



Lignin-Assisted Water Electrolysis for Energy-Saving Hydrogen Production With Ti/PbO₂ as the Anode

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Replacing the oxygen evolution reaction (OER), which is of high energy consumption and slow kinetics, with the more thermodynamically favorable reaction at the anode can reduce the electricity consumption for hydrogen production. Here we developed a lignin-assisted water electrolysis (LAWE) process by using Ti/PbO₂ with high OER overpotential as the anode aimed at decreasing the energy consumption for hydrogen production. The influence of key operating parameters such as temperature and lignin concentration on hydrogen production was analyzed. Compared with alkaline water electrolysis (AWE), the anode potential can be decreased from 0.773 to 0.303 (V vs. Hg/HgO) at 10 mA/cm² in LAWE, and the corresponding cell voltage can be reduced by 546 mV. With increasing the temperature and lignin concentration, current density and H₂ production rate were efficiently promoted. Furthermore, the anode deactivation was investigated by analyzing the linear sweep voltammetry (LSV) and cyclic voltammetry (CV) tests. Results showed that the anode deactivation was affected by the temperature.

Keywords: hydrogen, water electrolysis, lignin, electrooxidation, lead dioxide

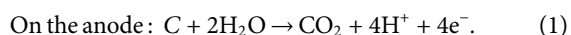
INTRODUCTION

Hydrogen is an ideal secondary energy and energy carrier (Yang et al., 2015; Lu et al., 2019; Nairan et al., 2021). The calorific value of hydrogen is 142.3 MJ/kg, which is 3 times higher than that of oil, and the theoretical combustion production of hydrogen is only water. Hydrogen is regarded as one of the cleanest fuels without carbon emissions (Wang et al., 2021a; Wang et al., 2021b; Wang and Astruc, 2021). Compared with hydrogen production by using fossil fuels, hydrogen production by water electrolysis (WE) has various advantages such as high hydrogen production purity, simple and clean process (Hosseini et al., 2015; Vandyshev and Kulikov, 2017; Wang et al., 2020). Moreover, WE has capability to couple with renewable electricity to transform surplus and fluctuating electricity into stable hydrogen energy (Liu et al., 2020a; Zhao et al., 2021). Therefore, hydrogen is the most promising energy carrier to replace fossil fuels and is an important part of the future energy structure (Hu et al., 2018; Wang and Astruc, 2021).

The high electricity consumption of hydrogen production is the main obstacle limiting the large-scale application of water electrolysis (Yang et al., 2017; Sun et al., 2021; Qian et al., 2022). The theoretical voltage of hydrogen production by water electrolysis is 1.23 V at 25°C, and the power consumption is 2.94 kWh/Nm³ (H₂) (Badwal et al., 2014). However, due to the existence of overpotential and internal resistance, and the actual operation must ensure a certain hydrogen production rate, so that the actual cell voltage reaches 2.0–2.2 V, and the actual power consumption is 4.5–5 kWh/Nm³, which is 50–70% higher than the theoretical value (Wang et al., 2014; Li et al., 2018). Anodic oxygen evolution reaction (OER) is a four-electron transfer process with slow reaction

kinetics and high overpotential (Reier et al., 2017; Li et al., 2021; Ren et al., 2021; Yu et al., 2021). 90% of the electric consumption of water electrolysis comes from the OER reaction (Ju et al., 2018; Shan et al., 2019; Verma et al., 2019).

In the biomass-assisted water electrolysis system, the OER is replaced by the oxidation reaction of biomass, which can occur at a lower potential to achieve the purpose of reducing the electricity consumption of hydrogen production (Chen et al., 2014; Zhao et al., 2021). Ideally, organic molecules are oxidized to CO₂, as shown in Eq. 1. The standard electrode potential of this reaction is 0.21 V, which is much lower than the anode potential required for the OER reaction (Yu et al., 2019). At present, a variety of substances have been used to reduce the electricity consumption for hydrogen production by assisting water electrolysis (Guo et al., 2011; Yu et al., 2018; Liu et al., 2020b). Among them, lignin is abundant and cost-effective, which has attracted the attention of researchers (Rinaldi et al., 2016). As the most abundant natural aromatic polymer, lignin is produced by plant growth up to 150 billion tons per year (Li et al., 2015; Du et al., 2020). However, lignin has not been efficiently used, which is mostly seen as low-rank fuel and pollutes the environment (Holade et al., 2020). In lignin-assisted water electrolysis, a new electrooxidation path was proposed. Lignin can be oxidized to low molecular weight aromatics (LMWA) which are high-value chemicals, such as vanillin, benzoic acid, and so on (Shao et al., 2014; Wang et al., 2015). Thus, apart from reducing the electricity consumption of hydrogen production, LAWE can also achieve the synergistic production of high-value chemicals (Song et al., 2019; Ghahremani et al., 2020). Mahtab et al. used NiCo/TiO₂ as the anode to oxidize lignin in an anion-exchange membrane electrolytic cell (NaderiNasrabadi et al., 2019). It was found that the electrochemical oxidation of lignin was more favorable than the OER reaction at the lower cell voltage when the cell voltage was 1.4–1.6 V. Once OER occurred, the oxidation reaction of lignin is in direct competition with OER. Deng et al. used polyoxometalate and FeCl₃ as the catalyst and charge-transfer agent to oxidize lignin (Du et al., 2017). With the LAWE, the electricity consumption could be 40% lower than the AWE.



In addition to precious metal or non-noble metal NiCo catalysts, cheap metal oxides such as PbO₂ were used to electrooxidize lignin (Caravaca et al., 2019; NaderiNasrabadi et al., 2019). PbO₂ has high conductivity, high catalytic oxidation capacity, and high chemical stability (Chai et al., 2014; Shao et al., 2014; Zhao et al., 2016). For example, Liang et al. used Ti/PbO₂ as the anode to achieve electrochemical oxidation of lignin (Shao et al., 2014). By analyzing the CV curves, the Ti/PbO₂ is a kind of active electrode, which means lignin degradation and OER on the anode share the same active sites. Besides, the Ti/PbO₂ could efficiently degrade lignin into low molecular weight aromatic and the mechanism was investigated. Bateni et al. used β-PbO₂/MWNT (multi-walled carbon nanotubes) as the anode, which improved the conversion rate of lignin and the rate of hydrogen evolution in the cathode, saving 20% energy compared with AWE for hydrogen production

(Bateni et al., 2019). Then the mechanism of lignin oxidation with this electrode was analyzed (Bateni et al., 2021). When lignin was added to the solution, the oxidation peak was slightly shifted to the cathodic directions in the CV curves. Vanillin and methyl salicylate were found to be the main oxidation products.

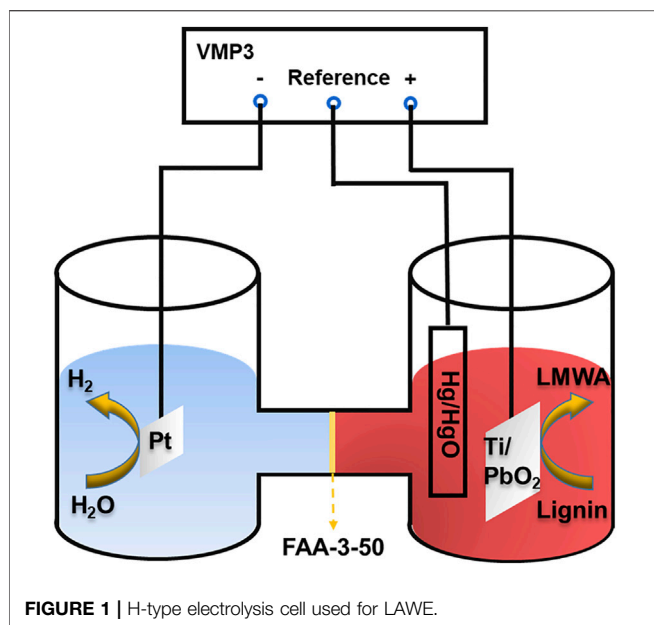
Furthermore, the electrolysis temperature is a key factor for LAWE. At low temperatures, the conversion rate of lignin and the rate of hydrogen evolution reaction (HER) is generally low (Caravaca et al., 2019; Li et al., 2020). But both of them can be promoted evidently when the temperature is increased from ambient temperature to about 100°C (Zirbes and Quadri, 2020). Temperature can change the intrinsic reaction rate of the chemical reaction and the mass transfer rate of reactants/products, so it can have a great influence on the LAWE. Caravaca et al. used Pt/C as the cathode and Pt-Ru as the anode for LAWE (Caravaca et al., 2019). When the temperature increased from 30°C to 90°C, the current density generated at the same potential increased significantly, the hydrogen production rate increased, and the onset potential decreased significantly from 0.75 to 0.45 V. Hibino et al. investigated the cellulose-assisted water electrolysis to produce hydrogen at 75–150°C (Hibino et al., 2017). It was also found that with the increase of temperature, the onset potential of HER decreased and the current density increased. Higher temperature reduced the polarization resistance of the electrode and the ohm resistance of the system. The resulting electrolysis cell could realize the onset voltage at 0.25 V and the current density of 290 mA/cm² at the cell voltage of only 1 V with the 100% current efficiency of HER.

This study aims to analyze the key operating parameters of the LAWE, such as the electrolysis temperature and the concentration of lignin. In this study, we constructed the anion exchange membrane H-type electrolysis cell to compare the LAWE with the AWE. Ti/PbO₂ and Pt were used as anode and cathode, respectively. First, the electrocatalysis performance of the Ti/PbO₂ anode was measured using the linear sweep voltammetry (LSV) and cyclic voltammetry (CV) techniques. The current density could be promoted at low cell voltage with the addition of lignin. With increasing the electrolysis temperature and lignin concentration, current density and H₂ production rate can be efficiently promoted. At last, this work analyzed the anode deactivation mechanism by electrochemical tests.

EXPERIMENTAL

Chemicals and Materials

Reagents used in this paper: sodium hydroxide (Aladdin chemical reagent Co., Ltd., 99%), sodium lignosulfonate (Aladdin chemical reagent Co., Ltd., 98%). The water used in all experiments was deionized water purified by a Millipore Milli-Q device. The cathode was Pt electrode (1.5 cm × 1.5 cm). Ti/PbO₂ electrode with the size of 3 cm × 2 cm was used as the anode, which was purchased from Xinfeng Technology Co., Ltd., and the area of a single titanium mesh hole was 0.25 cm². The interval between the two electrodes was 6 cm. The anion exchange membrane



was Fumapem FAA-3-50. Before use, the anion exchange membrane was soaked in 1 mol/L NaOH at room temperature for 24 h and then washed with deionized water. The electrochemical reaction device is an H-type electrolysis cell, and the volumes of the anode and cathode chamber were both 100 ml, shown in **Figure 1**.

Electrochemical Measurements

In all experiments, 85 ml of 1 mol/L NaOH solution was added to the anode and cathode chambers. The stirring rate was controlled at 800 r/min when carrying out chronoamperometry (CA) experiments. The linear sweep voltammetry (LSV) and cyclic voltammetry (CV) tests were carried out without stirring. Hg/HgO was used as the reference electrode. The electrochemical characteristics of the reaction were investigated by CA, LSV, and CV in a three-electrode or two-electrode system by electrochemical Workstation (Bio-Logic, VMP3). LSV was measured from 0 V vs. Hg/HgO to 1.0 V (control group 1.2 V) vs. Hg/HgO with a scan rate of 5 mV/s. The two-electrode system LSV has a measuring range from 0.6 to 1.8 V and a scan rate of 5 mV/s. CV is measured from 0 V vs. Hg/HgO to 1.0 V vs. Hg/HgO with a scan rate of 20 mV/s.

To reveal the deactivation mechanism of Ti/PbO₂ anode, LSV curves were tested at 60°C under different conditions 6 times. 1) First, 1 mol/L NaOH solution was added to the anode chamber to complete the LSV test. 2) Then, 850 mg sodium lignosulfonate was added to complete the LSV test. 3) After the CA test at 1.6 V cell voltage for 6 h, the rest remained unchanged to complete the LSV test. 4) The LSV test was completed by only replacing the deactivated Ti/PbO₂ with fresh Ti/PbO₂ which is of the same size. 5) Using deactivated Ti/PbO₂, the solution in the anode chamber was replaced with fresh 1 mol/L NaOH solution to complete the LSV test. 6) At last, the LSV test was completed by adding 850 mg sodium lignosulfonate into fresh 1 mol/L NaOH solution using deactivated Ti/PbO₂.

RESULTS AND DISCUSSION

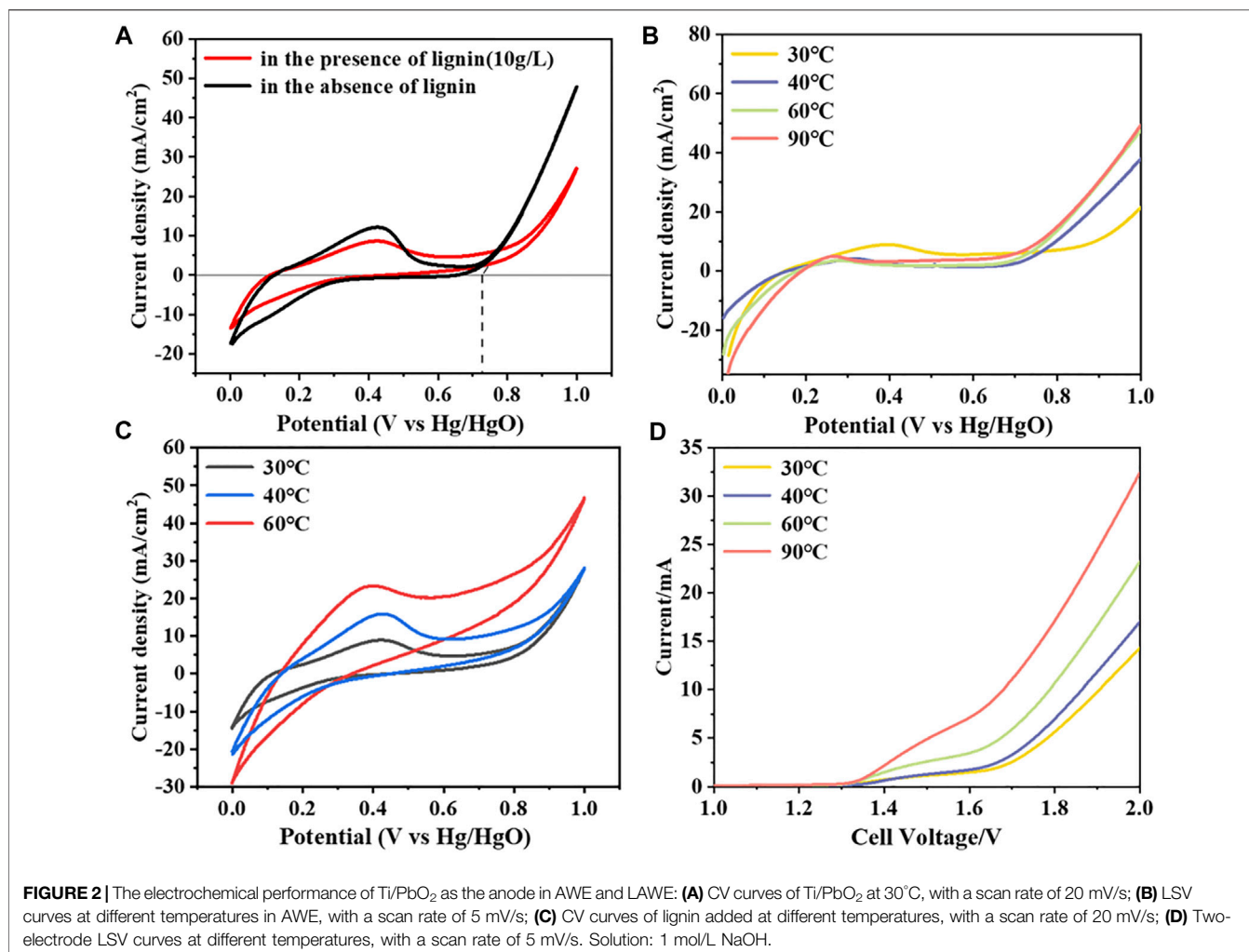
Electrochemical Properties of Ti/PbO₂

The oxidation reaction of lignin at the anode occurs at the anode-electrolyte heterogeneous interface, and the oxidation efficiency of lignin is closely related to the electrode materials. This section focuses on the electrochemical properties of Ti/PbO₂ as the anode to oxidize water or lignin. The oxidation reaction of lignin and OER are competitive, and the oxygen evolution potential (OEP) of the anode is also important to further understand the mechanism of the anodic reaction. The CV test of Ti/PbO₂ in 1 mol/L NaOH solution was performed to analyze its OEP, and the results are shown in **Figure 2A**. At 30°C without lignin, the OEP of Ti/PbO₂ was 0.73 V vs. Hg/HgO (1.65 V vs. RHE), which showed a high oxygen evolution overpotential. After adding 10 g/L lignin, no new oxidation peak appeared, the OEP increased and OER reaction kinetics decreased. But at lower anode potential (0.5–0.7 V vs. Hg/HgO), the CV curves had a higher current response, which indicated that the oxidation reaction of lignin was thermodynamically more favorable than OER. The addition of lignin inhibits the occurrence of OER because the oxidation reaction of lignin occupies the active site of oxygen evolution reaction, and the reaction kinetics of lignin oxidation is worse than that of OER, resulting in a reduced current response at higher potential (Shao et al., 2014). In consideration of this effect, the experiments involved in the following experiments should try to ensure a low anode potential to avoid the occurrence of competitive OER. **Figure 2C** shows the CV curves of lignin at different temperatures of 30°C, 40°C, and 60°C. With the increase of temperature, the oxidation peak around 0.4 V vs. Hg/HgO gradually moved to the opposite direction to the negative potential, and the peak current gradually increased, and the anode-lignin reaction activity gradually increased.

This study mainly focuses on the influence of temperature on hydrogen production rate, lignin oxidation efficiency, etc. The temperature also affects the occurrence of anodic OER. **Figures 2B,D** show the LSV curves of water electrolysis at different temperatures and the polarization curves of the two-electrode system respectively. With the increase of temperature, the OEP of Ti/PbO₂ decreased, and the current density of the same potential increased, indicating that the increase of temperature could reduce the cell voltage and improve the rate of hydrogen production. The cell voltage could decrease from 2.04 to 1.77 V at 5 mA/cm² as the temperature increased from 30°C to 90°C.

Effect of the Temperature and Lignin Concentration on the LAWE

In this study, some tests were carried out in the two-electrode system. In the LAWE, the influence of temperature and lignin concentration on hydrogen production rate was emphatically investigated. **Figure 3** shows the LSV curves at different temperatures of 30, 40, 60, and 90°C, in the meantime, to compare the LAWE and AWE. All the experiments were operated with the addition of 10 g/L lignin. Under all temperature conditions, the current density of LAWE was

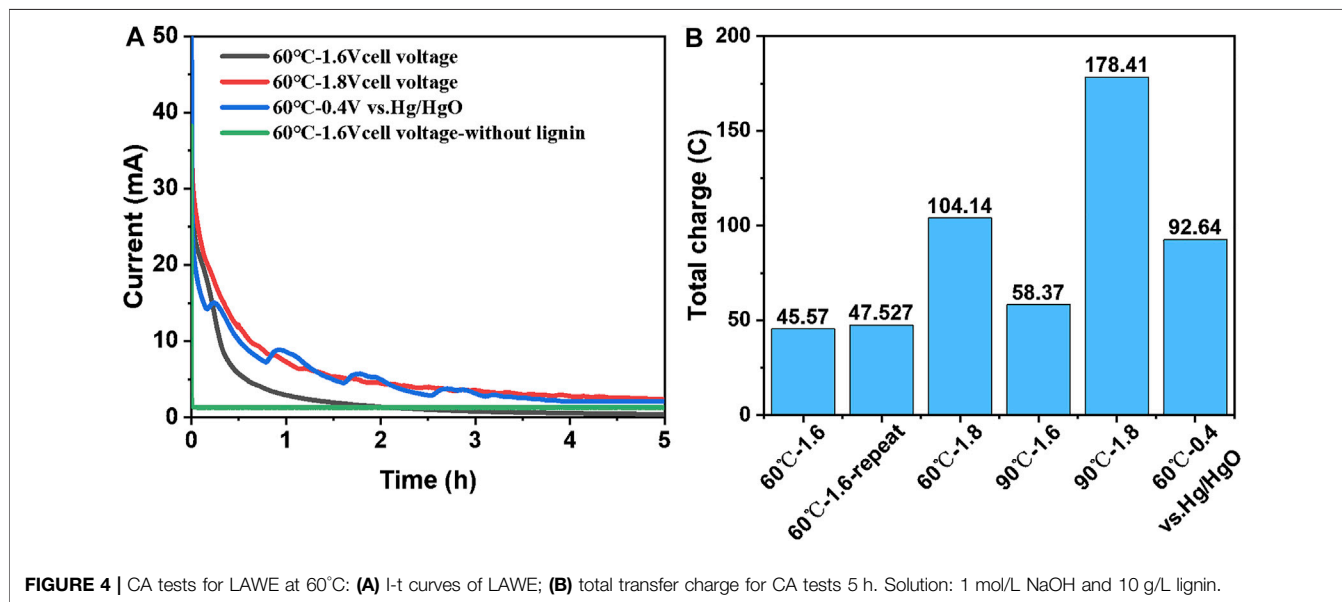
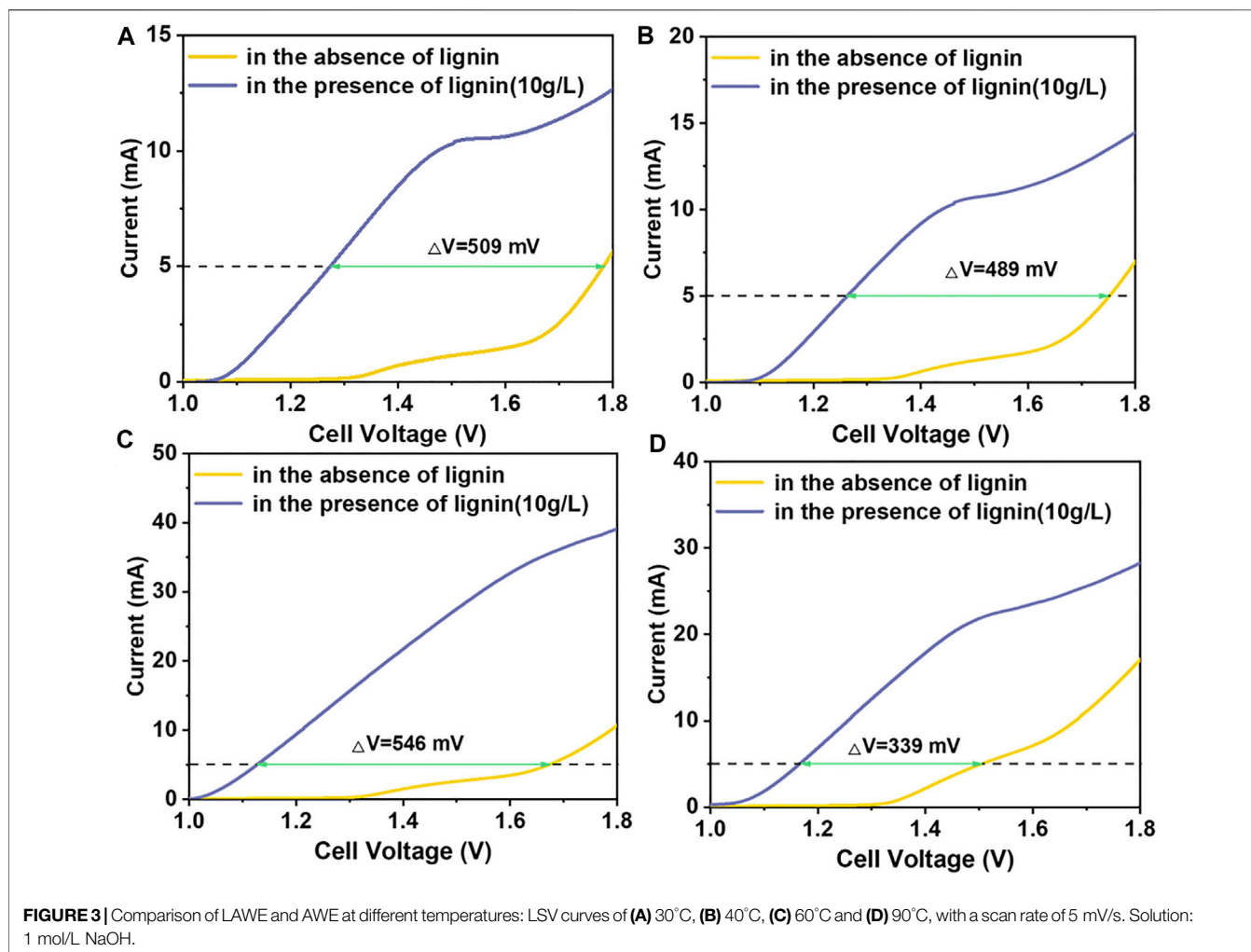


obviously higher than that of AWE at the same cell voltage. For example, when the current was 10 mA at 60°C, the cell voltage of water electrolysis for hydrogen production was 1.79 V, while it was only 1.23 V for LAWE. And when the current is 5 mA, compared the LAWE and AWE, the difference of cell voltage was 509 mV, 489 mV, 546 mV, 339 mV under the temperature of 30, 40, 60, and 90°C, respectively. The maximum difference occurred at 60°C, so the later CA tests were almost under the condition of 60°C. Therefore, it can be concluded that replacing the OER reaction with anodic lignin oxidation reaction can reduce the energy consumption of hydrogen production.

Figure 4A shows the I-t curves of LAWE under different conditions at 60°C. Except for the control test, 10 g/L lignin was added to the anode chamber. Compared with AWE, LAWE for hydrogen production had a higher current response, but with the extension of electrolysis time, there was a trend of a slow decline of current, and the anodic oxidation reaction of lignin is a diffusion control process. Possible reasons include the anode deactivation and the consumption of lignin. Detailed analysis of related reasons is given in hereafter this text. **Figure 4B** shows the total amount of charge transferred by CA tests for 5 h under different working conditions, where 60°C-1.6-repeat refers to the

repeated experiment. As the temperature or the cell voltage increased, the total amount of transfer charge increased. The cell voltage or anode potential had a greater effect on the total transfer charge. When the cell voltage increased from 1.6 to 1.8 V, the total transfer charge could be more than doubled. With the increase of cell voltage, more adsorbed hydroxyl radicals could be generated on the surface of the anode, which improves the oxidation efficiency of lignin macromolecules and the rate of hydrogen production.

To investigate the effect of lignin concentration on hydrogen production rate, LSV and CA (60°C-1.6 V) tests with different lignin concentrations were carried out. The experimental results are shown in **Figure 5**. With the increase of lignin concentration, the current response gradually increased, and the total charge transferred gradually increased. When the concentration of lignin is 1 g/L, the LSV curve is almost the same as that of water electrolysis, and the concentration of lignin is too low for the anode to effectively oxidize lignin. When the lignin concentration increased from 10 to 20 g/L, the LSV curve had little difference relative to the condition of lignin concentration increased from 1 to 10 g/L. In the absence of



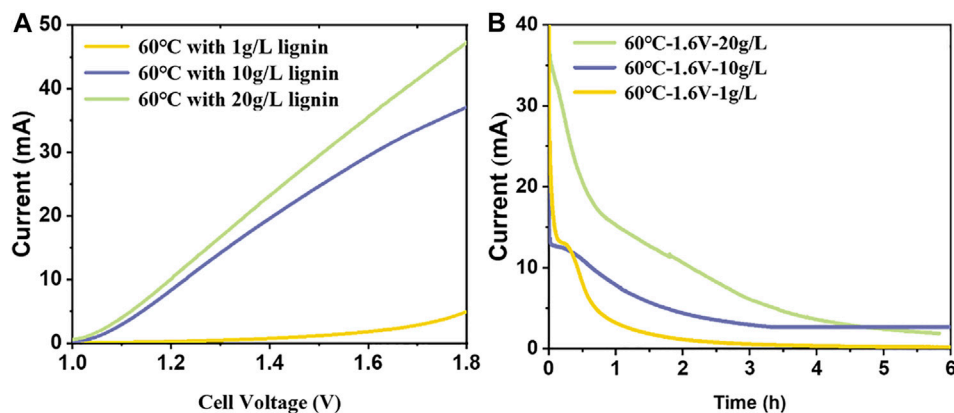


FIGURE 5 | The influence of lignin concentration on LAWE: **(A)** LSV curves, with a scan rate of 5 mV/s; **(B)** I-t curves. 60°C with different lignin concentrations. Solution: 1 mol/L NaOH.

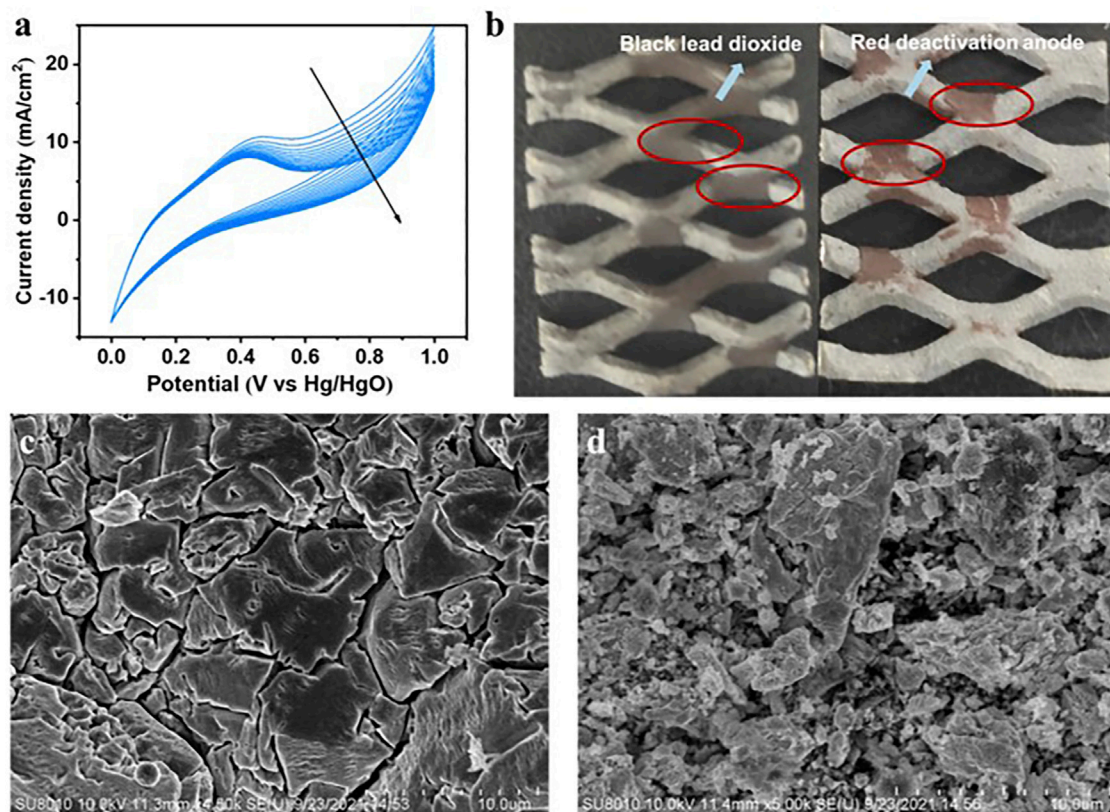


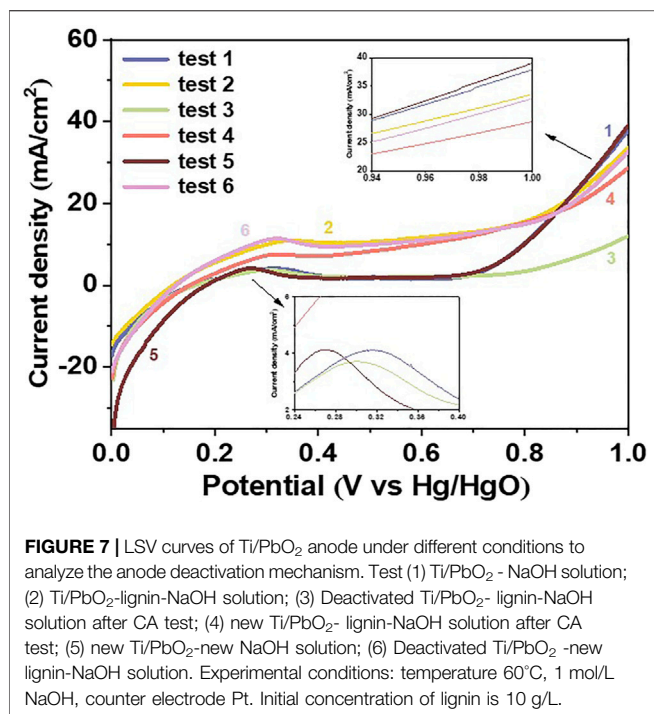
FIGURE 6 | Anode deactivation: **(A)** CV curves of the anode with the addition of lignin at 40°C, with a scan rate of 5 mV/s, 15 cycles; **(B)** deactivation anode with the red substance on the electrode surface; **(C)** SEM image of normal Ti/PbO₂ anode; **(D)** SEM image of deactivated Ti/PbO₂ anode.

stirring, the anodic reaction is controlled by diffusion, which increases the overall solution concentration and fails to replenish the anodically oxidized lignin effectively. In addition, the total transferred charges of the two were 47.53 and 185.45°C, respectively. When the concentration of lignin doubled, the total transferred charges increased about four times, which did not show

a proportional relationship, which may be related to the low oxidation degree of lignin at a low concentration.

Anode Deactivation

Anode deactivation occurs in most heterophase lignin oxidation systems. Some studies suggested that small generated molecules,



after lignin was oxidized and depolymerized, would adhere to the electrode surface (Du et al., 2020), while others suggested that the recondensation of small molecules would hinder the further occurrence of the reaction (Ezerskis and Jusys, 2001; Shiraishi et al., 2012). Some studies also used the lignin model substrate to investigate the oxidation mechanism of lignin on the anode, and gradual deactivation of the anode was also found (Beliaeva et al., 2020). **Figure 6A** shows the CV curves of the anode after the addition of lignin at 40°C, with a scan rate of 20 mV/s, which was accompanied by stirring. With the increase of CV cycle number, the current density decreased significantly and the anode deactivation occurred. Among them, CV had a high scan rate, so the current drop caused by lignin consumption could be ignored. Moreover, anode deactivation was also found in the above experiments. In the CA tests at a low temperature (30, 40°C), the current eventually dropped to 0, and the anode material was attached to red substances, as shown in **Figure 6B**. But under the temperature of 60°C and 90°C, the formation of red substance could not be observed. However, if the electrode is not cleaned in time and the temperature is naturally cooled, the surface of the electrode will also be attached with the red substance. Among them, part of the red material dissolved in water, could be cleaned by deionized water, but part of the red material would be firmly attached to the surface of the anode, even using ultrasonic cleaning could not be removed. Compared with the normal anode, the SEM image of deactivated Ti/PbO₂ showed that the film was mostly covered and original PbO₂ film could not be observed (**Figures 6C,D**).

In this paper, the mechanism of anode deactivation was investigated by electrochemical tests, as shown in **Figure 7**. LSV tests were carried out at 60°C with a scan rate of 5 mV/s. The six curves represent: 1) Ti/PbO₂ - NaOH solution; 2) Ti/PbO₂-lignin-NaOH solution; 3) Deactivated Ti/PbO₂- lignin-NaOH solution

after CA test; 4) new Ti/PbO₂- lignin-NaOH solution after CA test; 5) new Ti/PbO₂-new NaOH solution; 6) Deactivated Ti/PbO₂ -new lignin-NaOH solution. Compared tests 3) with 1) and 2), the current density of curve 3) which involved the deactivated anode and lignin-NaOH solution after CA test was even lower than that of water electrolysis. By only changing the electrode, comparing curve 4) with curve 1) and curve 2), it can be concluded that there is still a certain current density under the condition of low potential, and the lignin in the solution still has the potential to be oxidized, so that the lignin cannot be completely oxidized by one time CA test. According to the comparison of curves 1) and 6), 2) and 5), the activity of the deactivated electrode could be regenerated after replacing it in fresh NaOH or lignin-NaOH solution. No red substance was observed on the surface of the electrode during CA tests at 60°C, and before test 5) and 6) the deactivated electrode was not cleaned.

To sum up, 1) Lignin cannot be completely oxidized by a one-time CA test at 60°C due to anode deactivation; 2) The small molecules generated by lignin oxygenation depolymerization will deactivate the anode, whether or not they are polycondensation. 3) The material that can deactivate the anode is attached to the surface of the anode; 4) The material attached to the anode surface is water-soluble to a certain extent, so the activity of the anode can be regenerated by replacing the anolyte. The composition and formation path of anode products need to be further studied.

CONCLUSION

This work investigated the effects of temperature and lignin concentration on hydrogen production rate in LAWE, and the Ti/PbO₂ anode deactivation mechanism was analyzed. The main conclusions are as follows:

- 1) Ti/PbO₂ anode has high OEP, and with the rise of temperature, the OEP shows a trend of decline. The anodic oxidation of lignin occupies the active site of the OER reaction, so the addition of lignin can inhibit the OER reaction. However, by replacing the OER reaction with the oxidation reaction of lignin, the H-type electrolytic cell can produce hydrogen at a lower cell voltage. The hydrogen production rate can be effectively increased by increasing the temperature and lignin concentration.
- 2) The internal resistance (i.e., anion exchange membrane resistance, electrolyte internal resistance) of the H-type electrolytic cell used in this study is large, and the lignin consumption cannot be replenished in time. The hydrogen production rate under the two-electrode system is low. However, the anode potential of 0.303 V vs. Hg/HgO can achieve a current density of 10 mA/cm², under the condition of 10 g/L lignin and 60°C, which is far lower than the potential needed for OER reaction (0.773 vs. Hg/HgO). The development of more suitable electrolytic devices, such as the application of flow-through electrolytic cells, reducing the distance between anode and cathode, can potentially improve the rate of hydrogen production.

- 3) Temperature can affect the deactivation of the electrode, and the substance attached to the anode surface at 60°C was colorless and soluble in alkaline solution. The deactivation mechanism of the Ti/PbO₂ anode needs to be quantitatively characterized and further analyzed.

DATA AVAILABILITY STATEMENT

All datasets generated for this study are included in the article.

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AUTHOR CONTRIBUTIONS

JL: Writing-original draft; WZ: Writing-review and editing; YH: review and editing; JG: Supervision, review and editing.

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