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Abstract. Thermodynamic data indicate that the oxidation of oxygenated organic species originating form biomass instead of water at the anode of an electrolysis cell should allow decreasing the cell voltage below 1.23 V. Bio-sourced alcohols, polyols, sugars, lignocellulosic compounds, and their derivatives are then electro-reformed to produce clean hydrogen at the cathode and compounds at the anode of electrolysis cells. The reported studies highlight the main challenges to make electro-reforming a future industrial process: higher reaction kinetics and hydrogen evolution rate, better selectivity of anode catalysts towards the formation of CO_2 or added-value compounds, and utilization of non-strategical metals. An attractive solution to decrease hydrogen production costs and to make bankable other economic activities consists in directly valuing wastes from agriculture/forestry (lignocellulosic raw materials) and/or wastes from biofuel industries.

Keyword: Biomass, Electro-reforming, Hydrogen, Oxidation, thermodynamics

1. Introduction.

According to a report of the International Energy Agency in 2018, the world production of hydrogen in 2014 was ca.100 million tons, with almost 44 % as by-product (fatal hydrogen)[1]. The world consumption of hydrogen in 2018 was estimated around 74 million tons, with 5 to 10 % growth forecast[2] supported by the increasing demands of ammonia for fertilizers and of methanol for fine chemistry, the refinery of heavier and dirtier oil sources, the more drastic environmental regulations on sulfur emission, and the increasing interest for hydrogen as energy carrier[3]. Indeed, the hydrogen molecule has a very high specific energy density (33 kWh kg^{-1}, which is twice that of methane and about 3 times that of gasoline). Nowadays, 96 % of hydrogen is produced from non-sustainable thermochemical routes using fossil resources[4] (ca. 48 % from natural gas or methane steam reforming, 30 % from oil partial oxidation and 18 % from coal gasification), generating high amounts of CO_2[5]. Only 4 % of hydrogen is manufactured by water electrolysis. However, classical thermochemical technologies for hydrogen production being already implemented in oil refinery, their adaptation for the production of hydrogen from lignocellulosic biomass has been proposed[1,6,7] (the annual production of lignocellulosic biomass is 4.6 billion tons from agricultural residues and 7 billion tons from grass and forests)[8].

Biological and electrochemical processes with lower TRLs (technology readiness levels) are also considered for hydrogen production[6]. Hydrogen electrochemical production through proton reduction in acidic media and water reduction in alkaline media at the cathode, and oxidation of oxygenated organic compounds (OOCs) from biomass at the anode of an electrolysis cell (EC)[9] is equivalent to an electro-reforming reaction. Although electro-reforming processes are less mature than thermochemical routes and water electrolysis (TRL 9 for alkaline electrolyzers and TRL 5-7 for proton

exchange membrane electrolyzers), they have important advantages: mild operating

conditions, lower energy consumption, clean hydrogen production without downstream

purification processes, and the possibility of co-production of value-added compounds

at the anode of the EC.[10] The present contribution is focused on recent developments

and trends concerning the electro-reforming of biomass.

2. Thermodynamics and kinetics[11]

The electrooxidation of an OOC with general formula $C_xH_yO_z$ into gaseous CO_2 and

protons at the anode of an EC (Fig. 1 shows the working principle of a proton exchange

membrane electro-reforming cell -PEMEC-) occurs on appropriate catalysts according

to the following reaction:

$$C_xH_yO_z + (2x-z)\ H_2O \rightarrow x\ CO_2 + (4x + y - 2z)\ (H^+ + e^-) \tag{1}$$
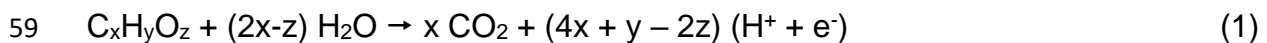
Protons formed at the anode cross the electrolyte and are reduced into dihydrogen at

the cathode of the EC in the presence of electrons coming from the external electric

circuit:

$$(4x + y - 2z)\ (H^+ + e^-) \rightarrow (4x + y - 2z)/2\ H_2 \tag{2}$$
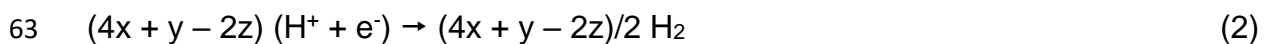
The electrical equilibrium between both electrodes implies the overall reaction (3),

which corresponds to the electrochemical reforming of $C_xH_yO_z$ into H_2 and CO_2:

$$C_xH_yO_z + (2x-z)\ H_2O \rightarrow x\ CO_2 + (4x + y - 2z)/2\ H_2 \tag{3}$$
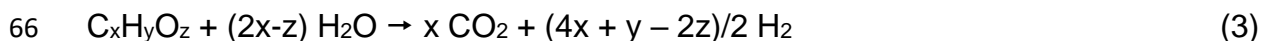
From the thermodynamic data at $T = 298$ K under standard conditions ($p = 0.1$ MPa,

compounds considered in their standard state) related to the formation of H_2O, CO_2,

and $C_xH_yO_z$ ($\Delta G°_f$ and $\Delta H°_f$), the Hess's law allows calculating the thermodynamic data

$\Delta G°_{rev}$ and $\Delta H°_{rev}$ associated to the electrolysis of water and electro-reforming of OOCs

into CO_2 and H_2, and further the reversible cell voltage $U°_{rev}$. Water electrolysis and

OOC electro-reforming being endothermic reactions ($\Delta H°_{rev} > 0$ kJ mol^{-1}), energy must

be provided to the systems to initiate the reactions. The standard enthalpy of formation

74   of compounds, that is $\Delta H^{\circ}_{f,C_xH_yO_z}$, has then to be considered instead of $\Delta G^{\circ}_{f,C_xH_yO_z}$, and

75   the additional overvoltage related to the entropy change $\Delta S^{\circ}_{f,C_xH_yO_z}$ ($\Delta H^{\circ}_{f,C_xH_yO_z}=$

76      $\Delta G^{\circ}_{f,C_xH_yO_z}$ + $T\Delta S^{\circ}_{f,C_xH_yO_z}$) leads to the so-called standard thermoneutral cell voltage

77   U°_{therm}.
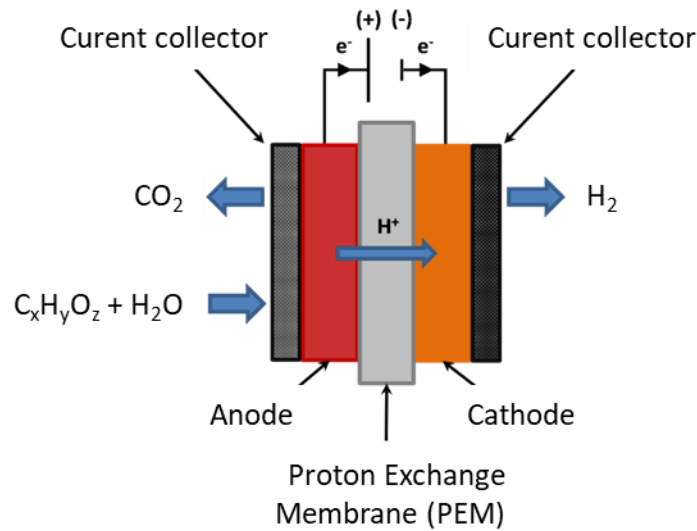
78

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 $U_{elec}(I)$

88   will then exceed the values calculated from the thermoneutral cell voltage:

89
$$W_e \ (\text{kWh Nm}_{H_2}^{-3}) = \frac{nF}{3600 \times V_m} \times U_{elec}(I) = 2.191 \times U_{elec}(I) \tag{4}$$

90
$$W_e \ (\text{kWh kg}_{H_2}^{-1}) = \frac{nF}{3600 \times M_{H_2}} \times U_{elec}(I) = 26.8 \times U_{elec}(I) \tag{5}$$

where n is the number of moles of electrons involved for the production of one mole of H$_2$ (n = 2), F is the Faraday constant (F = 96485 C mol^{-1}), V_m is the molar volume of a perfect gas (V_m = 24.465 dm^3 mol^{-1} at 298 K), M_{H_2} is the molar weight of H$_2$ (M_{H_2} = 0.002 kg mol^{-1}) and I is the current crossing the EC.

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

$$I = \mathrm{n}F v = 2F \times \frac{\mathrm{d}[\mathrm{H_2}]}{\mathrm{d}t} \tag{6}$$

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

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

$$\frac{\mathrm{d}V_{H_2}}{\mathrm{d}t} = V_\mathrm{m} \times \frac{\mathrm{d}[\mathrm{H_2}]}{\mathrm{d}t} = V_\mathrm{m} \times \frac{I}{2F} \tag{7}$$

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

$$V_{H_2} = V_\mathrm{m} \times \frac{I \times \Delta t}{2F} \tag{8}$$

Tableau 1. Thermodynamic data for the formation of H$_2$O, CO$_2$, and C$_x$H$_y$O$_z$ molecules ($\Delta H°_f$ and $\Delta G°_f$) at 298 K under standard conditions, values of $\Delta H°_{rev}$ et $\Delta G°_{rev}$, and cell voltages ($U°$ and $U°_{therm}$).

	Carbon dioxyde CO$_2$	Water H$_2$O	Methanol CH$_3$OH	Ethanol CH$_3$CH$_2$OH	Glycerol C$_3$H$_8$O$_3$	Glucose C$_6$H$_{12}$O$_6$
$\Delta G°_f$ (kJ mol^{-1})	-394.4	-237.2	-166.3	-174.8	-438.5	-917.2
$\Delta H°_f$ (kJ mol^{-1})	-393.5	-285.8	-238.9	-277.7	-669.6	-1273.3
$\Delta G°_{rev}$ (kJ mol^{-1})	-	+237.2	+9.1	+97.6	-33.1	-26
$\Delta H°_{rev}$ (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
$\Delta h°_{rev}$ (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

3. Electroreforming of oxygenated organic compounds from biomass

Particular attention was brought to alcohols as hydrogen sources because they were thoroughly studied for applications in direct alcohol fuel cells[12]. Methanol was first considered due to its simplicity and high reactivity. The electro-conversion of 2 M methanol solution at 90 °C in a PEMEC fitted with PtRu/C as anode catalyst, a Nafion®117 membrane and Pt-WC/C as cathode catalyst allowed reaching current densities as high as 0.5 A cm^{-2} at a cell voltage of +0.6 V[13]. Lamy et al.[14] analyzed the kinetics of methanol oxidation on the PtRu(1:1)/C anode catalyst of a PEMEC as a function of methanol concentration and working temperature, and evaluated the hydrogen evolution rate at the Pt/C cathode of the PEMEC. They reached current densities of 0.1 A cm^{-2} for a cell voltage of +0.8 V at 85 °C. But methanol is a toxic compound generally obtained from partial oxidation of methane. Amongst alcohols presented in Table 1, ethanol is bio-sourced. Caravaca et al.[15] reported the electrochemical reforming of a 6 M ethanol solution in a PEMEC (40%Pt - 20%Ru/C as anode catalyst, 20% Pt/C as cathode catalyst and a proton conducting Sterion® membrane as electrolyte). They obtained an onset cell voltage of ca. +0.4 V. At a cell voltage of +1.0 V the current densities increased from 0.05 to 0.2 A cm^{-2} with temperature increasing from 40 °C to 80 °C. Lamy et al.[16] decreased the onset cell voltage down to +0.25 V in a PEMEC fitted with a PtSnRu anode, a Pt/C cathode, and a Nafion® 117 membrane; they obtained a current density of 0.13 A cm^{-2} at +1.0 V and 20 °C.

For kinetics reasons the electro-oxidation of alcohols and polyols is often performed in alkaline media[17]. The electro-reforming of biomass-derived alcohols (2 M ethanol and glycerol in 2 M KOH electrolyte) was studied at 60 °C on Rh/C[18] and Au–Pd/C[19] anode catalysts, with a Pt/C cathode for the H$_2$ evolution reaction. The onset voltage was +0.3

V, and hydrogen was produced with energy consumptions lower than 20 kWh kg_{H2}^{-1}.

Gonzales-Cobos et al.[20] carried out glycerol electro-reforming (2 M glycerol in 0.5 M NaOH electrolyte) at 20 °C in an EC fitted with a Pt_9Bi_1/C anode and a Pt/C cathode; they obtained hydrogen production rates of 0.11 and 0.23 $(Nm_{H2})^3$ $h^{-1}m^{-2}$ and electrical energy consumptions of 15.0 and 20.2 kWh $(kg_{H2})^{-1}$, for cell voltages of +0.55 V and +0.70 V, respectively.

Bio-sourced alcohols and polyols are often obtained from sugar fermentation. This supplementary step increases the cost for the whole hydrogen production process. The direct feeding of an electro-reformer with glucose and xylose for hydrogen production has then been considered[21]. Glucose and xylose (0.1 and 0.5 M in 0.1 M NaOH aqueous electrolyte) were electro-reformed at 20 °C using a Pd_3Au_7/C anode catalyst and a Pt/C cathode catalyst at +0.4 V, +0.6 V and +0.8 V, with hydrogen production costs ranging from 1.60 € to 3.20 € kg_{H2}^{-1}, lower than those from wind, solar or nuclear water electrolysis (between 4.15 \$ kg^{-1} and 23.27 \$ kg^{-1}). Replacing the Pd_3Au_7/C anode catalyst by a Pt_9Bi_1/C one allowed electro-reforming 0.1 M glucose in 0.1 M NaOH electrolyte at +0.3 V[22] with an energy consumption of only 7 kWh kg_{H2}^{-1}.

Raw biomass, i.e., lignin[23] and cellulose[24], were also considered for the electrochemical production of hydrogen. For example, electro-reforming of lignin and cellulose using a polyoxometalate as anode catalyst was performed[24] with an electric consumption of ca. 8.5 kWh kg_{H2}^{-1} for a current density of 0.2 A cm^{-2}.

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

Electro-reforming of OOCs leads to EC voltages much lower than those for water electrolysis. But the achieved current densities, i.e., the hydrogen evolution rates, are 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 catalysts[26], 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 strategical, making the technology expensive as in the case of fuel cells[27]. PGM-

163 based catalysts display low selectivity towards CO_2 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 CO_2 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-reforming[28].

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

	PGM					Non-PGM	
Metal	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 breaking[29]. The reaction is driven by the Ni^{2+}/Ni^{3+} 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 CO_2 at moderate anode potentials

178 is not achieved and remains then the Grail Quest for electrochemists.

Fig. 2. Flow charts of integrated biorefineries to produce biofuels, hydrogen, and fine chemicals from (a) first generation of biofuels and (b) second generation of biofuels.

The small organic molecules that can be further electro-reformed into H_2, must first be produced from raw biomass by depolymerization or fermentation processes. The production of these small OOCs impacts the energy and cost balance of the whole electro-reforming process for hydrogen production[6]. Electro-reforming of raw biomass (lignin, cellulose, hemicellulose, chitin)[30,31] into CO_2 and H_2 would represent a very interesting perspective for the future, but also an important challenge due to the high stability of biopolymers.

9

On the other hand, biofuel industries generate important amounts of small OOCs as bioproducts. The production of first-generation biofuels from vegetal oil methanolysis generates ca. 10 wt% glycerol as by-product[32]. The production of second-generation biofuels from lignocellulosic biomass (cellulose, hemicellulose, and lignin) thermal treatment generates long-chain OCCs (for biofuel synthesis by hydrodeoxygenation reactions -HDO-) and small-chain OOCs (C5 and C6 sugars and derivatives)[33,34]. The C-C bond being difficult to break at low anode potentials, e.g., at low cell voltages, the electro-reforming of these by-products allows producing hydrogen simultaneously with value-added compounds of industrial interest[20,21,22]. Such approaches could make the biofuel industry more profitable and allow developing full integrated biorefineries generating zero waste. Figures 2a and 2b display the flow chart of the production of biofuels, hydrogen, and fine chemicals from raw biomass conversion.

5. Conclusion

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

OOCs produced as by-products/wastes by the biofuels industry, for example, can be 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 CO_2

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.

229 **Declaration of interest:** none

230

231

232   **References**

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