbon structure with alternately bright and dark stripes and very little stacking was observed, suggesting that B,O-C-900 had a distinct disordered structure without apparent long-range ordering. Moreover, the impact of pyrolysis temperature on the porous structure of the B,O-C catalysts was not significant in the pyrolysis temperature range of 700–1100 °C (Fig. S2, ESI†).

The X-ray diffraction (XRD) patterns of B,O-C catalysts at different pyrolysis temperatures (700–1100 °C) were displayed in Fig. 3(a). Only two distinct peaks located at around 25° and 44° were observed regardless of the pyrolysis temperature,

which are attributed to (002) and (100) diffractions of graphite, indicating their amorphous states.²⁶ The XRD results were consistent with that observed in TEM images. Moreover, the intensity of distinct peaks increased at higher temperatures, demonstrating the increase in the degree of graphitization of the catalysts. Raman spectroscopy was utilized to examine the concentration of defects in the catalysts (Fig. 3(b)). Two clear peaks at around 1350 cm^{-1} and 1600 cm^{-1} were observed, which corresponded to the disordered amorphous carbon (D band) and crystalline graphic carbon (G band).¹⁹ The peak intensity ratios of the D and G bands of B,O-C-700, B,O-C-900, and B,O-C-1100, which are widely used for evaluating the defect concentration in graphitic materials,²⁷ were 0.948, 1.053, and 1.160 respectively, demonstrating that more surface defects were generated at higher pyrolysis temperatures. Nitrogen (N_2) adsorption-desorption isotherms were carried out to analyze the pore characteristics of the prepared catalysts (Fig. 3(c)). The adsorption isotherms of the prepared catalysts belonged to type IV with a hysteresis loop, which was associated with capillary condensation taking place in mesopores. The type H3 loop was observed, which usually existed in slit-shaped pores formed by aggregates of plate-like particles, corresponding to micropores.²⁸ A sharp increase in N_2 adsorption capacity at relative low pressures also indicated their microporous structures.²⁹ The corresponding pore size distribution curves (Fig. 3(d)) with three peaks at 1.3 nm, 4.8 nm, and 16.7 nm, further confirmed the existence of micropores and mesopores. To confirm the role of SiO_2 hard template (size of 15 ± 5 nm) in the formation of mesopores, carbon materials without using SiO_2 were prepared at a pyrolysis temperature of 900 °C. It was found that the obtained materials (B,O-C-900 without SiO_2) did not show a clear hysteresis loop (Fig. 3(c)). Moreover, no peak at 16.7 nm was observed in the pore size distribution curves (Fig. 3(d)), which corroborated the important role of SiO_2 in the generation of the mesoporous structure of the prepared catalysts. The Brunauer-Emmett-Teller (BET) surface areas of B,O-C-700, B,O-C-900, and B,O-C-1100 were 907 $\text{m}^2 \text{g}^{-1}$, 737 $\text{m}^2 \text{g}^{-1}$, and 513.2 $\text{m}^2 \text{g}^{-1}$, respectively, indicating that the pyrolysis at a relatively low temperature was beneficial to the formation of pore structure (Fig. 3(e)). Moreover, B,O-C-700 also possessed the highest total pore volume, followed by B,O-C-900 and B,O-C-1100.

X-ray photoelectron spectroscopy (XPS) analysis was further conducted to investigate the chemical composition and bonding structure of the prepared catalysts (Fig. 3(f)). The main elements in the B,O-C catalysts were C, O and B. The high-resolution XPS of C1s could be fitted to four peaks (Fig. 3(g)) at 284.8, 285.6, 289.5, and 292.1 eV, corresponding to C-C/C=C, C-B-O/C-O, C=O, and O-C=O, respectively.³⁰ For O1s (Fig. 3(h)), three peaks corresponding to C=O (531.2 eV), C-OH/C-O-B (532.4 eV), and O-C=O (533.6 eV)^{30,31} could be observed. The B1s spectra featured only one peak mainly attributed to O-BC₂ at 192 eV (Fig. 3(i)).³² The above results clearly indicate that B and O atoms were successfully incorporated into the carbon matrix structure. The FTIR spectrum of the B,O-C-900 further confirmed the effective doping of B and O

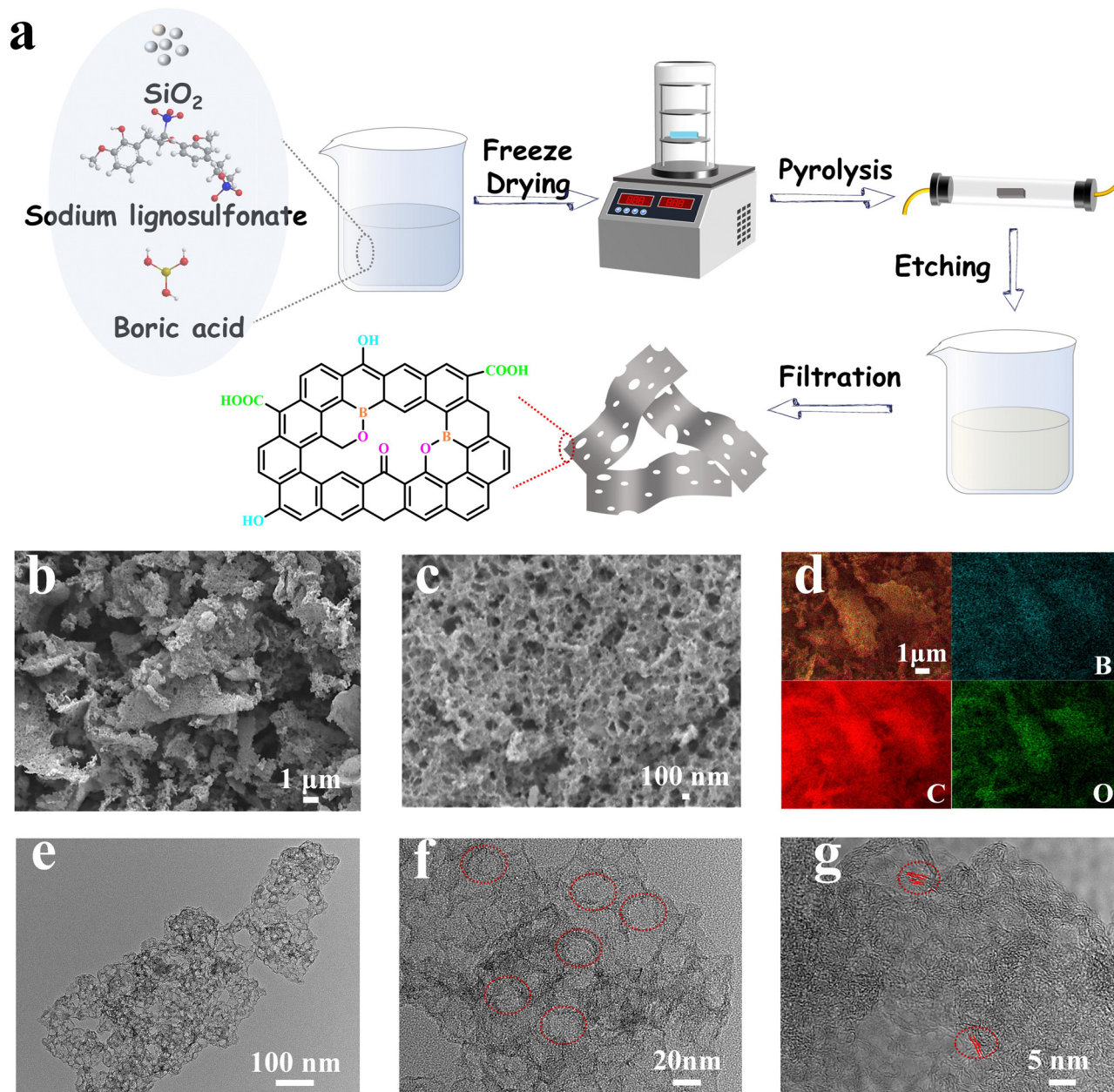


Fig. 2 Preparation and morphology of the lignin-based B,O-C catalysts. (a) Schematic diagram of the procedure for the preparation of B,O-C catalysts. (b) and (c) SEM images of the B,O-C-900. (d) EDS elemental mapping of the B,O-C-900. (e)–(g) TEM images of the B,O-C-900 with different magnification.

into the carbon materials (Fig. S3a, ESI[†]). The high-resolution XPS spectra of Na 1s were recorded as shown in Fig. S3b (ESI[†]), and the signal was very weak, indicating that no salts was present in the prepared catalysts.

Electrochemical performance of the lignin-based B,O-C catalysts

The intrinsic ORR activities and corresponding H₂O₂ selectivity of the B,O-C catalysts have been evaluated in a rotating ring-disc electrode system (RRDE) in an O₂-saturated 0.1 M KOH solution (Fig. 4(a) and (b)), which varied significantly with the pyrolysis temperatures. B,O-C-700 exhibited the highest ORR

activity with the earliest onset potential of 0.85 V vs. RHE, while the selectivity was much poorer, which may have to do with the relatively higher surface areas but lowest surface defect concentration and B doping amount.¹⁹ B,O-C-900 seemed to be the best candidate with the superior catalytic performance of the second earliest onset potentials and the highest H₂O₂ molar selectivity of over 90% across a broad potential window, because it had a moderate specific surface area, surface defect concentration, and B,O doping amount. A series of control experiments were further performed to analyze the effects of SiO₂ and boric acid (H₃BO₃) addition on 2e-ORR performance and H₂O₂ selectivity at a constant pyrolysis temperature of

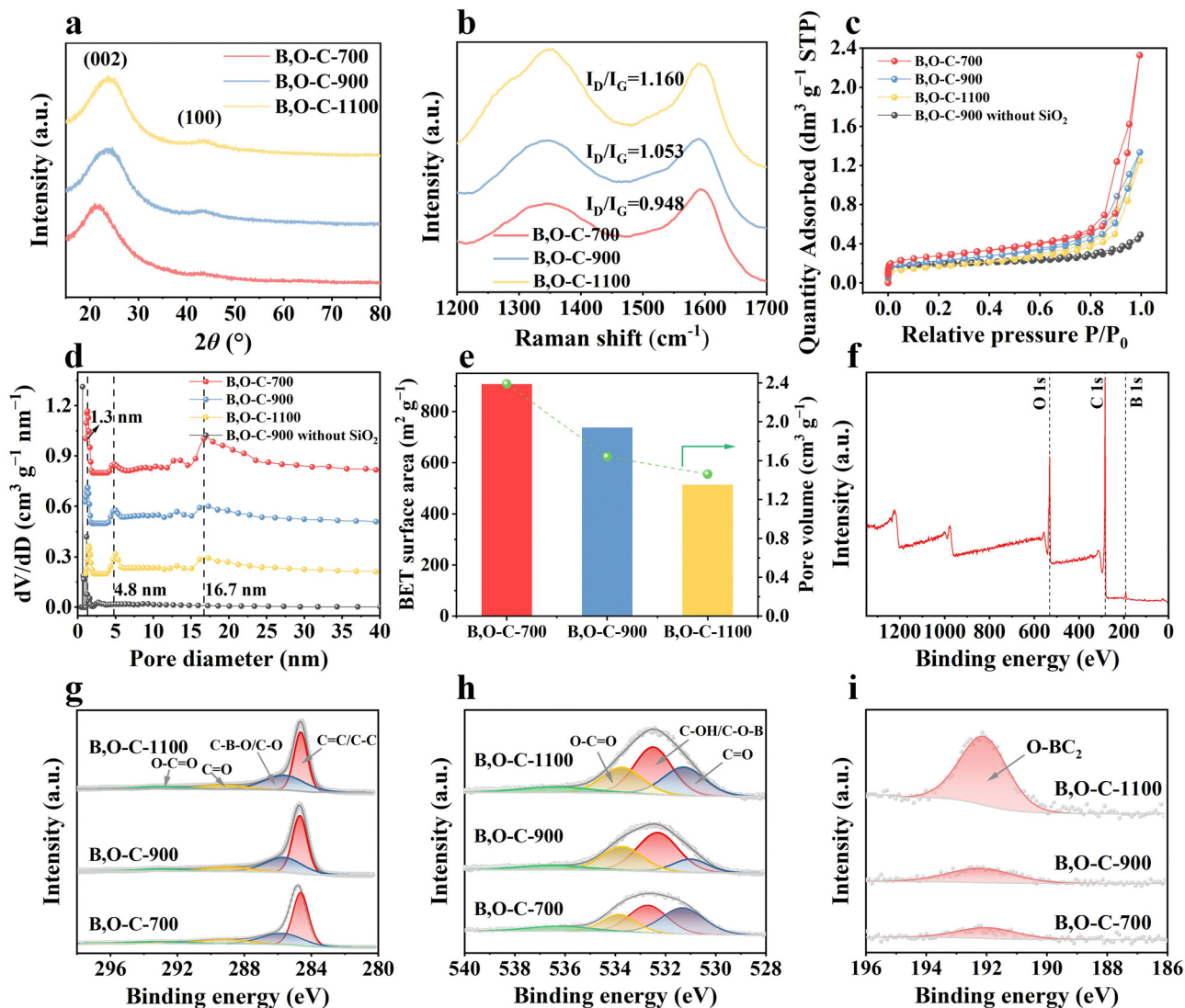


Fig. 3 Characterization of the B,O-C-700, B,O-C-900 and B,O-C-1100. (a) XRD patterns. (b) Raman spectra. (c) N₂ adsorption–desorption isotherms. (d) Pore size distribution from the density functional theory (DFT) model (with Y-axis offsets of 0.8, 0.5, and 0.2 cm³ g^{−1} nm^{−1} for B,O-C-700, B,O-C-900 and B,O-C-1100, respectively). (e) BET surface area and total pore volume. (f) Full XPS spectrum of B,O-C-900. (g)–(i) High-resolution XPS spectra of C1s, O1s and B1s, respectively.

900 °C. Significant improvement of disk current could be observed when SiO₂ was added as the hard templates, indicating the effectiveness of this strategy for pore-making (Fig. S4a and b, ESI†). With regards to the impacts of the addition of H₃BO₃, the prepared carbon materials without addition of H₃BO₃ exhibited an onset potential of 0.78 V vs. RHE and a half-wave potential of 0.70 V vs. RHE, which were about 30 mV and 50 mV smaller, respectively, than those obtained with the addition of 2 g H₃BO₃/g LS, corroborating the effectiveness of H₃BO₃ addition for improving the 2e-ORR activity (Fig. S4c and d, ESI†). Hence, the optimal condition for preparing the 2e-ORR carbon-based catalyst was one part of LS with one equal mass part of the SiO₂ template followed by the addition of two parts of H₃BO₃, which was mainly used in the subsequent electrolysis experiments.

Moreover, a linear sweep voltammetry (LSV) test and constant potential electrolysis were conducted in a typical H-type cell to evaluate the performance of B,O-C catalysts for H₂O₂ electrosynthesis. The electrolytic current was less than 1 mA cm^{−2} under the N₂ atmosphere (Fig. 4(c)), while the current response was much greater under the O₂ atmosphere, indicating the occurrence of the ORR. The onset potential was estimated as 0.8 V vs. RHE, consistent with the RRED test results. The subsequent electrolysis at constant potential further verified that the catalysts possessed excellent 2e-ORR activities in a wide potential range (Fig. 4(d)), in which B,O-C-900 obtained the highest H₂O₂ concentration during 30-min electrolysis at 0.71 V, 0.51 V, and 0.31 V vs. RHE, respectively, with a faradaic efficiency (FE) of 93–99%, and an average H₂O₂ productivity of 1009 mmol g^{−1} h^{−1}. The B,O-C-1100 also

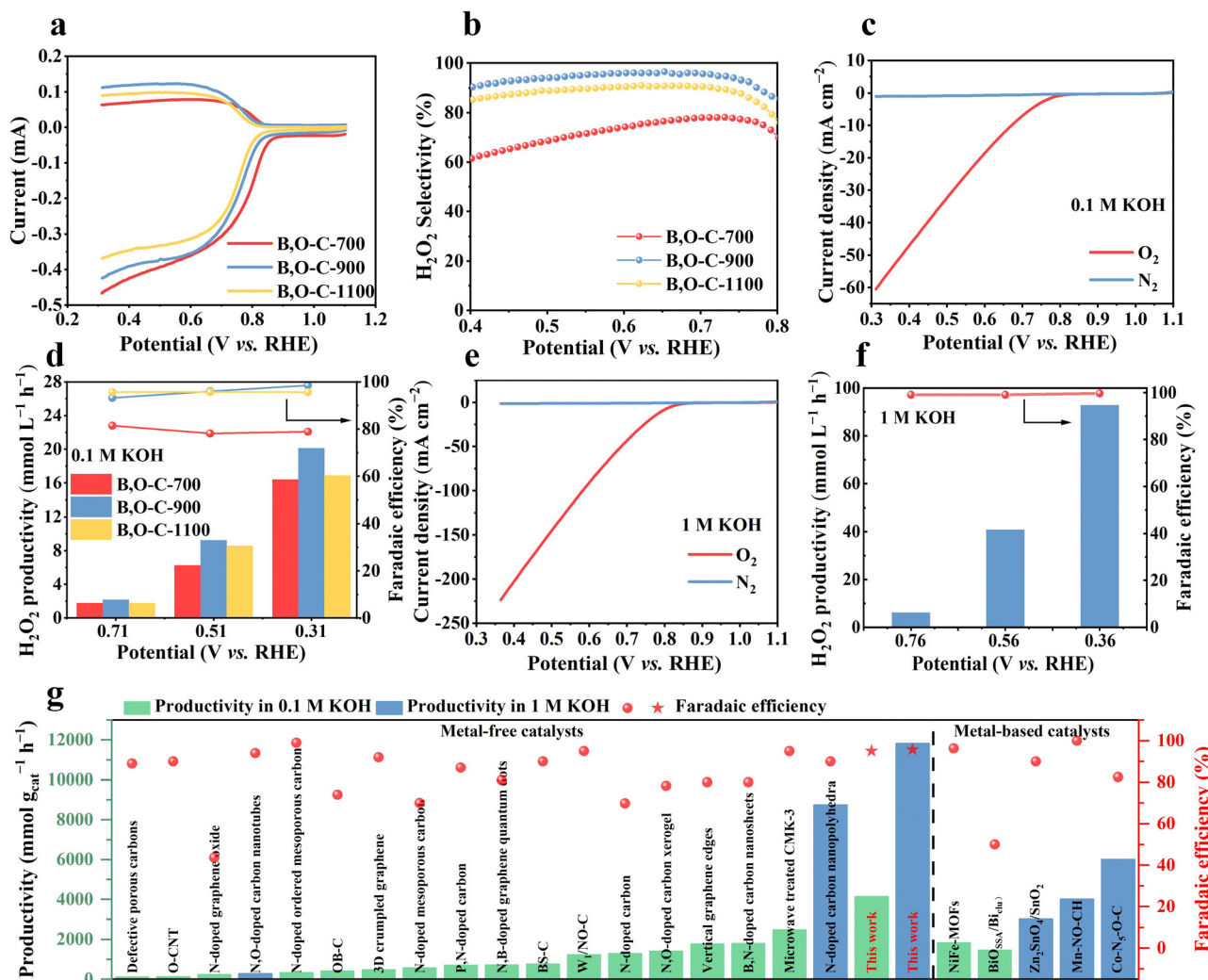


Fig. 4 Electrochemical performance of the lignin-based B,O-C catalysts. (a) Linear sweep voltammetry (LSV) curves recorded in RRDE at a rotation rate of 1600 rpm in O₂-saturated 0.1 M KOH and (b) the calculated H₂O₂ selectivity based on the corresponding LSV curves. (c) LSV curves of B,O-C-900 recorded in a typical three-electrode electrolytic system in O₂ or N₂-saturated 0.1 M KOH. (d) H₂O₂ concentration and FE at different constant potential electrolysis for 30 min in O₂-saturated 0.1 M KOH. (e) LSV curves of B,O-C-900 in a typical three-electrode electrolytic system in O₂ or N₂-saturated 1 M KOH. (f) H₂O₂ concentration and FE at different constant potential electrolysis for 30 min in O₂-saturated 1 M KOH solution with B,O-C-900 as the catalyst. (g) Comparison on H₂O₂ productivity and FE with some recently reported studies by using different carbon-based and metal-based catalysts (further refer to Tables S1 and S2 in the ESI†).

achieved a high FE of over 95%. The results were in good agreement with those of the RRED test.

Several biomass-derived organic carbon precursors including glucose, fructose, and alkali lignin were further used for the preparation of carbon-based catalysts using the same synthetic process. The catalysts prepared with glucose and fructose as carbon precursors also possessed excellent 2e-ORR activities (Fig. S5a, ESI†) with H₂O₂ selectivity of higher than 90% (Fig. S5b, ESI†). However, the performance of the catalysts obtained from alkali lignin was relatively poor, probably due to the poor solubility of alkali lignin leading to non-uniform mixing of dopants and templates. The results were further confirmed by electrolysis experiments at a constant potential of 0.31 V vs. RHE (Fig. S5c, ESI†). The catalysts obtained from glucose and

fructose exhibited FE of higher than 95% with H₂O₂ productivity of higher than 950 mmol g⁻¹ h⁻¹, while slightly lower productivity (836 mmol g⁻¹ h⁻¹) was obtained for alkali lignin as the precursor. This suggested that the synthetic process developed in this work was universal for preparing carbon-based 2e-ORR catalysts with good performance.

A higher KOH concentration in electrolyte was used to study whether the efficiency of H₂O₂ production could be further enhanced. In O₂-saturated 1 M KOH solution, the onset potential of B,O-C-900 was 0.81 V vs. RHE, which was slightly larger than that in 0.1 M KOH electrolyte (Fig. 4(e)). Moreover, a significantly enhanced current density reaching 200 mA cm⁻² at 0.4 V vs. RHE was observed, which was about 4 times higher than that in 0.1 M KOH electrolyte. The subsequent constant

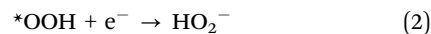
potential electrolysis test of 0.36 V *vs.* RHE further confirmed the higher H₂O₂ productivity (4635 mmol g⁻¹ h⁻¹) and better FE (99%) at a higher KOH concentration (Fig. 4(f)).

It should be noted that all of the three-electrode electrolysis tests above were conducted without iR compensation, which was closer to the actual situation, but it was difficult to demonstrate the inherent catalytic activity of the catalysts due to the existence of the contact resistance, charge transfer resistance, and intrinsic resistance of the H-type cell.³³ Hence, the effect of iR compensation was investigated on the electrolysis performance. Under 85% iR compensation, the B,O-C-900 showed excellent ORR activities in 1 M KOH solution, with reduction currents exceeding 100, 370, and 680 mA cm⁻² at 0.76 V, 0.66 V and 0.56 V *vs.* RHE, respectively, which was significantly enhanced compared with those obtained without iR compensation (Fig. S6a, ESI†). Moreover, through iR compensation, the improvement of the catalytic performance became more significant at higher KOH concentration. For example, the current density increased from 220 to 680 mA cm⁻² at 0.56 V *vs.* RHE with KOH concentration increasing from 0.1 to 1 M. Therefore, using iR compensation can well analyze the intrinsic catalytic activity of the catalysts with better accuracy. Long-term electrolysis at a constant potential of 0.56 V *vs.* RHE under 85% iR compensation was further carried out (Fig. S6b, ESI†). In 1 M KOH electrolyte, the electrolytic current was stable at about 650 mA cm⁻² within 30 min, and 59.1 mmol L⁻¹ of H₂O₂ was produced. The FE and H₂O₂ productivity reached 95.7% and 11 812 mmol g⁻¹ h⁻¹, respectively. In addition, in 0.1 M KOH solution, the H₂O₂ production rate still reached 4122 mmol g⁻¹ h⁻¹. These H₂O₂ productivities were at the highest level, compared to those in recently reported 2e-ORR studies with similar catalyst loads (Fig. 4(g)). It was suggested that the method developed in this work for preparing carbon-based electrocatalysts was effective in producing H₂O₂.

Mechanism of oxygen reduction over the B,O-doped carbon-based catalysts

In situ attenuated total reflection infrared (ATR-IR) spectroscopy was used to analyze the adsorbed oxygen intermediates on the B,O-C-900. ATR-IR spectra were recorded by stepwise varying the applied potential from 0.91 to 0.31 V *vs.* RHE in O₂-saturated 0.1 M KOH electrolyte. An adsorption band at 1250 cm⁻¹ was observed (Fig. 5(a)), which was attributed to the O–O stretching of surface-adsorbed *OOH.³⁴ Moreover, the intensity of this adsorption band increased with the decrease in the applied potential. It is known that the *OOH intermediate is crucial in the 2e-ORR process. Typically, the 2e-ORR proceeds through a one-electron reduction to form *OOH firstly (eqn (1)) and a subsequent one-electron reduction of *OOH to form H₂O₂ (eqn (2)). Hence, the 2e-ORR/4e-ORR activity of an electrocatalyst is determined by the binding strength of the *OOH to the active site. In general, lower adsorption energy is beneficial to the production of H₂O₂; however, if the adsorption strength is too low, the formation of *OOH intermediate from the hydrogenation of O₂ would be difficult to occur. Hence, the

active site with the best catalytic performance for 2e-ORR should have a moderate *OOH adsorption strength.¹³ Therefore, the B,O-C-900 with excellent catalytic performance was probably due to its moderated adsorption strength of *OOH intermediate.



Density functional theory (DFT) calculations were carried out to further study the active sites of B,O-C-900. Based on the results of XPS spectra, six active sites were considered (Fig. 5(b) and Fig. S7, ESI†), including three oxygen-containing functional groups: carbonyl (C=O), carboxyl (COOH), and hydroxyl (OH); and three active sites in the C–O–B–C structure: B atom (B), C atom connecting with B atom (C1), and C atom connecting with O atom (C2). $\Delta G_{\text{*OOH}}$ can be used to describe the activities of different sites. The limiting potential (U_L), as a metric of activity, was defined as the lowest potential at which all the reactions were decreased stepwise in free energy. The theoretical overpotential was defined as the maximum difference between the limiting potential and equilibrium potential.²⁷ The volcano-type relationship of $\Delta G_{\text{*OOH}}$ with the U_L was shown in Fig. 5(c). The top of the volcano plot corresponded to the maximum limiting potential and the thermodynamic equilibrium potential (0.70 V), indicating a zero overpotential required for the 2e-ORR into H₂O₂. Typically, for the active site with the best catalytic activity, the *OOH should be bound in a thermodynamically neutral way, close to the top of the volcano. Among those six possible active sites, the C1 site showed the smallest overpotential and a moderate $\Delta G_{\text{*OOH}}$, suggesting that the C1 site had the highest 2e-ORR activity.³⁵ Moreover, the superior 2e-ORR activity of the C1 site could be further verified by the reaction free energy diagrams under different applied potentials (Fig. 5(d)). When the applied potential was 0 or 0.2 V, thermodynamically, the free energy of the substances decreased as the reaction progressed, suggesting that the reaction could occur spontaneously from a thermodynamic perspective. When the applied potential was raised to 0.7 V, the free energy decreased first for the formation of *OOH and then increased for the formation of H₂O₂, suggesting that the first reaction step (eqn (1)) could spontaneously occur, but the second step (eqn (2)) with a rather low energy barrier needed some external energy.³⁶ Therefore, the above results revealed that the excellent activity and selectivity performance of the B,O-C-900 could be expected with the C atom connecting with the B atom.

H₂O₂ production in a flow electrolytic cell with air as the O₂ source

A flow electrolytic cell was employed with air as the O₂ source for H₂O₂ production (Fig. 6(a) and (b)). An acid-alkali asymmetric design was employed, with H₂SO₄ solution as the anolyte and KOH solution as the catholyte. The H⁺ produced on the anode could diffuse through the ion exchange

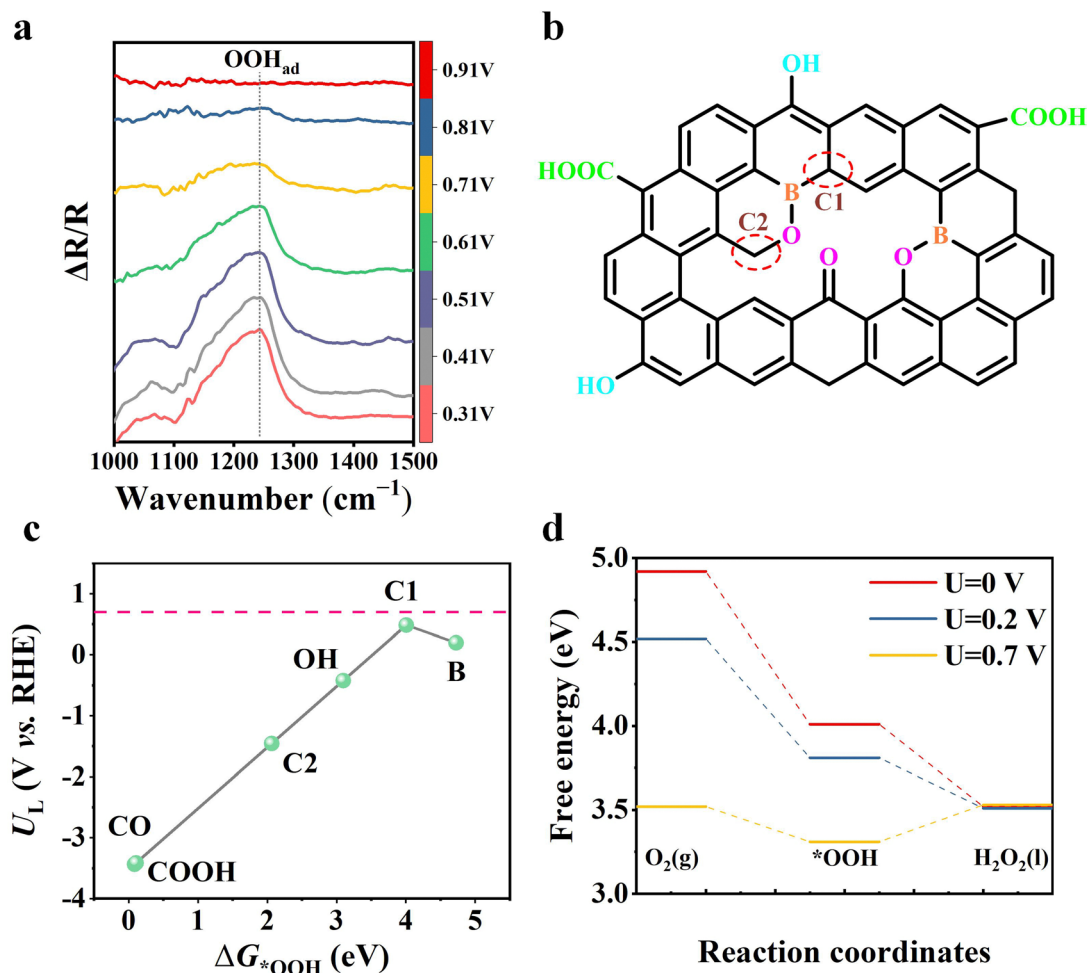
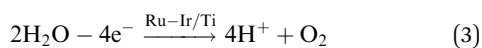


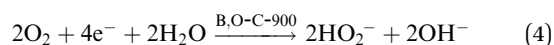
Fig. 5 The mechanisms for the B,O-C-900 catalysed 2e-ORR with regards to the adsorption of intermediates and active sites. (a) *In situ* ATR-IR spectra of B,O-C-900 in O₂-saturated 0.1 M KOH. (b) Schematic diagram of the six active sites of B,O-C-900 for DFT calculation. (c) Catalytic activity volcano plot of different active sites for 2e-ORR based on DFT calculations. (d) Free energy diagram of the 2e-ORR over the C1 atom at various applied potentials.

membrane and react with the OH[−] produced on the cathode, thus maintaining the acidity and alkalinity of the anolyte and catholyte to keep a stable acidic-alkaline bias. Hence, the reactions taking place in the flow electrolytic cell could be described as follows:

On the anode:



On the cathode:



In the absence of O₂, a hydrogen evolution reaction (HER) occurred on the cathode when the applied voltage was higher than −2.5 V (Fig. 6(c)). However, in the air atmosphere, the LSV curve significantly moved forward, suggesting the occurrence of the 2e-ORR. The onset voltage that ORR occurred was estimated as −1.47 V and the current density reached 100 mA cm^{−2} when the cell voltage was −2.91 V.

A relatively long-term electrolysis was conducted at a constant current of 100 mA cm^{−2} for 120 h (Fig. 6(d)). The FE maintained around 95% with ignorable fluctuation. In the first 24-h electrolysis, the applied voltage increased from 2.9 V to about 3.2 V but recovered after replacing the catholyte. A total of 2 L alkaline H₂O₂ solution with an H₂O₂ mass fraction of 1.1% was obtained from the 120-h electrolysis, which could be directly used for disinfection, pulp bleaching, and biomass pretreatment in a biorefinery. Overall, those results clearly demonstrated that the developed B,O-C-900 was a promising candidate for electrochemical synthesis of H₂O₂ towards industrial application.

H₂O₂ production by a paired electrolytic system with lignin oxidation on the anode

The cathodic ORR is typically paired with the OER on the anode in conventional electrolytic systems, which is kinetically sluggish with the generation of low value-added product, O₂.^{37,38} To reduce the overall energy consumption of the system, we employed a thermodynamically favourable organic molecule

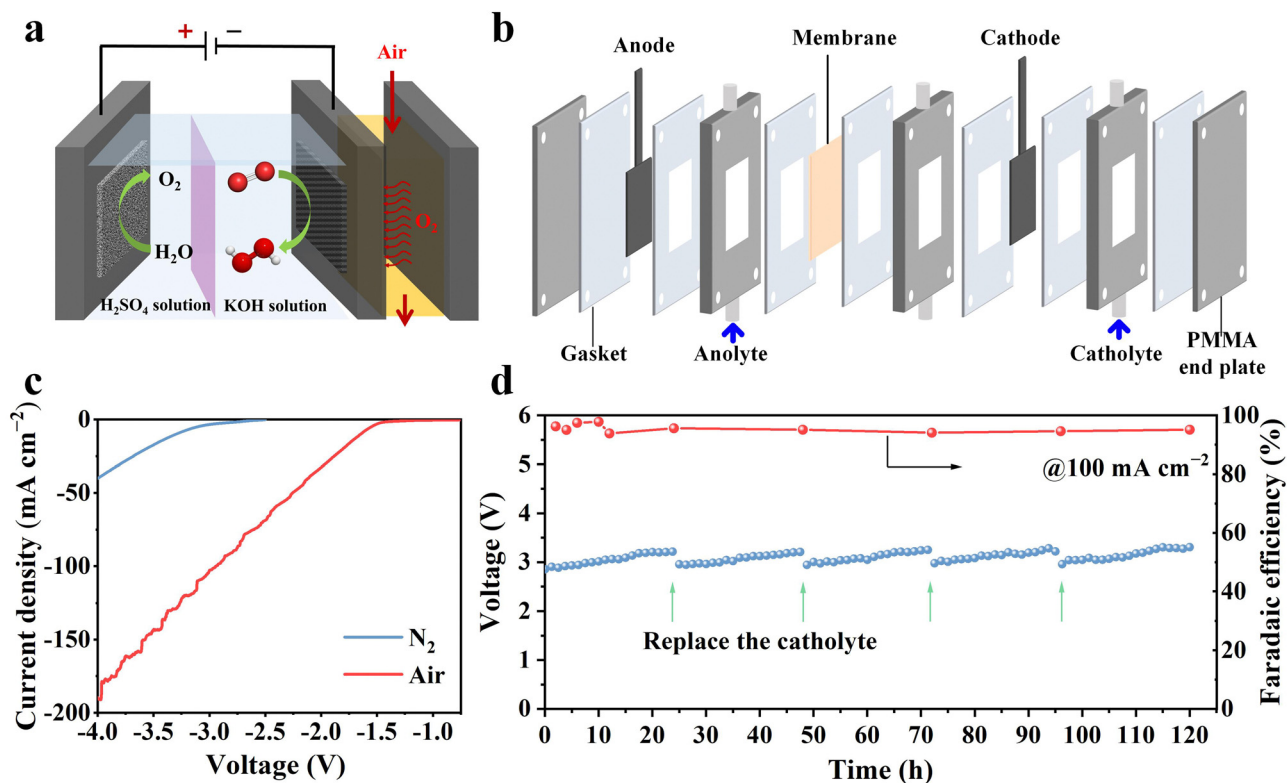


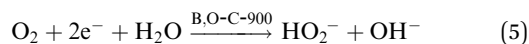
Fig. 6 Production of H_2O_2 by using B,O-C-900 as the catalyst with a flow electrolytic cell. (a) Schematic diagram of the electrolysis process. (b) Structure diagram of the flow electrolytic cell. (c) LSV curves of the flow electrolytic cell. (d) Electrolytic voltage and FE during a relatively long-term electrolysis at a constant current of 100 mA cm^{-2} , with 400 mL 1 M KOH as the catholyte, 2000 mL 0.5 M H_2SO_4 as the anolyte and the electrode area of 3 cm^2 .

oxidation reaction to replace the OER at the anode. As a by-product of the pulping industry and lignocellulose biorefinery, lignin is low cost and abundantly available. Moreover, the direct discharge of high-concentration lignin black liquor from pulping mills could cause serious environmental pollution problems.³⁹ Therefore, pairing lignin electro-oxidation not only improves H_2O_2 productivity but also removes the lignin from the black liquor and even valorises the lignin into high-value phenolic compounds through the electrochemical depolymerization of lignin.⁴⁰

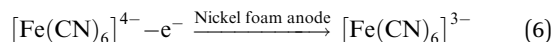
However, lignin is difficult to oxidize at relatively low temperatures due to its complex structure. Moreover, the mass transfer resistance between the solid electrocatalysts and lignin further decreases the rate of electron transfer and oxidation efficiency of lignin. Recently, we developed a direct biomass fuel cell that employed a soluble redox couple such as $[\text{Fe}(\text{CN})_6]^{3-}/[\text{Fe}(\text{CN})_6]^{4-}$ as electron carriers to mediate the electron transfer thus achieving efficient oxidation of lignin for electricity generation.⁴¹ $[\text{Fe}(\text{CN})_6]^{3-}$ could rapidly oxidize lignin in an alkaline medium and extract electrons. About 93% of lignin was oxidized to CO_2 by $[\text{Fe}(\text{CN})_6]^{3-}$ at a relatively high weight ratio of $[\text{Fe}(\text{CN})_6]^{3-}$ to lignin. Moreover, as the widely used redox-active species in redox flow batteries, the $[\text{Fe}(\text{CN})_6]^{3-}/[\text{Fe}(\text{CN})_6]^{4-}$ redox couple possesses rapid electron transfer kinetics without any special catalyst. Therefore, in this work, we selected the $[\text{Fe}(\text{CN})_6]^{3-}/[\text{Fe}(\text{CN})_6]^{4-}$ redox couple to

promote lignin oxidation on the anode in the paired system (Fig. 7(a)). The reactions taking place in the paired system could be described as follows:

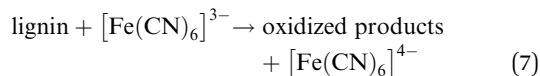
On the cathode:



On the anode:



In the external anode reactor, lignin is oxidized and depolymerized by $[\text{Fe}(\text{CN})_6]^{3-}$ in alkaline electrolyte:



The LSV curves of $[\text{Fe}(\text{CN})_6]^{4-}$ oxidation and the OER on the anode in a typical three-electrode system with 1 M KOH as the supporting electrolyte was shown in Fig. 7(b) for comparison. Ni foam without any pretreatment was used as an electrode for $[\text{Fe}(\text{CN})_6]^{4-}$ oxidation. As expected, a significantly negative shift of onset potential was observed for $[\text{Fe}(\text{CN})_6]^{4-}$ oxidation, compared with that for the OER. The modification of Ni foam with the deposition of NiFe-LDH could significantly accelerate the OER and thus decrease the overpotential. However, the $[\text{Fe}(\text{CN})_6]^{4-}$ oxidation reaction on the Ni foam anode exhibited

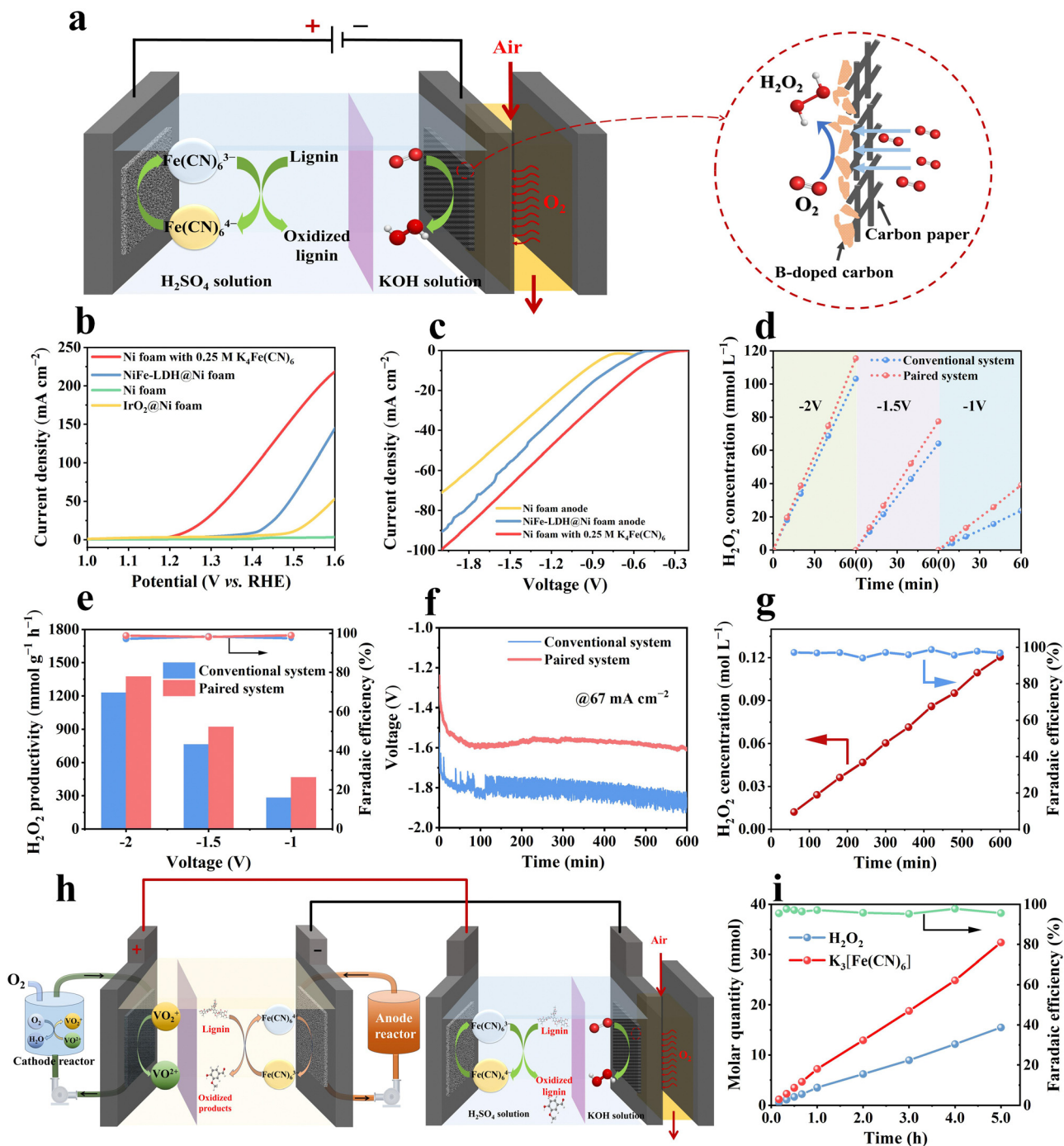


Fig. 7 Paired electrolytic system and coupled power-supply system for electrooxidation of lignin and electrosynthesis of H_2O_2 . (a) Schematic diagram of $[\text{Fe}(\text{CN})_6]^{3-} / [\text{Fe}(\text{CN})_6]^{4-}$ mediated electron transfer for lignin oxidation and the 2e-ORR. (b) LSV curves of $\text{K}_4[\text{Fe}(\text{CN})_6]$ oxidation and the OER in a three-electrode system with 1 M KOH as the supporting electrolyte. (c) LSV curves in a two-electrode flow electrolytic cell using different anodes. (d) H_2O_2 concentration and (e) productivity and FE of the conventional system and paired system during constant voltage electrolysis. (f) Voltage change of the conventional and paired system during constant current electrolysis. (g) H_2O_2 concentration and FE of the paired system during a relatively long-term electrolysis. (h) Schematic diagram of DLFC as a power source for the electrochemical synthesis of H_2O_2 with $[\text{Fe}(\text{CN})_6]^{3-} / [\text{Fe}(\text{CN})_6]^{4-}$ and $\text{VO}_2^+ / \text{VO}^{2+}$ as the anode and cathode electron mediators, respectively. (i) The molar quantity of $[\text{Fe}(\text{CN})_6]^{3-}$ in the anolyte of DLFC and H_2O_2 in the catholyte of the electrolytic cell during 5-h electrolysis.

the lowest onset potential, which was about 200 mV lower than the OER reaction catalysed by the NiFe-LDH@Ni foam electrode, suggesting that the $[\text{Fe}(\text{CN})_6]^{4-}$ oxidation reaction was thermodynamically more feasible than the OER. The

performance of the paired system was further investigated by LSV (Fig. 7(c)). The onset potential decreased from -0.56 to -0.36 V with $[\text{Fe}(\text{CN})_6]^{4-}$ oxidation, compared with the OER catalysed by NiFe-LDH@Ni foam. Moreover, an improvement

in current density of about 10 mA cm^{-2} could be observed in a wide voltage range between -0.6 and -2 V . The above results indicated that oxidation of $[\text{Fe}(\text{CN})_6]^{4-}$ on the anode indeed had a higher reaction rate and thus could improve the efficiency of the paired system.

In our previous works, we found that $[\text{Fe}(\text{CN})_6]^{3-}$ could efficiently oxidize lignin and was reduced to $[\text{Fe}(\text{CN})_6]^{4-}$ at $80\text{--}90^\circ\text{C}$.⁴¹ However, the electrochemical synthesis of H_2O_2 should be carried out at room temperature due to the unstable nature of H_2O_2 . Therefore, the reaction between $[\text{Fe}(\text{CN})_6]^{3-}$ and lignin at room temperature was further explored. To analyze the efficiency of electron extraction by $[\text{Fe}(\text{CN})_6]^{3-}$, the ratio of the produced $[\text{Fe}(\text{CN})_6]^{4-}$ to the initial amount of $[\text{Fe}(\text{CN})_6]^{3-}$ was defined as the degree of $[\text{Fe}(\text{CN})_6]^{3-}$ reduction. The degree of reduction could reach 0.7 within 240 min at room temperature when the electrolyte consisted of 0.25 M $[\text{Fe}(\text{CN})_6]^{3-}$ and 4 g L^{-1} lignin (Fig. S8a, ESI†). A higher degree of reduction of 90% could be achieved within 120 min when the lignin concentration increased to 8 g L^{-1} . These results demonstrated that $[\text{Fe}(\text{CN})_6]^{3-}$ could efficiently oxidize lignin at room temperature. The oxidative depolymerization products were phenolic compounds phenol, guaiacol, vanillin, ferulic acid, apocynin, syringaldehyde, *p*-hydroxybenzaldehyde, vanillic acid, syringic acid *etc.*⁴¹ These high value-added products could be isolated by extraction and further employed for the synthesis of derived products such as antioxidants.⁴²

Electrolysis experiments at 1.32 V vs. RHE in a typical three-electrode system were performed to confirm that the $[\text{Fe}(\text{CN})_6]^{3-}/[\text{Fe}(\text{CN})_6]^{4-}$ redox couple could act as electron carriers to mediate the electron transfer (Fig. S8b, ESI†). The electrochemical reaction on the anode was the oxidation of $[\text{Fe}(\text{CN})_6]^{4-}$ to $[\text{Fe}(\text{CN})_6]^{3-}$. In the absence of lignin, the current density decreased to near zero within 7 h, and the total transferred charge was 428.5 C after 10 h. When 8 g L^{-1} lignin was added, the trend of current density decline became much more gentle, and the total transferred charges increased to 1203 C , being about 2.5 times higher than that without lignin, suggesting that lignin was continuously oxidized by the *in situ* generated $[\text{Fe}(\text{CN})_6]^{3-}$ on the electrode.

To further verify the improved performance of the paired system, electrolysis experiments at constant voltages of -2 V , -1.5 V , and -1 V were conducted (Fig. 7(d) and (e)). The conventional system using NiFe-LDH as the catalyst for the OER was compared. Both the conventional and paired systems exhibited outstanding FE of about 98%. The H_2O_2 concentration in the electrolyte increased almost linearly, which further demonstrated the excellent performance of the prepared catalysts. Regardless of the electrolytic voltage, the H_2O_2 productivity of the paired system was always higher than that of the conventional system. For example, at a constant voltage of -1 V , the H_2O_2 productivity was $465.8 \text{ mmol g}^{-1} \text{ h}^{-1}$, which was about 1.6 times higher than that of the conventional system ($282.4 \text{ mmol g}^{-1} \text{ h}^{-1}$). A constant current electrolysis further verified the good stability of the paired system. During a 600-min electrolysis at 67 mA cm^{-2} , the cell voltage was stable at around 1.6 V , which was about 0.2 V lower than that of the

conventional system (Fig. 7(f)). As a result, the energy consumption of the paired system was decreased by 11.4%, compared with the conventional system. Moreover, the paired system exhibited impressive H_2O_2 productivity and FE (Fig. 7(g)). The accumulated H_2O_2 concentration reached 0.12 mol L^{-1} after 600-min electrolysis, and FE remained at 98%. The results indicated that the paired system achieved higher H_2O_2 productivity in a flow electrolytic cell by using lignin as an electron donor with ferricyanide as an electron carrier. This paired system not only decreased the energy consumption of electrochemical synthesis of H_2O_2 , but also could potentially use the lignin-rich waste liquor from a pulping mill or biorefinery as feedstock for simultaneous treatment of the pollutant (lignin waste).

In this paired system, under the driving of an external electric field, the electrons from lignin could be transferred to O_2 thus forming H_2O_2 . Generally, the process of electron transfer could be divided into three steps, namely: from lignin to the electron mediator ($[\text{Fe}(\text{CN})_6]^{3-}$, step I), from the reduced electron mediator ($[\text{Fe}(\text{CN})_6]^{4-}$) to cathode through the anode and external circuit (step II), and from the cathode to O_2 to form H_2O_2 (step III). Step I was a chemical oxidation process where lignin was oxidized by $[\text{Fe}(\text{CN})_6]^{3-}$ in alkaline medium, and the rate of electron transfer can be determined separately. 69.0% of the $[\text{Fe}(\text{CN})_6]^{3-}$ (0.25 M) in 1 M KOH electrolyte could be reduced by oxidation of lignin (8 g L^{-1}) within 30 min (Fig. S8a, ESI†), indicating an electron (charge) transfer rate of $33\,278 \text{ C L}^{-1} \text{ h}^{-1}$. For Step II, the rate of electron transfer was affected by electrooxidation conditions including the voltage, electrode materials, active areas, *etc.* It was found in our previous work that the electron transfer rate during oxidation of $[\text{Fe}(\text{CN})_6]^{3-}$ on a graphite anode could reach $0.190 \text{ mol electron L}^{-1} \text{ h}^{-1}$, corresponding to $18\,332 \text{ C L}^{-1} \text{ h}^{-1}$.⁴¹ For step III, the electron (charge) transfer rate was calculated as $58\text{--}895 \text{ C L}^{-1} \text{ h}^{-1}$ at a cathode potential of 0.76 to 0.36 V vs. RHE (Fig. 4(f)), which was significantly lower than those of step I and II. It was indicated that step III was a rate-limiting step of the electron transport chain. This conclusion was reasonable because the ORR took place in a solid-liquid-gas (catalyst-electrolyte- O_2) tri-phase system, and would be significantly impacted by local concentration of reactants (O_2), diffusion of products, interfacial hydrophilicity and pH value.⁴³ For better match of the electrode reaction rates to achieve high FE and productivity of the paired system, it is necessary to design highly efficient catalysts and electrolyzers, as well as optimize conditions such as reaction voltage, concentration of reactants at both the anode and cathode. Studying the kinetics of electron transfer would also be very helpful to match the electrode reaction rates.

Currently, no reported works on the electrooxidation of lignin paired with 2e-ORR for the synthesis of H_2O_2 have been found. One of the major reasons is the heterogeneity and recalcitrance of lignin's aromatic heteropolymer structure, making it not a suitable organic substrate for anodic oxidation to replace the OER. However, as compared in Table S3 (ESI†), using oxidation reactions of small molecules such as ethylene

glycol and furfural have been found to well improve the efficiency of the paired system. Moreover, by pairing water oxidation on the anode can achieve the synthesis of H_2O_2 on both the anode and cathode, which needs a higher cell voltage but avoids using a membrane to separate the anolyte and catholyte. In contrast, the present work employs an electron mediator to facilitate the oxidation of lignin and achieves excellent cathodic FE (98%) and productivity ($\sim 12 \text{ mmol L}^{-1} \text{ h}^{-1}$) for the synthesis of H_2O_2 , indicating the success of the paired system. The constructed electron transport chain may also inspire future works for pairing electro-oxidative conversion of more complex polymers such as lignocellulose and waste plastics with 2e-ORR.

Direct lignin fuel cell as a power source to drive the electrolytic cell

The paired electrolytic system still needed the input of external electric energy. To achieve a more efficient transfer of the endogenous electrons from lignin to O_2 , a coupled system was further developed by incorporating the DLFC (Fig. S9, ESI†) as a power source to drive the electrolytic cell. In this system, lignin was converted to electricity by the DLFC *via* transferring the chemical energy of lignin to electric energy, which was then used to power the electrochemical reactions in the electrolytic cell. Therefore, no “external electricity” was needed. Due to the relatively complex structure of lignin and poor contact between the lignin “fuel” and electrode, electron mediators should be used to improve the rate of electron transfer from lignin to the electrode. In our previous studies, we developed two types of DLFCs depending on the electron mediators (catalysts) used for anodic oxidation of lignin, namely soluble electron mediators such as $[\text{Fe}(\text{CN})_6]^{3-}/[\text{Fe}(\text{CN})_6]^{4-}$ and solid electrocatalysts such as cobaltous sulfide. Because of the higher electrode reaction rate, the DLFC using soluble electron mediators can usually obtain higher power density. For example, the DLFC with $[\text{Fe}(\text{CN})_6]^{3-}/[\text{Fe}(\text{CN})_6]^{4-}$ as the electron mediators obtained a higher power density of 200.3 mW cm^{-2} , compared to 176 mW cm^{-2} obtained with $\text{Co}^{3+}/\text{Co}^{2+}$ as the electron mediators.^{41,44} Therefore, we selected the DLFC with $[\text{Fe}(\text{CN})_6]^{3-}/[\text{Fe}(\text{CN})_6]^{4-}$ as electron mediators for powering the electrolytic cell, and $\text{VO}_2^+/\text{VO}^{2+}$ redox couples were used as the cathode electron mediators to transfer electrons to O_2 (Fig. 7(h)). In order to provide enough high output voltage for the electrolytic cell, two DLFCs were used in series with a total area of 8 cm^2 . During a 5-h operation, the mole quantity of both $[\text{Fe}(\text{CN})_6]^{3-}$ in the anolyte of DLFC and H_2O_2 in the catholyte of the electrolytic cell increased continuously (Fig. 7(i)), indicating that electrons were steadily transferred from lignin to air (O_2) to achieve the production of H_2O_2 in the coupled system. For H_2O_2 production, the FE remained above 95%, corroborating the excellent selectivity of B-O-C-900. A total of 50 mL 1.05 wt% H_2O_2 solution was obtained. According to the molar quantity change of $[\text{Fe}(\text{CN})_6]^{3-}$ and H_2O_2 , the electron transfer efficiency from $[\text{Fe}(\text{CN})_6]^{4-}$ to air was estimated as 95.6%. In our previous work on DLFC, the electron transfer efficiency from lignin to $[\text{Fe}(\text{CN})_6]^{3-}$ could reach 98%.⁴¹ Therefore, the total efficiency of electron transfer in the coupled system was 93.7%, *i.e.*,

93.7% of the electrons extracted by $[\text{Fe}(\text{CN})_6]^{3-}$ from lignin were used for the 2e-ORR to produce H_2O_2 in the electrolytic cell. This high electron transport efficiency suggested the high efficiency of the developed electron transport chain and superior performance of B-O-C-900 for the 2e-ORR. The results also demonstrated the feasibility of integrating DLFC with an electrolytic cell using lignin-based catalysts to achieve H_2O_2 production from air. This coupled system avoided using an external electricity supply and thus showed good potential in decreasing the net CO_2 emission.

In situ use of H_2O_2 for the production of biomass-based chemical

The obtained H_2O_2 in the catholyte was of low concentration (1.1 wt%). To recover and concentrate H_2O_2 to 27.5 wt% that can be obtained by the conventional anthraquinone process,⁹ a process was designed to recover H_2O_2 from the catholyte by extraction with diethyl ether (Fig. S10, ESI†).⁴⁵ The most important factors affecting the recovery rate of H_2O_2 were the volume ratio of extractant to the reaction solution, temperature, pressure, and distillate rate (Fig. S11, ESI†). The simulation results (Fig. S12a, ESI†) revealed that 27.5 wt% H_2O_2 indeed could be obtained by extraction, though the energy consumption was relatively high. However, it was difficult to obtain concentrated H_2O_2 from alkaline electrolyte (Fig. S12b, ESI†). Therefore, it was better to develop novel process for *in situ* use of the generated alkaline H_2O_2 .

As a green oxidant, H_2O_2 shows great promise for the oxidation of organic molecules. In this work, HMF, one of the top twelve important biomass-based platform chemicals, was oxidized with the *in situ* generated H_2O_2 to produce HMFCa with commercial Ag_2O catalyst (Fig. S13a, ESI†). HMF conversion reached above 95% within half an hour in both flow and H-type cells, but only 80.7% in a control system without H_2O_2 (Fig. S13b, ESI†). The HMFCa yield reached 84.5% and 94.8% in the flow and H-type cells, respectively, but only 44.7% in the control system (Fig. S13c, ESI†), indicating that the *in situ* generation of H_2O_2 could significantly improve the conversion rate of HMF and selectivity of HMFCa. In triplicate experiments of the flow cell, HMF conversion reached 94.2–99.6% in 1 h with an HMFCa yield of 80.9–86.9%, while the by-product 2,5-bis(hydroxymethyl)furan (BHMF) formed *via* disproportionation of HMF was also detected with a yield of 9.7–13.8%. The carbon balance was $\sim 99\%$, indicating that little humin was produced. The mechanisms for the Ag_2O -catalyzed oxidation of HMF have been proposed (Fig. S13d, ESI†). In the initial step, an aldehyde group in HMF was oxidized by Ag_2O followed by nucleophilic attack of a hydroxide anion (OH^-), resulting in the formation of metallic Ag and a tetrahedral intermediate. The intermediate subsequently undergoes hydrogen shift to form a gem-diol intermediate, in which a hydrogen ion in one of the hydroxyl groups was stripped away by OH^- under alkaline conditions, to form a carboxylic acid group with the reduction of Ag_2O to form metallic Ag again, followed by the final formation of a carboxylate anion.⁴⁶ The generated metallic Ag then could be oxidized by H_2O_2 to regenerate Ag_2O . The above results demonstrated that biomass-based chemicals could be

produced *via in situ* use of the H_2O_2 , which provided a novel route for biomass conversion to biochemicals. However, the reactor should be further designed to improve mass transfer and contact between the substrate and catalysts.

Conclusions

In summary, we have developed a novel approach for the preparation of B and O doped carbon-based electrocatalysts with lignin as the carbon precursor to boost the reaction kinetics and selectivity of the 2e-ORR for the synthesis of H_2O_2 with air as the oxygen source. Among the prepared catalysts, B,O-C-900 showed the highest 2e-ORR activity. The method showed good universality to prepare the catalysts with different biomass derivatives as the carbon precursors. Remarkably, the B,O-C-900 exhibited a high H_2O_2 selectivity of over 90% and superior long-term stability of 120 h in the flow cell. The FE reached 95.7%, and the H_2O_2 productivity could be as high as 11 812 mmol $\text{g}^{-1} \text{h}^{-1}$. *In situ* ATR-IR spectroscopy revealed that B,O-C-900 had moderated adsorption strength of the *OOH intermediate. DFT calculation revealed that the C atom connecting with the B atom had the smallest overpotential and a moderate ΔG_{OOH} , suggesting its highest 2e-ORR activity. A novel paired system was further developed by pairing electrooxidation of lignin on the anode under the assistance of electron mediators, $[\text{Fe}(\text{CN})_6]^{3-}/[\text{Fe}(\text{CN})_6]^{4-}$ redox couple. This paired system well increased the synthesis rate of H_2O_2 and reduced the energy consumption by 11.4%, compared to the conventional system. Furthermore, by using DLFC as the power source, the endogenous electrons of lignin could be transferred to O_2 , achieving the production of H_2O_2 from air without external electric energy. The Aspen plus simulation indicated the difficulty in recovering and concentrating the generated H_2O_2 from the alkaline electrolyte by extraction. Hence, a novel coupled system was further developed by *in situ* use of H_2O_2 for the oxidation of HMF to produce HMFCa. This work provided an innovative process for lignin-based catalyst preparation and production of H_2O_2 from air with lignin as the carbon precursor and electron donor.

Author contributions

Y. L. and D. O. prepared and characterized the catalysts, and performed most of the experiments. X. L. contributed partially to the characterization of the catalysts; Y. Z. contributed to the DFT calculation, and provided discussion on the mechanism interpretation; Z. N. provide discussion on the H_2O_2 production; X. Z. conceived and supervised the project; Y. L. and D. O. co-wrote the draft manuscript. J. Y. Z., X. P. and X. Z. revised the finalized manuscript.

Data availability

The essential data supporting the major conclusions of this study are present in the article and the ESI.† Requests for

additional information related to the study can be directed to the authors.

Conflicts of interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Acknowledgements

This work was supported by the National Key R & D Program of China (2022YFC2105900) and the National Natural Science Foundation of China (No. U23A6005; 22178197; and 22478222). The theoretical computation part of this research was supported by the Centre for High Performance Computing, Tsinghua University.

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