



HAL
open science

Towards a sustainable technology for H-2 production: Direct lignin electrolysis in a continuous-flow Polymer Electrolyte Membrane reactor

A. Caravaca, W. Eunice Garcia-Lorefice, S. Gil, A. de Lucas-Consuegra, P. Vernoux

► To cite this version:

A. Caravaca, W. Eunice Garcia-Lorefice, S. Gil, A. de Lucas-Consuegra, P. Vernoux. Towards a sustainable technology for H-2 production: Direct lignin electrolysis in a continuous-flow Polymer Electrolyte Membrane reactor. *Electrochemistry Communications*, 2019, 100 (–), pp.43-47. <10.1016/j.elecom.2019.01.016>. <hal-02099436>

HAL Id: hal-02099436

<https://hal.science/hal-02099436v1>

Submitted on 21 Oct 2021

HAL is a multi-disciplinary open access archive for the deposit and dissemination of scientific research documents, whether they are published or not. The documents may come from teaching and research institutions in France or abroad, or from public or private research centers.

L'archive ouverte pluridisciplinaire HAL, est destinée au dépôt et à la diffusion de documents scientifiques de niveau recherche, publiés ou non, émanant des établissements d'enseignement et de recherche français ou étrangers, des laboratoires publics ou privés.



Distributed under a Creative Commons CC BY-NC 4.0 - Attribution - Non-commercial use - International License

Towards a sustainable technology for H₂ production: Direct lignin electrolysis in a continuous-flow Polymer Electrolyte Membrane reactor

Angel Caravaca^{a}, Wendy Eunice Garcia-Lorefice^{a, b}, Sonia Gil^a, Antonio de Lucas-Consuegra^b,
Philippe Vernoux^a*

*^aUniversité de Lyon, Institut de Recherches sur la Catalyse et l'Environnement de Lyon, UMR 5256,
CNRS, Université Claude Bernard Lyon 1, 2 avenue A. Einstein, F-69626 Villeurbanne, France*

*^bDepartment of Chemical Engineering, School of Chemical Sciences and Technologies, University of
Castilla-La Mancha, Avenida Camilo José Cela 12, 13005 Ciudad Real, Spain*

Keywords: Hydrogen production; lignin valorization; Polymer Electrolyte Membrane electrolyser; biomass electrolysis

*Corresponding author: angel.caravaca@ircelyon.univ-lyon1.fr

Abstract

We have performed, for the very first time in literature, the production of pure H₂ via “electrolysis of lignin solutions in continuous-flow mode in a Polymer Electrolyte Membrane (PEM) reactor”. A Pt-Ru//Fumapem (OH⁻ conductor)//Pt/C (Anode//Anion Exchange membrane//Cathode) electrochemical cell was used. Under the explored conditions, we have demonstrated that lignin can be electrolyzed at much lower electrical potentials (from ~0.45 V) compared to that of water electrolysis (thermodynamically favored from ~1.2 V). In addition, we observed that increasing the reaction temperature gives rise to an enhanced activity towards the electrolysis of lignin, increasing therefore the production of pure H₂. Finally, *in-situ* cyclic voltammetry experiments were performed in the PEM cell to demonstrate that lignin electro-oxidation takes place at potentials lower than that for O₂ evolution. These experiments also showed that the whole system did not suffer a significant deactivation during the electrolysis experiments, which pointed out the **promising** stability and reproducibility of the proposed technology. Further studies should be performed to identify the products of the lignin electro-oxidation at the anode.

This study establishes a very important step-forward towards the direct electrochemical valorization of lignin (usually considered as a biomass residue) for a sustainable production of pure H₂ using renewable sources.

1. Introduction

To this date it is well known that H₂ is an excellent energy carrier, which is expected to play a key role in near-future energy systems. In this sense, H₂-fuel cells are on the verge of creating a revolutionary change in the field of production of energy due to their excellent properties [1]. They allow to transform the chemical energy of the electrochemical reaction within hydrogen and oxygen into clean electrical power, with zero emissions. As an example, since 2015, H₂-fuel cell-based vehicles are commercialized by some of the main manufacturers.

Currently, steam reforming of fossil fuels (mainly natural gas) is used for large scale H₂ production [2]. However, it requires high reaction temperatures (> 600 °C), and produces low purity H₂ with a high concentration of carbonaceous species (CO, CO₂). Therefore additional separation units are required to obtain pure H₂. Hence, the water electrolysis process has gained much attention lately, since it allows to produce pure H₂ quick and conveniently without any greenhouse gas emissions. In addition, this technology is compatible with renewable resources. When abundant renewable energy is available, the excess of energy could be stored in form of H₂ via water electrolysis [3].

The main drawback of water electrolysis is related to its high electrical energy requirements, which makes the process economically unattractive. In this sense, the electrolysis of organic molecules has been proposed as a promising method for onsite pure H₂ production with much lower power demands, since the minimum thermodynamic potential needed for the electro-oxidation of the organic molecules is much lower than that for water electrolysis (~1 order of magnitude). For instance, it has been reported that pure H₂ can be produced by the electrolysis of methanol [4–7] and ethanol [8–12] as well as bio-ethanol [13] solutions. However, some alcohols are already considered as important bio-fuels (e.g. bioethanol-gasoline blends are widely sold in USA for vehicles). Therefore, their further transformation to H₂ is unattractive for practical purposes.

New resources should be found for real and sustainable H₂ production. In this sense, lignin is one of the most abundant bio-polymers in nature. Nowadays, about 50 million tons of lignin are produced annually as a waste stream of the Kraft pulping industry for cellulose production [14]. The Kraft lignin is characterized by its inertness and robustness, making tricky its selective oxidation into fine chemicals. Therefore, lignin is currently incinerated for energy applications.

In order to valorize the lignin, in the last years it has been widely reported that this biopolymer can be efficiently depolymerized into mono-aromatic high added-value

compounds [15–18] (such as vanillin) by electro-catalytic methods. Most of these studies have been recently summarized in a review by Zirbes and Waldvogel [19]. Electrochemistry allows to work under less severe conditions (lower pressure and/or temperature) compared to conventional thermolysis, hydrolysis, and catalytic processes.

However, to this date, only a few studies have reported the production of H₂ by direct lignin (or black liquor, an effluent from the kraft pulping process, with ~40 % lignin) electrolysis. Table 1 shows, to the best of the authors' knowledge, the main scientific works carried out in this field [20–25]. Most of them [20–24] were performed in conventional 3-electrode electrochemical cells working in batch operation mode using Pt-based, mild steel or NiCo-based electrodes. **However, working in batch operation in 3 electrode-cells is highly unattractive for practical purposes, mostly due to the fact that it does not allow to work in continuous-flow operation mode.** Thus, **different** electro-catalytic reaction devices easy to scale up should be used and developed for the practical application of this technology.

In this sense, a recent study published by Hibino et al. [25] reported the electrolysis of **alkaline** lignin on Polymer Electrolyte Membrane-based reactors (PEM). This architecture is normally composed of 2 catalyst-electrodes (anode and cathode) and a solid polymer electrolyte membrane to form the so-called membrane electrode assembly (MEA). The membrane enables the separation of anodic and cathodic compartments. This configuration allows to work in continuous mode by the use of a compact/modular system easy to scale up by commercial PEM stacks for large production of pure H₂. However, in the above mentioned study, lignin was not directly fed to the anode in a continuous operation mode. Instead, lignin was impregnated on the anode before it was assembled to the membrane. Even though the production of H₂ was significant, this configuration exhibits important limitations in view of their further practical implementation. Once the pre-added lignin is consumed, the MEA should be dismantled in order to impregnate a new batch.

To enhance the potential of biomass-derived molecules (such as lignin) as a H₂ resource, this technology should be clearly improved. In this study we propose, for the very first time in literature (to the best of our knowledge), to **use a different configuration for H₂ production from lignin.** **We will** perform the direct electrolysis of lignin-based solutions in Polymer Electrolyte Membrane reactors under continuous operation mode. For the majority of applications, continuous flow operation mode saves time, energy and costs, increasing the productivity and reducing the transportation costs. This study allows to advance a step

forward for the development of a sustainable technology towards the valorisation of biomass-derived resources for H₂ production.

2. Experimental

Commercial electrodes (FuelCellStore ®) and membranes were used in this study. The anode was composed of a bimetallic Pt-Ru catalyst (2 mg cm⁻², 50 % Pt-50 % Ru *wt/wt*, unsupported) impregnated on carbon cloth (with a 410 µm thick microporous layer). The cathode was composed of a Pt/C catalyst (0.2 mg cm⁻², 20 % *wt* Pt) impregnated on a similar carbon cloth. The geometric surface area of both electrodes was 25 cm². An alkaline (OH⁻) conductor polymeric membrane (Fumapem FAA-3-50 ®) of 45-50 µm thickness was used as electrolyte. Prior to use, it was immersed in an aqueous solution of 1 M NaOH for 24 hours at room temperature, to exchange its bromide functional groups (Br⁻) into OH⁻ groups.

All the experiments were performed in a commercial Polymer Electrolyte Membrane (PEM) electrolysis cell (Baltic fuel cells ®). The main components anode/membrane/cathode above described were separately introduced between two Teflon gaskets to ensure a proper sealing of the cell, without previous pre-assembly. Graphitic bi-polar plates with parallel grooves (flow channels) were used as current collectors. The cell was provided with a temperature control system and connections for reactants and products of anodic and cathodic compartments.

For the electrolysis experiments, the anode of the cell was continuously fed with a lignin alkaline aqueous solution (10 g L⁻¹ lignin, 1 M NaOH, 2.5 mL min⁻¹), and the cathode was supplied with a 1 M NaOH solution (2.5 mL min⁻¹). Several experiments were performed by feeding 1 M NaOH aqueous solution (under absence of lignin) to the anode for comparison purposes. Anode and cathode liquid flow-rates were controlled with a peristaltic pump. **Alkali (Kraft) lignin was purchased from Sigma Aldrich.** A potentiostat-galvanostat (Orignalys) was used for the polarization of the cell. **According to previous studies regarding the electrolysis of organic molecules on PEM cell configurations [8,13,26], the rate of H₂ production at the cathode follows the Faraday's Law based on the cell current. In this study we assumed therefore that the H₂ produced followed exactly the same rule, and it was proportional to the obtained current.**

3. Results and discussion

A first series of electrolysis experiments was performed in order to demonstrate the potential of lignin electrolysis in comparison with alkaline water electrolysis. In order to better understand the overall electro-catalytic process, Figure 1a shows a basic scheme for the PEM

electrolysis operation. Briefly, considering the alkaline membrane as a pure OH⁻ conductor, the application of positive polarizations (using the anode as working electrode) leads to the electro-reduction of H₂O in the cathode, with the subsequent production of pure gaseous H₂ and OH⁻ (H₂O + 1 e⁻ → OH⁻ + ½ H₂). The OH⁻ ions will then migrate, through the polymeric membrane, to the anode, leading to the electro-oxidation of the lignin (Lignin + OH⁻ → Lignin-ox + e⁻), and therefore to the production of lignin oxidation products (denoted as “lignin-ox”). When water is introduced in the anode instead of lignin, O₂ evolution takes place (2 OH⁻ → ½ O₂ + H₂O + 2e⁻) [27].

Figure 1b shows the variation of the obtained current and current density (in mA and mA cm⁻²) vs. the applied cell potential during a slow rate (0.5 mV s⁻¹) linear voltammetry experiment. The applied potential was varied between 0 and + 0.9 V, at a constant temperature of 80 °C, and by feeding either a lignin-NaOH solution or a NaOH solution (for water electrolysis) to the anode, as described in the experimental section. Starting with the water electrolysis experiments, it could be clearly observed that no significant electrical current was obtained at the explored potential range studied. This could be easily understood considering that the minimum thermodynamic cell voltage for water electrolysis (with H₂ evolution at the cathode and O₂ evolution at the anode) at this reaction temperature range is ~1.2 V. However, when the alkaline lignin solution was fed to the anode, a significantly different trend was observed. After an onset potential of ~0.45 V, the obtained current linearly increased with the applied potential.

According to previous studies [6,8–13], the electrolysis of organic molecules allows to obtain hydrogen at much lower potentials compared to water electrolysis, since the minimum thermodynamic potential required for the former is much lower. For lignin electrolysis, it was calculated to be equal to 0.21 V [21] (6 times lower than that for water electrolysis). A previous work dealing with electrolysis of C1-C3 alcohols on Pt-based electrodes in PEM configurations [6] reported that the overall cell over-potential is mainly due to the slow kinetics of the anodic electro-oxidation reactions (while the cathodic over-potential is almost negligible). Hence, the over-potential required to start the electrolysis process could be attributed to kinetic limitations up to 0.45 V, most likely due to the lignin electro-oxidation process.

The amount of pure hydrogen produced at the cathode was calculated following the Faraday law ($r_{H_2} = I/2F$, where I is the current obtained under the application of different potentials, and F is the Faraday constant). Maximum H₂ production rates of ~0.4 μmol s⁻¹ were obtained.

These values are lower than those obtained by Hibino et al. [25]. This could be explained on the basis of the residence time and the lignin/catalyst contact-type in the anodic compartment of the PEM cell. As previously explained in the introduction section, in the aforementioned study, a fixed amount of lignin was directly impregnated on the electrode before the preparation of the MEA, leading to a batch-type electro-catalytic reactor (infinite residence time) with a very intimate lignin/catalyst contact. In order to make the lignin electrolysis a sustainable technology, working in continuous flow, as in the current study, is a very important step-forward in view of its further practical application.

The impact of the reaction temperature was also studied (Figure 2) for the overall lignin electrolysis process. As expected, an increase in the reaction temperature from 30 to 90 °C gives rise to a significant and gradual increase of the produced current (and therefore of the pure hydrogen flow generated at the cathode of the cell). As previously reported for the electrolysis of alcohols in PEM configurations, it could be attributed to both, the increase of the ionic conductivity of the polymeric electrolyte membrane, and the enhanced kinetics of the electrochemical reactions involved in the overall electrolysis process [8,13] (water electro-reduction at the cathode, and lignin electro-oxidation at the anode).

Figure 2b shows the evolution of the onset potential with the reaction temperature. A significant evolution could be observed, with the onset potential decreasing from ~0.75 V to ~0.45 V as the temperature increased from 30 to 90 °C. In addition, no limiting current was observed at any reaction temperature in the potential range studied. It seems to indicate that the system is mostly controlled by activation and ohmic losses with no mass transport limitations in these operating conditions. The maximum current density of ~3.6 mA cm⁻² was obtained at the highest temperature (90 °C). Much higher current densities have been reported in literature for the electrolysis of low carbon chain alcohols on PEM-based reactors (most of them in acid media). For instance, current densities up to 2 A cm⁻² [4], 250 mA cm⁻² [8] and 170 mA cm⁻² [26] were observed under similar reaction temperatures and PtRu-based anodes for methanol, ethanol and glycerol respectively. As expected, the electrolysis kinetics of a more complex molecule, such as lignin, is much slower, probably due to the required cleavage and rupture of the complex bonds of this bio-polymer (C-C, ether, etc.), although further studies should be performed to clarify the cleavage of the different lignin bonds on PtRu-based electrodes in the range of electrical potentials studied. The lower activity with lignin compared to low carbon chain alcohols could be also attributed to the competitive adsorption of the organic molecules and water, where the steric effects are expected to be more

pronounced for larger organic molecules, or the formation of intermediate species that could poison the electro-catalytic activity of the anode [6]. However, the latter is not very likely, since the overall electrolysis performance was stable, as it was observed by cyclic voltammetry.

Even though the hydrogen production is not very high, the present study can be considered as a starting point for the direct electrochemical conversion of a biomass-residue into pure hydrogen in a continuous-flow PEM reactor. The development of more active anodic catalysts and the optimization of operation conditions may allow to achieve higher electro-catalytic activities, opening a new field in electrochemistry vs. the conventional catalytic routes, which typically requires from high reaction temperatures and pressures.

Cyclic voltammetry experiments (CV) were used to study the electrochemical behavior of the Pt-Ru//Fumapem (OH⁻)//Pt-C (Anode//Anion Exchange membrane//Cathode) electrochemical system under the presence of lignin solution at the anode. CV experiments (10 cycles) were in-situ performed in the PEM cell in continuous flow mode, at 90 °C at a sweep rate of 10 mV s⁻¹, under the application of positive polarizations from 0 to 1.1 V. The upper potential limit was chosen in order to avoid the O₂ evolution reaction at the anode (thermodynamically favored from ~1.2 V). **A similar CV experiment was performed by feeding an alkaline water solution to the anode (1 M NaOH) for further comparison (water electrolysis).**

Regarding the water electrolysis experiment (only 10th cycle shown), we can clearly observe one anodic peak and one cathodic peak. The onset potential for the anodic peak is observed at ~0.95 V. Considering O₂ evolution is thermodynamically unlikely at this potential, these peaks could be attributed to the formation of an oxide film on the surface of the metallic anodic electro-catalyst (anodic scan), and to its further reduction (cathodic scan). For instance, the passivation of Pt was previously observed by Parpot et al. [15] at potentials below the oxygen evolution (i.e. ~0.4 V vs the NHE in alkaline media). In other words, it might correspond to the “passivation”/reduction of the PtRu electro-catalyst, although further studies should be performed to clarify this point.

Regarding the lignin electrolysis, the characteristic CV curves shown on Figure 3 were reproducible after the second cycle. It seems to indicate that the system does not undergo a significant deactivation under these operating conditions. To ensure the long-term stability of the system, future chronoamperometric studies in the high range potential (0.7-0.9 V) will be performed for long-time periods. This experiment shows a first onset potential during the anodic scan at ~0.45 V, in good agreement with the potentiostatic experiments shown in

Figure 1 and 2. Then, during the forward scan different onset potentials were observed (at ~0.75 V and ~0.95 V). It could be attributed to the electro-oxidation of lignin and the formation of several intermediate oxidation products (while the last peak could be attributed to the metal passivation as previously explained). Previous studies on Pt [15,20,21] and Ni-based [24] electrodes have reported that lignin electro-oxidation takes place at potentials lower than the O₂ evolution potential. The electrochemical depolymerization of lignin into high added value organic products may also occurred at the explored conditions [19]. Hence, a wide variety of products could be produced by means of these reactions, including vanillin, vanillic acid and guaiacol. Therefore it is worth mentioning that the PEM configuration used in this study may allow, on the one hand, to produce pure hydrogen at the cathode via H₂O electro-reduction (at much lower potentials compared to conventional water electrolysis experiments) and, on the other hand, to separately produce a wide variety of organic products at the anode. Further electrochemical experiments and analysis of the anodic product streams should be performed in order to identify and quantify these products from lignin electro-oxidation.

4. Conclusions

The following conclusions could be obtained from this study:

- Polymer Electrolyte Membrane-based reactors have been, for the first time, used to perform the electrolysis of lignin-based alkaline solutions in continuous-flow mode.
- This configuration allows to obtain hydrogen at the cathode at much lower electrical potentials (starting at ~0.45 V) compared to conventional water electrolysis.
- Working at high temperatures (< 90 °C) allows to maximize the electrolysis performance (and therefore the production of H₂) due to the enhanced kinetics and conductivity of the polymeric membrane.
- Cyclic voltammetry experiments have demonstrated that lignin electro-oxidation undergo at potentials much lower than that needed for O₂ evolution. In addition, the electrolysis performance was stable along the different cycles, which seems to indicate that the system did not suffer a significant deactivation during the electrolysis experiments.

5. References

- [1] S.J. Peighambaroust, S. Rowshanzamir, M. Amjadi, Review of the proton exchange membranes for fuel cell applications, *Int. J. Hydrogen Energy*. 35 (2010) 9349–9384. doi:10.1016/j.ijhydene.2010.05.017.

- [2] A. Heinzl, B. Vogel, P. Hübner, Reforming of natural gas - Hydrogen generation for small scale stationary fuel cell systems, *J. Power Sources* 105 (2002) 202–207. doi:10.1016/S0378-7753(01)00940-5.
- [3] K. Zeng, D. Zhang, Recent progress in alkaline water electrolysis for hydrogen production and applications, *Prog. Energy Combust. Sci.* 36 (2010) 307–326. doi:10.1016/j.pecs.2009.11.002.
- [4] G. Sasikumar, A. Muthumeenal, S.S. Pethaiah, N. Nachiappan, R. Balaji, Aqueous methanol eletrolysis using proton conducting membrane for hydrogen production, *Int. J. Hydrogen Energy.* 33 (2008) 5905–5910. doi:10.1016/j.ijhydene.2008.07.013.
- [5] B. Hasa, J. Vakros, A.D. Katsaounis, Effect of TiO₂ on Pt-Ru-based anodes for methanol electroreforming, *Appl. Catal. B Environ.* 237 (2018) 811–816. doi:10.1016/j.apcatb.2018.06.055.
- [6] F.M. Sapountzi, M.N. Tsampas, H.O.A. Fredriksson, J.M. Gracia, J.W. Niemantsverdriet, Hydrogen from electrochemical reforming of C1–C3 alcohols using proton conducting membranes, *Int. J. Hydrogen Energy.* 42 (2017) 10762–10774. doi:10.1016/j.ijhydene.2017.02.195.
- [7] Y.X. Chen, A. Lavacchi, H.A. Miller, M. Bevilacqua, J. Filippi, M. Innocenti, A. Marchionni, W. Oberhauser, L. Wang, F. Vizza, Nanotechnology makes biomass electrolysis more energy efficient than water electrolysis, *Nat. Commun.* 5 (2014) 4036. doi:10.1038/ncomms5036.
- [8] A. Caravaca, F.M. Sapountzi, A. De Lucas-Consuegra, C. Molina-Mora, F. Dorado, J.L. Valverde, Electrochemical reforming of ethanol–water solutions for pure H₂ production in a PEM electrolysis cell, *Int. J. Hydrogen Energy* 37 (2012) 9504–9513. doi:10.1016/j.ijhydene.2012.03.062.
- [9] N. Gutiérrez-Guerra, M. Jiménez-Vázquez, J.C. Serrano-Ruiz, J.L. Valverde, A. de Lucas-Consuegra, Electrochemical reforming vs. catalytic reforming of ethanol: A process energy analysis for hydrogen production, *Chem. Eng. Process. Process Intensif.* 95 (2015) 9–16. doi:10.1016/j.cep.2015.05.008.
- [10] A.R. de la Osa, A.B. Calcerrada, J.L. Valverde, E.A. Baranova, A. de Lucas-Consuegra, Electrochemical reforming of alcohols on nanostructured platinum-tin catalyst-electrodes, *Appl. Catal. B Environ.* 179 (2015) 276–284. doi:10.1016/j.apcatb.2015.05.026.

- [11] A.B. Calcerrada, A.R. de la Osa, H.A.E. Dole, F. Dorado, E.A. Baranova, A. de Lucas-Consuegra, Stability testing of Pt_xSn_{1-x}/C anodic catalyst for renewable hydrogen production via electrochemical reforming of ethanol, *Electrocatalysis* 9 (2018) 293–301. doi:10.1007/s12678-017-0428-0.
- [12] A.B. Calcerrada, A.R. de la Osa, J. Llanos, F. Dorado, A. de Lucas-Consuegra, Hydrogen from electrochemical reforming of ethanol assisted by sulfuric acid addition, *Appl. Catal. B Environ.* 231 (2018) 310–316. doi:10.1016/j.apcatb.2018.03.028.
- [13] A. Caravaca, A. De Lucas-Consuegra, A.B. Calcerrada, J. Lobato, J.L. Valverde, F. Dorado, From biomass to pure hydrogen: Electrochemical reforming of bio-ethanol in a PEM electrolyser, *Appl. Catal. B Environ.* 134–135 (2013) 302–309. doi:10.1016/j.apcatb.2013.01.033.
- [14] O. Movil-Cabrera, A. Rodriguez-Silva, C. Arroyo-Torres, J.A. Staser, Electrochemical conversion of lignin to useful chemicals, *Biomass and Bioenergy*. 88 (2016) 89–96. doi:10.1016/j.biombioe.2016.03.014.
- [15] P. Parpot, A.P. Bettencourt, A.M. Carvalho, E.M. Belgsir, Biomass conversion: Attempted electrooxidation of lignin for vanillin production, *J. Appl. Electrochem.* 30 (2000) 727–731. doi:10.1023/A:1004003613883.
- [16] H. Zhu, L. Wang, Y. Chen, G. Li, H. Li, Y. Tang, P. Wan, Electrochemical depolymerization of lignin into renewable aromatic compounds in a non-diaphragm electrolytic cell, *RSC Adv.* 4 (2014) 29917–29924. doi:10.1039/c4ra03793f.
- [17] H. Zhu, Y. Chen, T. Qin, L. Wang, Y. Tang, Y. Sun, P. Wan, Lignin depolymerization via an integrated approach of anode oxidation and electro-generated H_2O_2 oxidation, *RSC Adv.* 4 (2014) 6232–6238. doi:10.1039/c3ra47516f.
- [18] S. Stiefel, J. Lölsberg, L. Kipshagen, R. Möller-Gulland, M. Wessling, Controlled depolymerization of lignin in an electrochemical membrane reactor, *Electrochem. Commun.* 61 (2015) 49–52. doi:10.1016/j.elecom.2015.09.028.
- [19] M. Zirbes, S.R. Waldvogel, Electro-conversion as sustainable method for the fine chemical production from the biopolymer lignin, *Curr. Opin. Green Sustain. Chem.* 14 (2018) 19–25. doi:10.1016/j.cogsc.2018.05.001.
- [20] S.B. Lalvani, P. Rajagopal, Lignin-augmented water electrolysis, *J. Electrochem. Soc.* 139 (1992) L1–L2. doi:10.1149/1.2069212.
- [21] S.B. Lalvani, R. Rajagopal, Hydrogen production from lignin-water solution by

- electrolysis, *Holzforschung*. 47 (1993) 283–286. doi:10.1515/hfsg.1993.47.4.283.
- [22] H. Roy Ghatak, Electrolysis of black liquor for hydrogen production: Some initial findings, *Int. J. Hydrogen Energy* 31 (2006) 934–938.
doi:10.1016/j.ijhydene.2005.07.013.
- [23] H.R. Ghatak, S. Kumar, P.P. Kundu, Electrode processes in black liquor electrolysis and their significance for hydrogen production, *Int. J. Hydrogen Energy* 33 (2008) 2904–2911. doi:10.1016/j.ijhydene.2008.03.051.
- [24] O. Movil, M. Garlock, J.A. Staser, Non-precious metal nanoparticle electrocatalysts for electrochemical modification of lignin for low-energy and cost-effective production of hydrogen, *Int. J. Hydrogen Energy* 40 (2015) 4519–4530.
doi:10.1016/j.ijhydene.2015.02.023.
- [25] T. Hibino, K. Kobayashi, M. Nagao, S. Teranishi, Hydrogen production by direct lignin electrolysis at intermediate temperatures, *ChemElectroChem*. 4 (2017) 3032–3036. doi:10.1002/celec.201700917.
- [26] J. de Paula, D. Nascimento, J.J. Linares, Influence of the anolyte feed conditions on the performance of an alkaline glycerol electroreforming reactor, *J. Appl. Electrochem.* 45 (2015) 689–700. doi:10.1007/s10800-015-0848-6.
- [27] F.M. Sapountzi, J.M. Gracia, C.J.K.-J. Weststrate, H.O.A. Fredriksson, J.W.H. Niemantsverdriet, Electrocatalysts for the generation of hydrogen, oxygen and synthesis gas, *Prog. Energy Combust. Sci.* 58 (2017) 1–35.
doi:10.1016/j.pecs.2016.09.001.

Table 1. State-of-the-art regarding the studies dealing explicitly with the production of H₂ via “direct lignin electrolysis”.

Electrochemical cell	Anode//Cathode//Electrolyte	Operation mode	Reference
3-electrode cell	Anode: Pt mesh 6.5 cm ² Reference: Ag/AgCl Electrolyte: 1 M NaOH	Batch	[20]
3-electrode cell*	Anode: Pt mesh 6.5 cm ² Cathode: Pt mesh 7.4 cm ² Reference: SCE Electrolyte: 1 M NaOH	Batch	[21]
Batch cell**	Anode: Mild steel Cathode: Mild steel Electrolyte: KOH	Batch	[22]
3-electrode cell**	Anode: 1 mm D Pt wire Cathode: Pt foil Reference: SCE Electrolyte: KOH	Batch	[23]
3-electrode cell	Anode: Ni/C, Co/C and NiCo/C 0.2 cm ² Cathode: Pt ring Reference: Hg/HgO Electrolyte: 1 M NaOH	Batch	[24]
PEM reactor	Anode: Pt/C and PtFe/C 2 cm ² Cathode: Pt/C 0.5 cm ² Electrolyte: PTFE-based acid membrane	Batch/Semi-continuous	[25]

* Anode and cathode separated by a fritted glass

** Production of H₂ via electrolysis of “Black liquor”

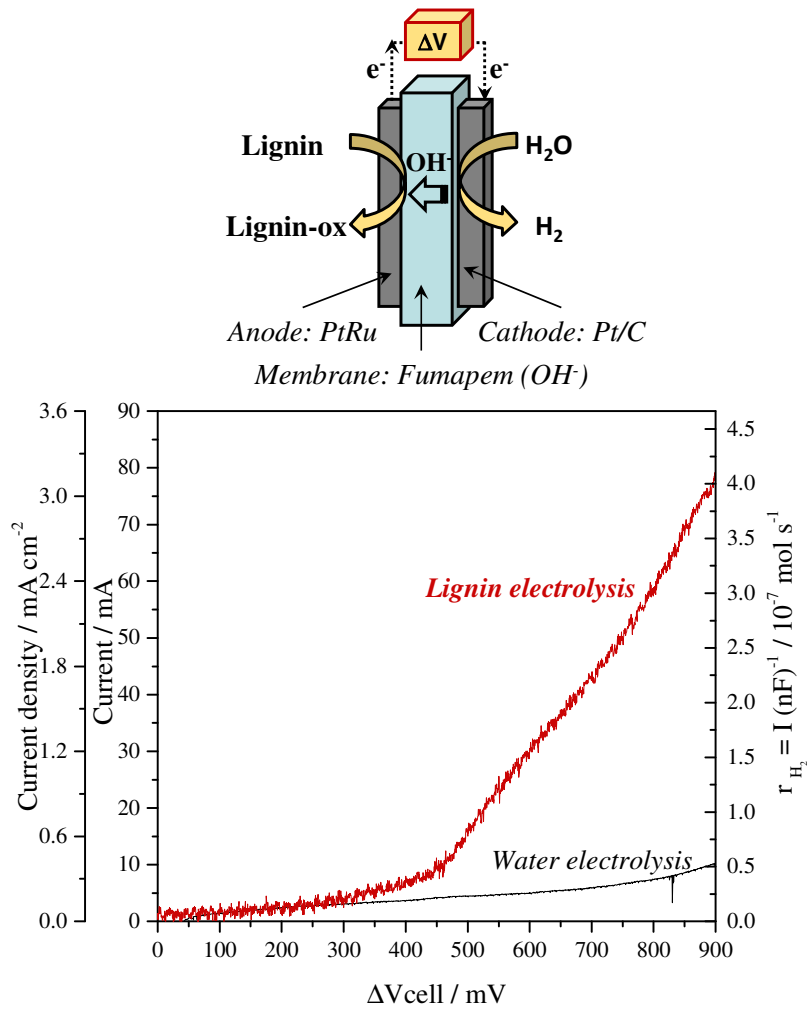


Fig 1. a) Scheme of the overall lignin electrolysis process in a PEM reactor working in continuous-flow mode; b) Influence of the presence of lignin in the anodic compartment at 80 °C: Linear sweep voltammetry from 0 V to 0.9 V; Sweep rate: 0.5 mV s⁻¹. Anode: Lignin 10 g L⁻¹ in NaOH 1 M, 2.5 ml/min (lignin electrolysis), or NaOH 1 M, 2.5 ml/min (water electrolysis). Cathode: NaOH 1 M, 2.5 ml/min.

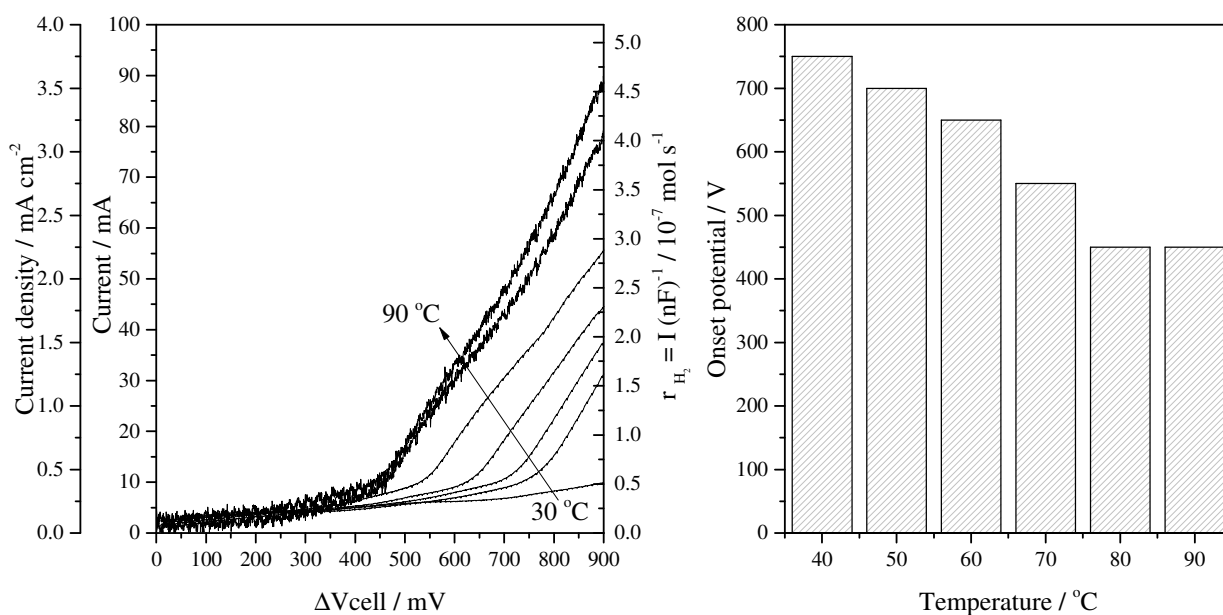


Fig 2. Influence of the reaction temperature on: a) the obtained current during the lignin electrolysis process. Linear sweep voltammetry from 0 V to 0.9 V. Sweep rate: 0.5 mV s⁻¹. Each curve represents an increase of 10 °C from 30 °C to 90 °C; b) the onset potential to start the lignin electrolysis. Anode: Lignin 10 g L⁻¹ in NaOH 1 M, 2.5 ml/min. Cathode: NaOH 1 M, 2.5 ml/min.

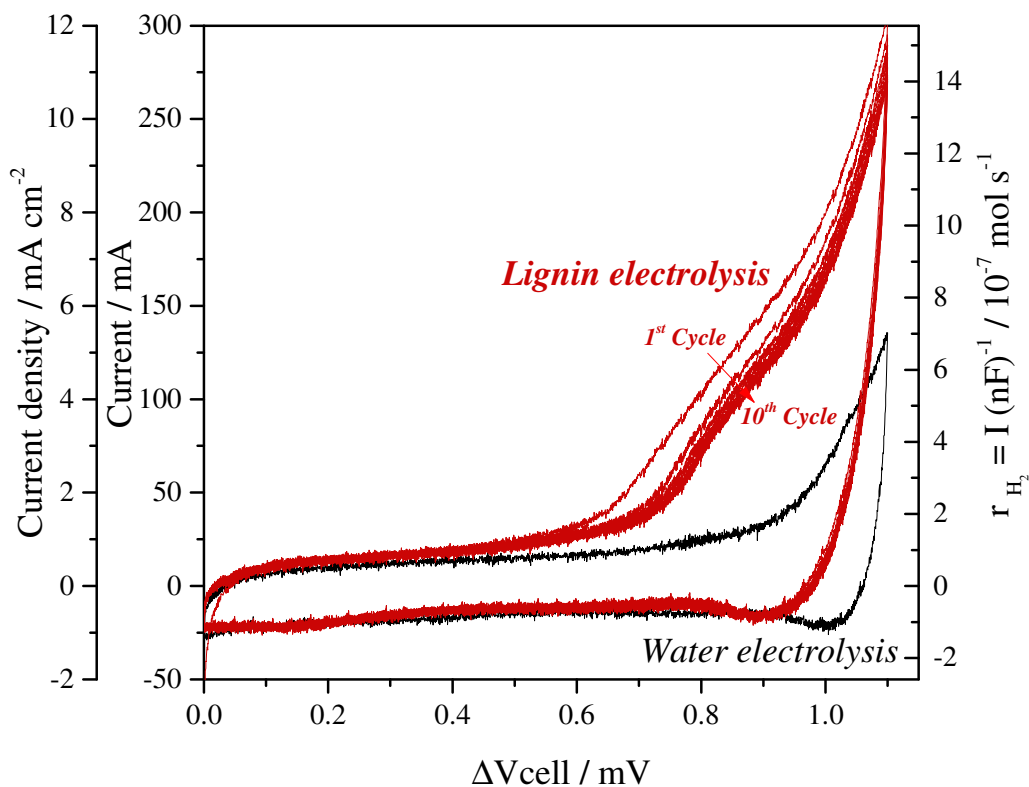


Fig 3. *In-situ* cyclic voltammetry (CV) experiment under the presence (10 cycles) and the absence (10th cycle) of lignin in the anodic side of the PEM cell. Potential range: from 0 V to 1.1 V. Sweep rate: 10 mV s⁻¹. Temperature: 90 °C; Anode: Lignin 10 g L⁻¹ in NaOH 1 M, 2.5 ml/min (lignin electrolysis), or NaOH 1 M, 2.5 ml/min (water electrolysis). Cathode: NaOH 1 M, 2.5 ml/min.

