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1 **Electrochemical hydrogen production from biomass**

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8
9 **Abstract.** Thermodynamic data indicate that the oxidation of oxygenated organic
10 species originating from biomass instead of water at the anode of an electrolysis cell
11 should allow decreasing the cell voltage below 1.23 V. Bio-sourced alcohols, polyols,
12 sugars, lignocellulosic compounds, and their derivatives are then electro-reformed to
13 produce clean hydrogen at the cathode and compounds at the anode of electrolysis
14 cells. The reported studies highlight the main challenges to make electro-reforming a
15 future industrial process: higher reaction kinetics and hydrogen evolution rate, better
16 selectivity of anode catalysts towards the formation of CO₂ or added-value compounds,
17 and utilization of non-strategical metals. An attractive solution to decrease hydrogen
18 production costs and to make bankable other economic activities consists in directly
19 valuing wastes from agriculture/forestry (lignocellulosic raw materials) and/or wastes
20 from biofuel industries.

21
22 **Keyword:** Biomass, Electro-reforming, Hydrogen, Oxidation, thermodynamics

24 **1. Introduction.**

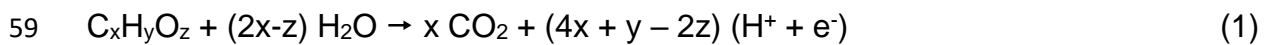
25 According to a report of the International Energy Agency in 2018, the world production
26 of hydrogen in 2014 was ca.100 million tons, with almost 44 % as by-product (fatal
27 hydrogen)¹. The world consumption of hydrogen in 2018 was estimated around
28 74 million tons, with 5 to 10 % growth forecast² supported by the increasing demands
29 of ammonia for fertilizers and of methanol for fine chemistry, the refinery of heavier and
30 dirtier oil sources, the more drastic environmental regulations on sulfur emission, and
31 the increasing interest for hydrogen as energy carrier³. Indeed, the hydrogen molecule
32 has a very high specific energy density (33 kWh kg⁻¹, which is twice that of methane
33 and about 3 times that of gasoline). Nowadays, 96 % of hydrogen is produced from
34 non-sustainable thermochemical routes using fossil resources⁴ (ca. 48 % from natural
35 gas or methane steam reforming, 30 % from oil partial oxidation and 18 % from coal
36 gasification), generating high amounts of CO₂⁵. Only 4 % of hydrogen is manufactured
37 by water electrolysis. However, classical thermochemical technologies for hydrogen
38 production being already implemented in oil refinery, their adaptation for the production
39 of hydrogen from lignocellulosic biomass has been proposed^{1,6,7} (the annual
40 production of lignocellulosic biomass is 4.6 billion tons from agricultural residues and
41 7 billion tons from grass and forests)⁸.

42 Biological and electrochemical processes with lower TRLs (technology readiness
43 levels) are also considered for hydrogen production⁶. Hydrogen electrochemical
44 production through proton reduction in acidic media and water reduction in alkaline
45 media at the cathode, and oxidation of oxygenated organic compounds (OOCs) from
46 biomass at the anode of an electrolysis cell (EC)⁹ is equivalent to an electro-reforming
47 reaction. Although electro-reforming processes are less mature than thermochemical
48 routes and water electrolysis (TRL 9 for alkaline electrolyzers and TRL 5-7 for proton

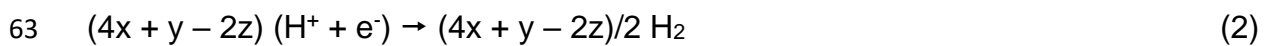
49 exchange membrane electrolyzers), they have important advantages: mild operating
50 conditions, lower energy consumption, clean hydrogen production without downstream
51 purification processes, and the possibility of co-production of value-added compounds
52 at the anode of the EC.¹⁰ The present contribution is focused on recent developments
53 and trends concerning the electro-reforming of biomass.

54 **2. Thermodynamics and kinetics**¹¹

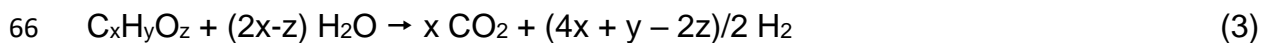
55 The electrooxidation of an OOC with general formula $C_xH_yO_z$ into gaseous CO_2 and
56 protons at the anode of an EC (Fig. 1 shows the working principle of a proton exchange
57 membrane electro-reforming cell -PEMEC-) occurs on appropriate catalysts according
58 to the following reaction:



60 Protons formed at the anode cross the electrolyte and are reduced into dihydrogen at
61 the cathode of the EC in the presence of electrons coming from the external electric
62 circuit:

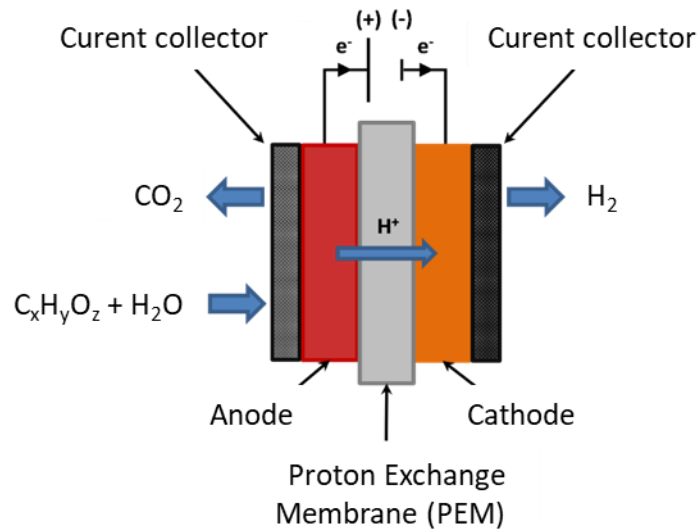


64 The electrical equilibrium between both electrodes implies the overall reaction (3),
65 which corresponds to the electrochemical reforming of $C_xH_yO_z$ into H_2 and CO_2 :



67 From the thermodynamic data at $T = 298$ K under standard conditions ($p = 0.1$ MPa,
68 compounds considered in their standard state) related to the formation of H_2O , CO_2 ,
69 and $C_xH_yO_z$ (ΔG°_f and ΔH°_f), the Hess's law allows calculating the thermodynamic data
70 ΔG°_{rev} and ΔH°_{rev} associated to the electrolysis of water and electro-reforming of OOCs
71 into CO_2 and H_2 , and further the reversible cell voltage U°_{rev} . Water electrolysis and
72 OOC electro-reforming being endothermic reactions ($\Delta H^\circ_{rev} > 0$ kJ mol⁻¹), energy must
73 be provided to the systems to initiate the reactions. The standard enthalpy of formation

74 of compounds, that is $\Delta H_{f,C_xH_yO_z}^\circ$, has then to be considered instead of $\Delta G_{f,C_xH_yO_z}^\circ$, and
 75 the additional overvoltage related to the entropy change $\Delta S_{f,C_xH_yO_z}^\circ$ ($\Delta H_{f,C_xH_yO_z}^\circ =$
 76 $\Delta G_{f,C_xH_yO_z}^\circ + T\Delta S_{f,C_xH_yO_z}^\circ$) leads to the so-called standard thermoneutral cell voltage
 77 $U_{\text{therm.}}$



78

79 **Fig. 1.** Working principle of a proton exchange membrane electrolysis cell for the electroreforming of
 80 oxygenated organic compounds.

81 All the OOCs in Table 1 lead to standard reversible and thermoneutral cell voltages
 82 much lower than those for water electrolysis. Then, the electrical energy theoretically
 83 needed (that is only proportional to the cell voltage) to produce one mole of hydrogen
 84 from $C_xH_yO_z$ is much lower than that for water electrolysis, and consequently the
 85 energy cost of hydrogen production is lowered.

86 When a current is crossing the EC, the cell voltage deviates from the reversible one
 87 towards higher values. The electrical energy (W_e) consumed at a cell voltage $U_{\text{elec}}(I)$
 88 will then exceed the values calculated from the thermoneutral cell voltage:

89
$$W_e \text{ (kWh Nm}_{\text{H}_2}^{-3})} = \frac{nF}{3600 \times V_m} \times U_{\text{elec}}(I) = 2.191 \times U_{\text{elec}}(I) \quad (4)$$

90
$$W_e \text{ (kWh kg}_{\text{H}_2}^{-1})} = \frac{nF}{3600 \times M_{\text{H}_2}} \times U_{\text{elec}}(I) = 26.8 \times U_{\text{elec}}(I) \quad (5)$$

91 where n is the number of moles of electrons involved for the production of one mole of
 92 H_2 ($n = 2$), F is the Faraday constant ($F = 96485 \text{ C mol}^{-1}$), V_m is the molar volume of a
 93 perfect gas ($V_m = 24.465 \text{ dm}^3 \text{ mol}^{-1}$ at 298 K), M_{H_2} is the molar weight of H_2 ($M_{H_2} =$
 94 $0.002 \text{ kg mol}^{-1}$) and I is the current crossing the EC.

95 The hydrogen production rate is directly related to the electrical current I crossing the
 96 cell:

$$97 \quad I = nFv = 2F \times \frac{d[H_2]}{dt} \quad (6)$$

98 where v is the reaction rate and $\frac{d[H_2]}{dt}$ the rate of hydrogen formation.

99 Then, the volume of hydrogen as a function of the electro-reforming time at constant
 100 current can be estimated as follows:

$$101 \quad \frac{dV_{H_2}}{dt} = V_m \times \frac{d[H_2]}{dt} = V_m \times \frac{I}{2F} \quad (7)$$

102 The volume of hydrogen produced over the period Δt is then:

$$103 \quad V_{H_2} = V_m \times \frac{I \times \Delta t}{2F} \quad (8)$$

104 **Tableau 1.** Thermodynamic data for the formation of H_2O , CO_2 , and $C_xH_yO_z$ molecules (ΔH°_f and ΔG°_f)
 105 at 298 K under standard conditions, values of ΔH°_{rev} et ΔG°_{rev} , and cell voltages (U° and U°_{therm}).

	Carbon dioxide CO_2	Water H_2O	Methanol CH_3OH	Ethanol CH_3CH_2OH	Glycerol $C_3H_8O_3$	Glucose $C_6H_{12}O_6$
ΔG°_f (kJ mol^{-1})	-394.4	-237.2	-166.3	-174.8	-438.5	-917.2
ΔH°_f (kJ mol^{-1})	-393.5	-285.8	-238.9	-277.7	-669.6	-1273.3
ΔG°_{rev} (kJ mol^{-1})	-	+237.2	+9.1	+97.6	-33.1	-26
ΔH°_{rev} (kJ mol^{-1})	-	+285.8	+131.2	+348.1	+343.5	+944.2
n_{e^-}	-	2	6	12	14	24
n_{H_2}	-	1	3	6	7	12
Δh°_{rev} ($\text{kJ mol}_{H_2}^{-1}$)		+285.8	+43.7	+58.0	+49.1	+78.7
U°_{rev} (V)	-	1.23	0.016	0.084	-0.024	-0.012
U°_{therm} (V)	-	1.48	0.227	0.301	0.254	0.265

106 **3. Electroreforming of oxygenated organic compounds from biomass**

107 Particular attention was brought to alcohols as hydrogen sources because they were
108 thoroughly studied for applications in direct alcohol fuel cells¹². Methanol was first
109 considered due to its simplicity and high reactivity. The electro-conversion of 2 M
110 methanol solution at 90 °C in a PEMEC fitted with PtRu/C as anode catalyst, a
111 Nafion[®]117 membrane and Pt-WC/C as cathode catalyst allowed reaching current
112 densities as high as 0.5 A cm⁻² at a cell voltage of +0.6 V¹³. Lamy et al.¹⁴ analyzed the
113 kinetics of methanol oxidation on the PtRu(1:1)/C anode catalyst of a PEMEC as a
114 function of methanol concentration and working temperature, and evaluated the
115 hydrogen evolution rate at the Pt/C cathode of the PEMEC. They reached current
116 densities of 0.1 A cm⁻² for a cell voltage of +0.8 V at 85 °C. But methanol is a toxic
117 compound generally obtained from partial oxidation of methane. Amongst alcohols
118 presented in Table 1, ethanol is bio-sourced. Caravaca et al.¹⁵ reported the
119 electrochemical reforming of a 6 M ethanol solution in a PEMEC (40%Pt - 20%Ru/C
120 as anode catalyst, 20% Pt/C as cathode catalyst and a proton conducting Sterion[®]
121 membrane as electrolyte). They obtained an onset cell voltage of ca. +0.4 V. At a cell
122 voltage of +1.0 V the current densities increased from 0.05 to 0.2 A cm⁻² with
123 temperature increasing from 40 °C to 80 °C. Lamy et al.¹⁶ decreased the onset cell
124 voltage down to +0.25 V in a PEMEC fitted with a PtSnRu anode, a Pt/C cathode, and
125 a Nafion[®] 117 membrane; they obtained a current density of 0.13 A cm⁻² at +1.0 V and
126 20 °C.

127 For kinetics reasons the electro-oxidation of alcohols and polyols is often performed in
128 alkaline media¹⁷. The electro-reforming of biomass-derived alcohols (2 M ethanol and
129 glycerol in 2 M KOH electrolyte) was studied at 60 °C on Rh/C¹⁸ and Au–Pd/C¹⁹ anode
130 catalysts, with a Pt/C cathode for the H₂ evolution reaction. The onset voltage was +0.3

131 V, and hydrogen was produced with energy consumptions lower than 20 kWh kg_{H2}⁻¹.
132 Gonzales-Cobos et al.²⁰ carried out glycerol electro-reforming (2 M glycerol in 0.5 M
133 NaOH electrolyte) at 20 °C in an EC fitted with a Pt₉Bi₁/C anode and a Pt/C cathode;
134 they obtained hydrogen production rates of 0.11 and 0.23 (Nm_{H2})³ h⁻¹m⁻² and electrical
135 energy consumptions of 15.0 and 20.2 kWh (kg_{H2})⁻¹, for cell voltages of +0.55 V and
136 +0.70 V, respectively.

137 Bio-sourced alcohols and polyols are often obtained from sugar fermentation. This
138 supplementary step increases the cost for the whole hydrogen production process.
139 The direct feeding of an electro-reformer with glucose and xylose for hydrogen
140 production has then been considered²¹. Glucose and xylose (0.1 and 0.5 M in 0.1 M
141 NaOH aqueous electrolyte) were electro-reformed at 20 °C using a Pd₃Au₇/C anode
142 catalyst and a Pt/C cathode catalyst at +0.4 V, +0.6 V and +0.8 V, with hydrogen
143 production costs ranging from 1.60 € to 3.20 € kg_{H2}⁻¹, lower than those from wind, solar
144 or nuclear water electrolysis (between 4.15 \$ kg⁻¹ and 23.27 \$ kg⁻¹). Replacing the
145 Pd₃Au₇/C anode catalyst by a Pt₉Bi₁/C one allowed electro-reforming 0.1 M glucose in
146 0.1 M NaOH electrolyte at +0.3 V²² with an energy consumption of only 7 kWh kg_{H2}⁻¹.
147 Raw biomass, i.e., lignin²³ and cellulose²⁴, were also considered for the
148 electrochemical production of hydrogen. For example, electro-reforming of lignin and
149 cellulose using a polyoxometalate as anode catalyst was performed²⁴ with an electric
150 consumption of ca. 8.5 kWh kg_{H2}⁻¹ for a current density of 0.2 A cm⁻².

151 **4. Drawbacks, advantages, and perspectives of biomass electro-reforming for** 152 **hydrogen production**

153 Electro-reforming of OOCs leads to EC voltages much lower than those for water
154 electrolysis. But the achieved current densities, i.e., the hydrogen evolution rates, are
155 also much lower (a few tens/hundreds mA cm⁻² for OOC electro-reforming against

156 several A cm⁻² for water electrolysis). Higher temperatures^{23,25} or bigger size of the
157 electro-reformer, as well as the development of more active catalysts²⁶, can help to
158 improve the hydrogen evolution rate.

159 Platinum group metals (PGMs) are often used as catalysts for electro-reforming
160 reactions: they allow decreasing the electrooxidation onset potential of OOCs and
161 reaching acceptable current densities at low cell voltages. But these materials are rare
162 and strategic, making the technology expensive as in the case of fuel cells²⁷. PGM-
163 based catalysts display low selectivity towards CO₂ formation owing to their low ability
164 to break the C-C bonds of OOCs. Therefore, the overall reaction efficiency is lowered.
165 To increase the selectivity towards CO₂ formation, higher cell voltages U (anode
166 potentials E_a , the cell voltage U being the difference between the anode potential E_a
167 and the cathode potential E_c , $U = E_a - E_c$) must be applied, which implies higher energy
168 consumption and hydrogen production cost. Here, the use of non-PGM-based
169 catalysts is certainly more relevant, making the electro-reformer less costly. Table 2
170 gives the prices of different metals used as catalysts for biomass electro-reforming²⁸.

171 **Tableau 2.** Prices of selected metals often used in anode of the EC for electro-reforming of oxygenated
172 organic compounds from biomass.

Metal	PGM					Non-PGM	
	Pt	Pd	Au	Rh	Ru	Ni	Co
Price (€ kg ⁻¹)	~34,500	~80,400	~49,000	~700,000	~8,500	~16	~47

173 The electro-reforming of glycerol on Ni-based catalysts occurs with very high selectivity
174 towards HCOO⁻ formation, i.e., much better efficiency for hydrogen production due to
175 C-C bond breaking²⁹. The reaction is driven by the Ni²⁺/Ni³⁺ redox transition that
176 imposes anode potentials (E_a) higher than +1.2 V vs. RHE, and therefore higher energy
177 consumption. In addition, the oxidation of OOCs into CO₂ at moderate anode potentials
178 is not achieved and remains then the Grail Quest for electrochemists.

191 On the other hand, biofuel industries generate important amounts of small OOCs as
192 bioproducts. The production of first-generation biofuels from vegetal oil methanolysis
193 generates ca. 10 wt% glycerol as by-product³². The production of second-generation
194 biofuels from lignocellulosic biomass (cellulose, hemicellulose, and lignin) thermal
195 treatment generates long-chain OCCs (for biofuel synthesis by hydrodeoxygenation
196 reactions -HDO-) and small-chain OOCs (C5 and C6 sugars and derivatives)^{33,34}. The
197 C-C bond being difficult to break at low anode potentials, e.g., at low cell voltages, the
198 electro-reforming of these by-products allows producing hydrogen simultaneously with
199 value-added compounds of industrial interest^{20,21,22}. Such approaches could make the
200 biofuel industry more profitable and allow developing full integrated biorefineries
201 generating zero waste. Figures 2a and 2b display the flow chart of the production of
202 biofuels, hydrogen, and fine chemicals from raw biomass conversion.

203 **5. Conclusion**

204 Electrochemical hydrogen production coupled with renewable energies is undoubtedly
205 an unavoidable alternative to thermoneutral methods based on fossil resources. In this
206 context, thermodynamic data clearly speak for electro-reforming of OOCs instead of
207 water electrolysis. However, hydrogen evolution rates remain very low compared with
208 water electrolysis. Larger amounts of PGM-based catalysts in anodes, bigger system
209 dimensions or higher metal loadings will increase the capital expenditure (CAPEX).
210 Replacement of PGMs by less costly Ni-based catalysts involves higher cell voltages,
211 increasing the operational expenditure (OPEX). Moreover, the previous production of
212 electro-reactive OOCs impacts the energy and cost balance of the electro-reforming
213 process.

214 OOCs produced as by-products/wastes by the biofuels industry, for example, can be
215 electro-reformed into hydrogen and value-added compounds, which can help to make

216 this industry more profitable and virtuous in the green chemistry point of view. In all
217 cases, development of very active catalysts, and very selective towards either CO₂
218 (highest efficiency of the electro-reformer), or a given value-added compounds (no
219 separation processes), is mandatory. The coupling with other activation methods
220 (sonochemistry, enzymes, bacteria, etc)^{35,36} can also help to improve activity and/or
221 selectivity.

222 The electro-reforming concept becomes very attractive in terms of sustainability,
223 energy saving, low hydrogen production cost, etc., and more and more research
224 groups get involved insuring the future development of this technology.

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229 **Declaration of interest:** none

230

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