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► **To cite this version:**

K. Beliaeva, M. Elsheref, D. Walden, F. Dappozze, A. Nieto-Marquez, et al.. Towards Understanding Lignin Electrolysis: Electro-Oxidation of a  $\beta$  -O-4 Linkage Model on PtRu Electrodes. Journal of The Electrochemical Society, 2020, 167 (13), pp.134511. 10.1149/1945-7111/abb8b5 . hal-02989635

**HAL Id: hal-02989635**

**<https://hal.science/hal-02989635v1>**

Submitted on 5 Nov 2020

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# Towards understanding lignin electrolysis: electro-oxidation of a $\beta$ -O-4 linkage model on PtRu electrodes

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**Keywords:** Lignin electrolysis,  $\beta$ -O-4 linkage model, hydrogen production

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## **Abstract**

The reaction mechanism for lignin electrolysis has been rarely studied. In a previous work, we reported the electrolysis of lignin on a Polymer Electrolyte Membrane (PEM) alkaline electrolyzer with PtRu-based anodes. Even though the performance of this technology was proven in a low range of applied potentials ( $< 1.2$  V) and reaction temperatures ( $< 90$  °C), the activity of the system was strongly hindered, leading to low H<sub>2</sub> production rates. The aim of this work is to study the main limitations of PtRu electrodes for lignin electro-oxidation. 2-Phenoxyethanol, 2-PE, has been chosen as a model molecule of the  $\beta$ -O-4 linkage, which represents  $\approx 60$  % of the lignin bio-polymer. The performed electrochemical experiments, together with the HPLC analysis of the anodic products and the thermodynamic DFT computations, suggest that the electro-oxidation of the 2-PE organic molecule is very limited and leads to the production of the carboxylic acid as the final reaction product. In addition, the electro-catalytic system was severely poisoned, probably owing to the presence of some reaction by-products. All in all, this study allows advancing one step-forward towards understanding the reaction mechanism and the main limitations of the lignin electrolysis technology in the above described system.

## 1. Introduction

Hydrogen-fuel-cells for energy storage and transportation are a potential key technology of a decarbonized energy sector [1]. The main issue nowadays remains the energy-efficient/environmentally friendly production of H<sub>2</sub>. Many efforts were performed in the last years to upgrade biomass-based by-products and wastes via electrolysis [2–8]. In these electrolyzers, H<sub>2</sub> is produced at the cathode by the electro-reduction of water ( $2 \text{ H}_2\text{O} + 2 \text{ e}^- \rightarrow \text{H}_2 + 2 \text{ OH}^-$ ), while the organic molecule is electro-oxidized at the anode ( $\text{C}_x\text{H}_y\text{O}_z + \text{OH}^- \rightarrow \text{C}_x\text{H}_y\text{O}_z + \text{CO} + \text{CO}_2 + \text{e}^-$ ), allowing for the co-production and separation of pure hydrogen and a wide variety of organic products. In addition, the production of hydrogen by these processes is potentially less energy-intensive than that for the state-of-the-art water electrolysis, since the electro-oxidation of the organic molecule (identified as the rate limiting step of the electrolysis process [9]) is thermodynamically favored compared to the oxygen evolution reaction ( $4 \text{ OH}^- \rightarrow \text{O}_2 + 2 \text{ H}_2\text{O} + 4 \text{ e}^-$ , thermodynamically allowed from  $V_{\text{cell}} = 1.23 \text{ V}$  [10]). In other words, the organic molecule behaves as a strong depolarizing agent, allowing for the production of H<sub>2</sub> in a range of electrical potentials where water electrolysis is not thermodynamically possible. Some of the most representative examples of this technology are the electrolysis of glycerol [3–5,11,12], vinasse [13] and lignin [6–8,14–19], being massive by-products of the bio-diesel production process, the fermentation process in the sugarcane industry, and the Kraft-paper industry, respectively.

With regards to lignin electrolysis, still an early-state exploratory technology, two main families of studies can be identified in literature: some solely focused on its electrochemical depolymerization, leading to the production of high value products, namely vanillin and vanillic acid, without considering the simultaneous production of hydrogen. These studies have been recently summarized in a review by Zirbes and Waldvogel [20]. Most of those works were

performed in a high range of electrical potentials ( $> 1.5$  V, sometimes as high as 12 V [21] and 15 V [22]) where the electro-oxidation of lignin ( $\text{lignin} + \text{OH}^- \rightarrow \text{lignin}_{\text{ox}} + \text{e}^-$ ) competes with the oxygen evolution reaction. At these very harsh conditions, reactive oxygen species might also be generated (e.g., hydroxyl radicals) that chemically oxidize lignin, accelerating the depolymerization. The main reason to work in such drastic energy-demanding conditions is most likely attributed to the challenge to cleave the C-C bonds of organic molecules in at low electrochemical potentials at temperatures below 90 °C. Analogous reports pertain to, for instance, for the electro-oxidation of ethanol [23–25] and glycerol solutions [4,5]. Nevertheless, several studies focused on  $\text{H}_2$  as the main product of interest [6–8,14–19]. This process is potentially less energy-intensive, considering that the depolarizing effect of lignin allows producing  $\text{H}_2$  from electrical cell potentials as low as 0.2 V. However, the valorization of the lignin electro-oxidation products and the yield of  $\text{H}_2$  might be limiting, considering that the depolymerization (i.e. the cleavage of C-C bonds) of lignin under such conditions is unlikely.

In a previous study [17], we reported the use of a PtRu//Fumapem<sub>membrane</sub> ( $\text{OH}^-$  conductor)//Pt cell (anode//electrolyte//cathode) for the electrolysis of lignin aiming at the production of pure  $\text{H}_2$  in continuous-flow in Polymer Electrolyte Membrane (PEM) reactors. Even though its performance was demonstrated for a wide range of reaction temperatures (up to 90 °C) upon the application of electrical cell potentials  $< 1.2$  V, the current densities obtained (and therefore the  $\text{H}_2$  production) were still rather low. It suggests very sluggish kinetics for the lignin electro-oxidation reaction under these conditions.

Most studies on lignin electrolysis (aiming either for the production of high value chemicals or  $\text{H}_2$ ) deal with the use of different electrode materials to demonstrate the feasibility of this technology as a potential alternative to valorize a biomass-waste resource. However, the reaction path and the mechanism for lignin electro-oxidation have been rarely studied on account of the

complexity of the lignin bio-polymer. While the formula of lignin is variable depending on the source, each of its monomers consists of one oxygenated aromatic unit, with hydroxyl-benzene, guaiacyl (4-alkyl-2-methoxyphenol), and syringyl (4-alkyl-2,5-dimethoxyphenol) units. The main inter-unit linkages are called  $\beta$ -O-4,  $\beta$ - $\beta$ ,  $\beta$ -5,  $\beta$ -1, etc. Among these linkages, the  $\beta$ -O-4 is the most abundant (providing more than half of the linkage structures) [26] and probably the most important substructure in lignin, affecting both its chemical and physical properties.

The aim of this study is, therefore, to use the simplest possible model compound (simplifying the identification of the reaction products) for the quintessential  $\beta$ -O-4 linkage to better understand the main limitations of the lignin electro-oxidation process on PtRu-based electrodes at low temperatures ( $< 90$  °C) and under the application of electrical potentials where water electrolysis is not possible ( $V_{\text{cell}} < 1.23$  V). *2-Phenoxyethanol (2-PE)*, with its aryl and alkyl ether function, was used as model molecule.

This study was performed on Polymer Electrolyte Membrane (PEM) reactors. One may think that conventional 3-electrode cells are better suited for this kind of comprehensive studies. However, PEM electrochemical cells offer several unique features, including: i) anode and cathode are properly separated by a polymeric membrane, and therefore anodic and cathodic electro-catalytic processes can be studied individually, ii) the catalyst/reactant contact is optimized by the use of flow-channels in the PEM architecture, iii) PEM reactors represent a more realistic electrochemical reactor in view of further practical applications, being a compact device easy to scale-up, iv) anode and cathode are separated by a short distance (a membrane of a few  $\mu\text{m}$  thickness), leading to a low ohmic resistance, and v) PEM cells allow to work at higher temperatures, since some reference electrodes commonly used in 3-electrode cells (e.g. Hg/HgO) are not stable over 60 °C. Eventually, the PEM cell could be equipped with an additional

compartment for a reference electrode [27,28]. Since in this study we pursue to solely analyze the chemical and electrochemical processes occurring at the anode (PtRu-based catalyst), we believe that the use of PEM reactors is the right choice. High Performance Liquid Chromatography (HPLC) analysis of the anodic product solution was performed and first-principles computations using Density Functional Theory (DFT) were used to corroborate the proposed reaction mechanism.

## 2. Experimental

As in our previous study [17], we used commercial electrodes (FuelCellStore ®) and membranes. Briefly, the anode consisted of a bimetallic Pt-Ru catalyst ( $2 \text{ mg cm}^{-2}$ , 50 % Pt-50 % Ru *wt/wt*, unsupported) impregnated on Carbon cloth (with a  $410 \text{ }\mu\text{m}$  thick microporous layer). The cathode was composed of a Pt/C catalyst ( $0.2 \text{ mg cm}^{-2}$ , 20 % *wt* Pt) impregnated on a similar Carbon cloth. Both electrodes had a geometric surface area of  $5 \text{ cm}^2$ . An alkaline ( $\text{OH}^-$ ) conductor polymeric membrane (Fumapem FAA-3-50 ®) of  $45\text{-}50 \text{ }\mu\text{m}$  thickness was used to separate anode and cathode. Prior to use, the membrane was pretreated in an aqueous solution of 1 M KOH for 24 hours at room temperature, to exchange its bromide functional groups ( $\text{Br}^-$ ) into  $\text{OH}^-$  groups. All the experiments were performed in a commercial Polymer Electrolyte Membrane (PEM) electrolysis device (Dioxide materials ®). The main components of the cell (anode/membrane/cathode) above described were separately introduced between two Teflon gaskets to ensure a proper sealing, without previous pre-assembly. Ni-based bi-polar plates with parallel grooves (flow channels) were used as current collectors.

The electrolysis experiments were performed in recirculation mode. The anode was fed with an alkaline aqueous solution of the model molecule (Volume of the solution: 20 mL,  $10 \text{ g L}^{-1}$  of 2-PE, 1 M KOH,  $1.3 \text{ mL min}^{-1}$ ), and the cathode was supplied with a 1 M KOH solution (Volume

of the solution: 20 mL, 1.3 mL min<sup>-1</sup>). Several experiments were performed by feeding alkali (Kraft) lignin supplied by Sigma Aldrich (20 mL, 10 g L<sup>-1</sup>, 1 M KOH, 1.3 mL min<sup>-1</sup>) or a 1 M KOH aqueous solution (in the absence of any organic molecule) to the anode for comparison purposes. Anode and cathode liquid flow-rates were controlled with a peristaltic pump. A potentiostat-galvanostat (Orignalys ®) was used for the polarization of the cell.

High-Performance Liquid Chromatography (HPLC, Agilent Technologies) allowed analyzing the anodic products after 2-PE electro-oxidation. A Nucleosil C18 column was used (Macherey Nagel, 250 x 4.6 mm, Particle size = 5 µm, Pore size = 100 Å), with “eighteen” being the length of carbon chain bonded on silica particles, suitable for analysis of organic compounds. All HPLC analysis were performed at 40 °C. The mobile phase was composed of 40 % methanol and 60 % Acidified Water (55 µL H<sub>3</sub>PO<sub>4</sub> in 1 L of H<sub>2</sub>O, pH = 3). A PDA detector (210 nm) was used.

The first-principles computations were performed using Density Functional Theory (DFT) as implemented in the Gaussian16 program package [29]. All geometries are fully optimized at the M06-2X/def2-TZVPP level of theory [30]. The free energy corrections are evaluated using default settings. Single-point energy evaluations with the SMD solvation [31] model have been used to correct the free energies for solvation effects. In order to closely match the experimental pK<sub>a</sub> values of the alcohols and acids present in the reaction network, we have applied an energy correction to charged species. The correction is based on a linear regression of the computed and experimental pK<sub>a</sub> values of 7 molecules (alcohols and acids, see Excel Sheet in the supplementary materials).

### **3. Results and discussion**

First of all, we studied the performance of the PEM electrolysis cell at 80 °C, by feeding the organic model molecule (2-PE), lignin or water to the anodic compartment. For every molecule studied, an in-situ cyclic voltammetry experiment was performed (10 cycles, sweep scan 10 mV



$s^{-1}$ ,  $V_{\text{cell}} = 0 - 1 \text{ V}$ ), followed by a chrono-amperometry upon the application of a constant cell potential  $V_{\text{cell}} = 1 \text{ V}$  for 30 minutes. Fig. 1a shows the 10<sup>th</sup> cycle of the cyclic voltammetry experiments. For water electrolysis, a weak anodic (at 1 V during the forward scan) ~~and cathodic~~ ( ~~$\sim 0.9 \text{ V}$  during the backward scan~~) peak could be observed. As discussed in our previous study [17], this feature can be attributed to the passivation (oxidation) of the PtRu anodic electro-catalyst. However, when lignin was introduced in the anodic compartment of the electrolyzer, a drastically different trend was observed. With an onset potential  $\sim 0.65 \text{ V}$ , lignin undergoes a significant electro-oxidation during the anodic forward scan, which seems to be irreversible, since only a very small peak was obtained during the backward scan. These results were in good agreement with those obtained in our previous study [17], with a maximum current density at 1 V of  $\sim 5 \text{ mA cm}^{-2}$ , which confirms the reproducibility of results with this experimental setup.

The most interesting part of this figure was obtained for the electrolysis of the 2-PE model molecule. With an onset cell potential at only  $\sim 0.25 \text{ V}$ , the molecule undergoes an important electro-oxidation, showing a first peak at  $\sim 0.6 \text{ V}$ . The intensity of this peak will be called " $I_{f1}$ " from now onwards. A second ascending trend could be observed at  $V_{\text{cell}} > 0.8 \text{ V}$  during the forward scan, leading to a peak at the highest applied potential (1 V). The intensity of this peak will be called " $I_{f2}$ ". During the backward scan, a first current decrease could be observed, followed by a new oxidation peak at  $V_{\text{cell}} \sim 0.5 \text{ V}$ . The intensity of this peak will be called " $I_b$ ". Similar trends were observed for the electro-oxidation of simpler organic alcohols, such as methanol [32], ethanol [23,33] and glycerol [34,35] on Pt-based electro-catalysts. However, the interpretation of such trend in cyclic voltammetry is still under debate. For instance, for methanol, as suggested by Goodenough's research team [36], both the second peak during the forward scan and the peak during the backward scan could be attributed to the oxidation of residual intermediate carbon species formed at lower potentials during the anodic scan. However, other

studies attribute them to the oxidation of freshly chemisorbed methanol [32]. For ethanol, Wang et al. [23] suggested that the first peak during the forward scan (on Pt electrodes) could be attributed to the formation of acetaldehyde (mostly) and acetic acid, while at higher potentials the electro-oxidation of the alcohol seemed to be hindered by the formation of PtO. During the backward scan, in the aforementioned ethanol system, the electro-oxidation reaction competes with the PtO reduction, leading to a first current decrease followed by the formation of a second oxidation peak (as we observed in our experiments), attributed again to the formation of acetaldehyde and/or acetic acid. The presence of a small redox couple, assigned to  $\text{Pt}^{\text{x+}}/\text{Pt}$ , was also observed in a similar range of applied potentials (although at temperatures over 200 °C) in a recent study dealing with the electro-oxidation of methane in PEM reactors [37].

To get more insights into the nature of the forward and backward peaks, a new cyclic voltammetry experiment was performed under the same reaction conditions, but in a smaller range of electrical potentials ( $V_{\text{cell}} = 0\text{-}0.65$  V, Fig. S1). Considering that the backward oxidation peak ( $I_b$ ) did not appear under such conditions, we can suggest that the peak observed during the cathodic scan in Fig. 1 was most likely due to: i) the electro-oxidation of some species produced during the anodic scan upon the application of electrical potentials  $> 0.6$  V ( $I_{f2}$ ), or ii)  $I_{f2}$  could be the result of the partial electro-oxidation of species produced during the  $I_{f1}$  at lower potentials, and  $I_b$  could be due to the continued electro-oxidation of such species.

Some researchers suggested that, if  $I_b$  is a consequence of the electro-oxidation of some reaction intermediate produced during the forward scan (as it seems to be the case of the present study), the peak ratio  $I_{f1}/I_b$  could be related to a tolerance/poisoning factor [32,34,38]. Therefore, high  $I_{f1}/I_b$  factors indicate efficient release of intermediate (potentially poisoning) species from the anodic active sites. According to the data shown in Fig. 1a,  $I_{f1}/I_b \sim 3$ . It suggests that an important

amount of the intermediate species, but not all of them, would be released to the reaction environment. Hence, some degree of poisoning of the anodic catalyst could be expected.

After the cyclic voltammetry experiment, a chrono-amperometry was performed under the application of a constant cell potential of  $V_{\text{cell}} = 1$  V. Based on the voltammetry, the maximum current density was obtained under these conditions for all molecules. Fig. 1b shows the trends for water, lignin and 2-PE electrolysis. Hydrogen production at the cathode by the electro-reduction of water was obtained by direct calculation using the Faraday's law (where  $nH_2 = Ix(2F)^{-1}$ , being  $nH_2$  the  $\text{mol}_{H_2} \text{ s}^{-1}$ ,  $I$  the obtained current upon the application of 1 V, and  $F$  the Faraday's constant). In general terms, we could observe, as expected, that the highest performance was obtained for the electrolysis of the organic model molecule, followed by that of lignin and then water. However, the current densities obtained were much lower compared to those of the cyclic voltammeteries. It suggests a significant deactivation of the system under medium-term reaction conditions, which could be attributed to the strong chemisorption of some of the reaction intermediates/products, as previously discussed.

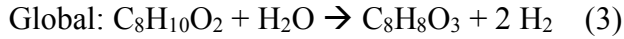
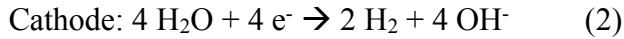
Considering the results obtained for the electrolysis of the 2-PE model molecule, together with previous works regarding the electrolysis of  $C_{2+}$  organic alcohols (e.g. ethanol [23,33,39,40] and glycerol [3–5,41,42]) on Pt-based electrodes, we can safely assume that: i) cleaving C-C bonds is very unlikely at low reaction temperatures (25-80 °C) and applied polarizations ( $V_{\text{cell}} = 0-1$  V), ii) the electro-oxidation of the terminal alcohol linkage will most likely lead to the production of aldehyde and acidic functional groups, and iii) adsorbed intermediate/final species might exhibit a detrimental effect on the performance of the anodic catalyst.

In order to get more insights into the electro-oxidation process, we studied the influence of the reaction temperature on: i) the electrochemical performance of the global electrolysis system, and ii) the anodic products owing to the 2-PE electro-oxidation. Therefore, at each temperature, a

cyclic voltammetry experiment (10 cycles, sweep scan  $10 \text{ mV s}^{-1}$ ,  $V_{\text{cell}} = 0 - 1 \text{ V}$ ) was performed, followed by a chrono-amperometry under the application of a constant cell potential  $V_{\text{cell}} = 1 \text{ V}$ . The accumulated anodic products were analyzed by HPLC.

Figs. 2a and b show, respectively, the 10<sup>th</sup> cycle of the cyclic voltammetry, and the current-potential curves at each temperature. Both figures demonstrate that the electro-oxidation of the organic molecule was negligible below  $50 \text{ }^\circ\text{C}$ . Similar results were obtained in our previous study for lignin electrolysis [17]. Nevertheless, as expected, an increase in the reaction temperature from  $50 \text{ }^\circ\text{C}$  to  $80 \text{ }^\circ\text{C}$  gave rise to an important and gradual increase of the produced current (and therefore the flow of pure  $\text{H}_2$  generated at the cathodic compartment of the electrolyser). In addition, Figure S2 shows the Arrhenius plots ( $\ln r_{\text{H}_2}$  vs.  $1/T$ ) of the 2-PE electrolysis process by collecting the  $\text{H}_2$  production rates after 30 minutes (Fig. 2b) at each temperature under the application of  $1 \text{ V}$ . Since the electro-oxidation of organic molecules has been considered in previous studies as the rate limiting step of the overall electrolysis process, we can attribute the activation energies observed to the electro-oxidation of 2-PE. The apparent activation energy was calculated from the slope of the straight line and was found to be  $34 \text{ kJ/mol}$ . This value is of the same order compared to the values found in previous studies about lignin electro-oxidation on  $\text{TiO}_2$ - [43] and  $\text{IrO}_2$ - [44] based catalysts, and to those reported for the electro-oxidation of methanol on Pt-based electrodes [45,46]. Hence, 2-PE electro-oxidation kinetics seem to share the characteristics for lignin electro-oxidation, validating its choice as a relevant model molecule, even though the raw CV data differs significantly.

On the other hand, as observed in Fig. 2c, the main product obtained in the anode after those experiments was phenoxy-acetic acid (PAA), with some traces of phenol. The production of both compounds increased with the reaction temperature. We suggest that PAA is produced from 2-PE following the electrochemical reactions:



Therefore, for every mol of PAA produced at the anode, 2 mol of pure H<sub>2</sub> should be produced at the cathode. According to the results of Fig. 2b, and using the Faraday's law, the total amount of pure H<sub>2</sub> produced during the chrono-amperometry experiment ( $n_{\text{H}_2 \text{ CA}}$ , in mol) could be calculated at each reaction temperature as:

$$n_{\text{H}_2 \text{ CA}} = \int I \times (2F)^{-1} dt \quad (4)$$

and according to reaction (3), the total amount of H<sub>2</sub> produced after the cyclic voltammetry experiment followed by the chrono-amperometry ( $n_{\text{H}_2 \text{ CV} + \text{CA}}$  in mol, Figs. 2 a-b) could be obtained as:

$$n_{\text{H}_2 \text{ CV} + \text{CA}} = 2 \times n_{\text{C}_8\text{H}_8\text{O}_3} \quad (5)$$

Fig. 2d shows the H<sub>2</sub> production according to eqs. 4 and 5. As expected, the production of hydrogen computed from the total production of PAA was of the same order as obtained based on the integration of the current. Nevertheless, the PAA-based estimates are slightly which might be attributed to the amount of hydrogen produced during the cyclic voltammetry experiment together with the experimental accuracy of the HPLC analysis. However, the close agreement between the two estimates excludes any other major electrochemical reaction to have occurred. According to these experiments, the following conclusions could be obtained: i) the main product for 2-PE electro-oxidation is a result of the oxidation of the OH- terminal linkage of the molecule into the carboxylic acid, ii) C-C bonds, as expected did not seem to cleave upon our working

conditions in the PtRu anode, and iii) a small cleavage of the C<sub>β</sub>-O linkage led to the production of phenol.

Fig. S3 shows a cyclic voltammetry experiment (10<sup>th</sup> cycle, sweep scan 10 mV s<sup>-1</sup>, 2-PE 10 g L<sup>-1</sup> in 1 M KOH, 150 mL) performed in a conventional 3-electrode cell at 55 °C. The same PtRu commercial electrode (supported on a carbon cloth with a 410 μm thick microporous layer, 2 x 2 cm<sup>2</sup>) was used as anode, and a Pt mesh (2 x 2 cm<sup>2</sup>) and Hg/HgO were used as counter and reference electrodes, respectively. We obtained a very similar trend in a range of potentials ( $\Delta V$  vs Hg/HgO = -0.8 – 0.1 V) compatible with the previously shown experiments in the PEM cell ( $V_{\text{cell}} = 0-1$  V). These results corroborate that the experiments performed in the PEM cell are representative and well suited for a comprehensive study of the electrochemical oxidation of 2-PE as a lignin model molecule. In addition, as previously highlighted in the introduction section, the PEM device allows to solely analyze the products obtained at the anode, avoiding any potential side-reaction on the cathode (as may happen in conventional 3-electrode cells).

Fig. 3 shows, for the same experiments described on Fig. 2a (cyclic voltammetry on PEM reactor) the 2<sup>nd</sup>, 5<sup>th</sup> and 10<sup>th</sup> cycle at each reaction temperature. At all the reaction temperatures studied we could observe a significant decrease in the performance of the electrolyzer. According to previous studies with simpler alcohol molecules, the deactivation of the system could be attributed to the poisoning of the anodic catalyst, since the electro-oxidation reaction is considered as the rate determining step in the overall electrolysis process [9]. For instance, in previous studies for ethanol/bio-ethanol electrolysis [39,40], we found that PtRu anodic materials suffered an important deactivation. In view of the results obtained in this study, we could suggest a deactivation of the PtRu electrocatalyst either on account of the production of the PAA

carboxylic acid as a final product, or some reaction intermediates leading to the production of PAA.

To study the poisoning effect of PAA on the anodic catalyst, a fresh similar Membrane Electrode Assembly (MEA) was prepared and tested under different conditions. Fig. S4 shows a cyclic voltammetry experiment (2<sup>nd</sup>, 5<sup>th</sup> and 10<sup>th</sup> cycle) at 80 °C by feeding different solutions to the anode: a) 2-PE (10 g L<sup>-1</sup>, 10 cycles, sweep scan 10 mV s<sup>-1</sup>, V<sub>cell</sub> = 0 – 1 V), b) 10 g L<sup>-1</sup> 2-PE + 2000 ppm PAA (10 cycles, sweep scan 10 mV s<sup>-1</sup>, V<sub>cell</sub> = 0 – 1 V), c) PAA (10 g L<sup>-1</sup>, 10 cycles, sweep scan 10 mV s<sup>-1</sup>, V<sub>cell</sub> = 0 – 1 V) and d) KOH (1 mol L<sup>-1</sup>, 10 cycles, sweep scan 10 mV s<sup>-1</sup>, V<sub>cell</sub> = 0 – 1 V). It is worth noting that, even though the electrolysis of 2-PE (Fig. S4a) followed a similar trend than that observed in Figs. 1-3, the current densities seemed to be slightly higher, probably owing to the use of a fresh MEA. In this figure, it could be clearly observed that: i) the addition of 2000 ppm of PAA to the 2-PE solution (Fig. S4b) did not have an important effect on the electrochemical performance of the system compared to that for 2-PE electrolysis, and ii) PAA did not undergo a significant electro-oxidation in the studied potential range (Fig. S4c), and therefore it seemed to be a final product of the 2-PE electro-oxidation. All in all, PAA itself did not seem to poison the catalytic performance of the anodic PtRu catalyst. The poisoning species might also be formed from the  $\beta$ -hydrogen oxidation of 2-PE, which might lead to coking-like residues on the electrode.

Fig. 4 shows the postulated reaction pathways and thermodynamic profiles according to the DFT calculations. We can differentiate between the hydration reactions (in blue) and the oxidation reactions (in red). The hydration reactions lead to the C-O bond dissociation of 2-PE and thus open the door to a more complete oxidation. However, their thermochemistry does not depend on the applied electrochemical potential, as opposed to the oxidation reactions, where the application

of an electrochemical potential higher than 0 V (vs RHE) reduces the free energies of reaction accordingly. For instance, reaction B, which is non-spontaneous ( $\Delta G > 0$ ) at 0 V becomes exothermic starting from 0.3 V, in good agreement with the onset potential observed in the electrochemical tests for 2-PE electrolysis. It is noteworthy that all the aldehydes involved in the reaction network are unstable and will readily be oxidized to the corresponding acid in alkaline conditions. Hydration reactions leading to the production of phenol are mildly exothermic but are likely to require a significant activation energy and thus favored at higher temperatures. However, as opposed to the oxidation reactions, they might also occur in the bulk solution (i.e., not only close to the electrode). This could explain the traces of phenol observed (Fig. 2c) on account of the thermodynamically favored C $\beta$ -O cleavage of the 2-PE molecule (Path A) or the PAA molecule produced under reaction conditions (Path J).

According to the electrochemical experiments and the thermodynamic calculations, we propose the following preliminary model: In a first step (path B), the 2-PE model molecule would be electro-oxidized (thermodynamically favored from 0.3 V) to the aldehyde function. Then, the thermodynamically unstable aldehyde gets further oxidized into PAA (path E). In view of the results obtained, and in good agreement with previous studies about ethanol electro-oxidation, we could argue that the first peak observed ( $I_{f1}$ ) during the cyclic voltammetry experiments with 2-PE (Fig. 1a, 2a and 3) could be attributed to the overlapping production of both, the aldehyde and PAA molecules. Even though the PAA itself did not seem to poison the PtRu anodic catalyst (Fig. S4), at higher potentials, the metallic surface might be partially blocked by adsorbed carboxylate species via a process like  $R-COO^- \rightarrow RCOO_{ad} + e^-$ . The temperature dependence (featureless at 30 °C, and gradually increased performance up to 80 °C, Fig. 2) might also suggest that the formation of the aldehyde is a chemically activated two-step process under these



conditions, i.e., the C-H hydrogen oxidation is associated with a non-negligible barrier. In this scenario, the first peak ( $I_{f1}$ ) would correspond to the first oxidation of the alcohol (or alcoholate), leading to a R-CH<sub>2</sub>-O<sub>ad</sub> bound species, while the second peak ( $I_{f2}$ ) would correspond to the generation of the aldehyde and PAA. This could explain why stopping the cyclic voltammetry at 0.6 V (Fig. S1) made the backward peak ( $I_b$ ) disappear. In any case, the thermodynamic considerations are fully consistent with PAA being the final oxidation product, in good agreement with the results observed in Fig. S4.

This study allowed advancing one step-forward toward understanding the electro-oxidation of one of the most common units in lignin: the quintessential  $\beta$ -O-4 linkage. Extrapolating these results, we can conclude that cleaving the C-C bonds in the lignin bio-polymer seems very unlikely at low potentials (< 1.2 V) and reaction temperatures < 90 °C, and the electrochemical activity of PtRu-based catalysts is mainly limited to the electro-oxidation of the terminal OH-bonds into aldehyde and carboxylic acid functional groups. In addition, the anodic electro-catalytic performance suffered in a significant manner on account of the poisoning of the catalytic material, most likely due to the strong chemisorption of some reaction intermediate species. All in all, the activity for lignin electro-oxidation under such conditions in PtRu catalysts is strongly hindered and limited, leading to an overall low performance of the electrolyzer, as we demonstrated in our previous study [17]. In order to promote the lignin electrolysis technology as an efficient/environmentally friendly route for H<sub>2</sub> production, understanding the limitation of anodic materials is crucial to enhance its efficiency. Future studies will be performed to understand the reaction mechanism for the electro-oxidation of model molecules of the  $\beta$ -O-4 linkage on other catalytic materials reported in literature (e.g. Ni and Fe [7]) under slightly more severe reaction conditions (i.e., higher reaction temperatures and electrical potentials) that should

allow for some cleavage of the C-C bonds, albeit the benefit compared to water electrolysis might be lost at these potentials.

Lignin is a tridimensional bio-polymer that is considered as a waste in the Kraft paper-making industry, with an annual production over 50 million tons. Lignin is usually incinerated to produce heat. However, the incineration is accompanied with the generation of dangerous emissions. Nevertheless, a small part of lignin waste is nowadays valorized into valuable chemicals by pyrolysis, gasification, catalytic oxidation and reduction. In this sense, we believe that the electrolysis of lignin could be a very competitive technology and will play a key role in the near future, and therefore further efforts should be carried out in order to find economic and active materials and to understand their main limitations in view of its practical implementation.

#### **4. Conclusions**

This study allowed, for the first time, to understand the main limitations of PtRu electrodes for the electro-oxidation of lignin in a range of low electrical potentials ( $V_{\text{cell}} = 0-1$  V) and reaction temperatures ( $< 90$  °C). The following conclusions could be summarized as:

- The electrolysis of a model molecule of the quintessential  $\beta$ -O-4 linkage present in lignin, 2-Phenoxyethanol (2-PE), follows a similar electro-oxidation trend than that observed for simpler alcohols, e.g., methanol, ethanol and glycerol.
- The analysis of the anodic electro-oxidation products depicted the production of phenoxyaceticacid (PAA) as the main product. In addition, the performance of the electrolysis system suffered from a significant deactivation with time.

- Thermodynamic DFT calculations suggest an electro-oxidation path where the 2-PE model molecule would be oxidized to the aldehyde, followed by its further oxidation into the carboxylic acid (PAA).
- All in all, extrapolating the results obtained in this study, the lignin electrolysis process is strongly limited by the lignin electro-oxidation reactions, mainly due to 2 reasons: i) depolymerization of lignin is very unlikely under the studied conditions (C-C cleavage is strongly hindered), and ii) the adsorption of reaction intermediates and products led to a strong deactivation of the anodic catalyst.

### **Acknowledgment**

The authors gratefully acknowledge the “Institut de Chimie de Lyon” (ICL, France) and the “Cellule Energie du Centre National de la Recherche Scientifique” (CNRS, France) for the financial support of this work. The authors also thank the SYSPROD project and AXELERA Pôle de Compétitivité for financial support (PSMN Data Center). Dr. A. Nieto-Marquez acknowledges IRCELYON and ETSIDI-UPM for financing a mobility grant in the frame of this work.

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