

## Supporting information

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### 1.1. Hydrogen quantification

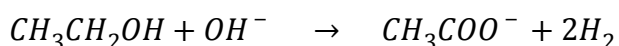
The amount of hydrogen evolved at the cathode was calculated by Faraday's laws (1), assuming that the coulombic efficiency of the hydrogen evolution reaction is close to 100%.

$$n = \frac{\int I(t)dt}{2F} \quad (1)$$

n is the number of hydrogen moles evolved at the cathode, I is the current load applied to the cell during the chronopotentiometric experiment and t is the duration time of this experiment. F is the Faraday constant (96485 C mol<sup>-1</sup>) and 2 is the number of electrons moles involved in the hydrogen evolution form water.

### 1.2 Energy balances for Ethanol electroreforming

The overall electro-reforming reaction for ethanol is:



According to the equation reported, for each mol of produced hydrogen 0.5 mol of ethanol and 0.5 mol of sodium hydroxide respectively are consumed; 1 kg of hydrogen corresponds to 495 mol whose production, require 247.5 mol of ethanol corresponding to a mass of 11.4 kg. In addition, 247.5 mol of for sodium hydroxide are required, corresponding to a mass of 9.9 kg (Table S1). A recent of investigation of the 'cradle to gate' life cycle assessment (LCA) determined the NaOH

energy cost to be 0.97 kWh kg<sup>-1</sup> [S1]; this value can be used to calculate an alkali-related energy expenditure of 9.7 kWh per kilogram of produced hydrogen. The electrical input needed for the electro-reforming of ethanol is 9.6 kWh kgH<sub>2</sub><sup>-1</sup>. Therefore, a net energy saving for H<sub>2</sub> production with respect to water electrolysis (47 kWh kg<sup>-1</sup>) will be achieved if the cost of ethanol contributes for less than 27.8 kWh per kilogram of produced H<sub>2</sub>. In order to achieve this goal, the ethanol energy cost shall be 2.4 kWh kg<sup>-1</sup> or lower. The assessment of renewable feedstock net energy cost is usually expressed in terms of the EROEI (Energy Return on Energy Invested), namely, the ratio between: (i) the output energy from ethanol and (ii) the energy input required for its production. According to the DoE the output energy density for ethanol is 7.4 kWh kg<sub>EtOH</sub> [S2]. On such a basis we can conclude that a bio-ethanol EROEI larger than 3.1 is required to obtain a net energy saving with respect to current water electrolysis technology. The DoE target for electrolyser stack electric energy input for 2020<sup>S4</sup>, 43 kWh kgH<sub>2</sub><sup>-1</sup>, is instead met for a bio-ethanol EROEI larger than 3.6. Hence, hydrogen production by electrolysis of bio-ethanol will be energetically convenient depending on the source of the alcohol, for example, using sugarcane (primary bioethanol) that is commonly reported to have an EROEI of 8 and higher. [S3,S4] and from cellulose (secondary bioethanol) with an EROEI potentially up to 35 depending on the production methods [S5]. In those cases, the total energy cost of 1kg of hydrogen produced by electroreforming is 29.9 and 21.7 kWh respectively.

It is important to mention that ethanol produced from cellulose (straw, wood chips) is particularly appealing as it can be obtained from the steam reforming of lignin. Lignin can be obtained even from spontaneously growing plants in lands not dedicated to agriculture, avoiding competition with the food chain supply.

Table S1: Electroreforming energy consumption at various (bio)ethanol EROEI values.

Electrical input (kWh/kgH <sub>2</sub> )	NaOH input		CH <sub>3</sub> CH <sub>2</sub> OH input			Total Energy cost (kWh/kgH <sub>2</sub> )
	Mass (kg/kgH <sub>2</sub> )	Energy cost (kWh/kgH <sub>2</sub> )	Mass (kg/kgH <sub>2</sub> )	EROEI	Energy cost (kWh/kgH <sub>2</sub> )	
9.6	9.92	9.62	11.43	3.1	27.65	46.9 <sup>[a]</sup>
				3.6	23.81	43.0 <sup>[b]</sup>
				7	12.25	31.5
				7.5	11.43	30.7
				8	10.72	29.9 <sup>[c]</sup>
				15	5.72	24.9
				33	2.60	21.8 <sup>[d]</sup>

<sup>[a]</sup> Current water-electrolysis-equivalent energy input

<sup>[b]</sup> DoE target for year 2020 for hydrogen production through electrolysis.

<sup>[c]</sup> Energy input of hydrogen production through electroreforming of primary (sugar cane) bioethanol.<sup>[S5]</sup>

[d] Energy input of hydrogen production through electroreforming of secondary (cellulose) bioethanol.<sup>[S5]</sup>

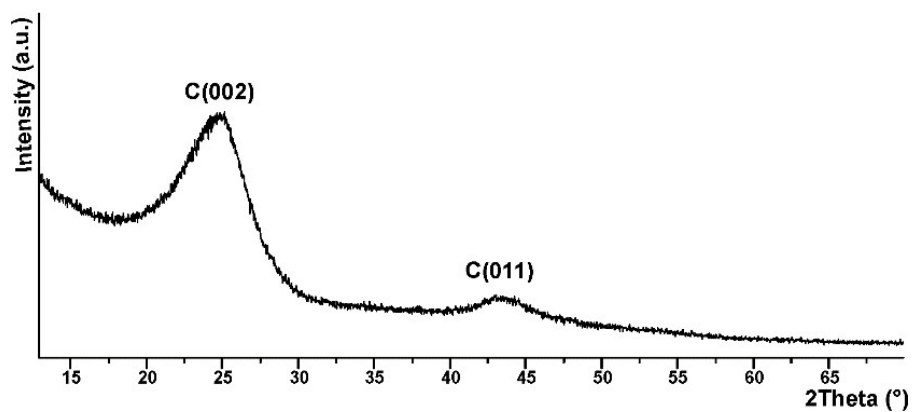


Figure S1. XRD of Rh/C.

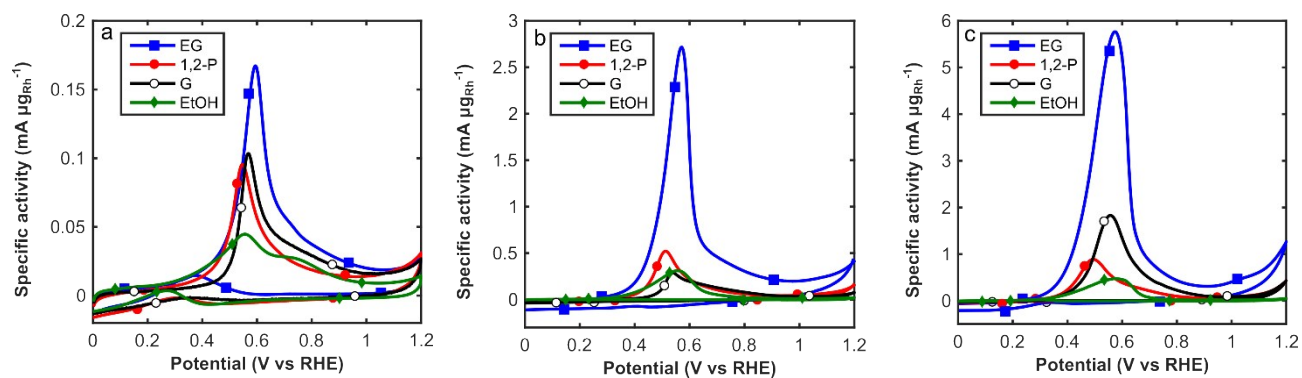


Figure S2. CVs of Rh/C in N<sub>2</sub> sat. 2M KOH and 2M alcohol solutions: (a) 25 °C, (b) 60 °C and (c) 80 °C. 0.2-1.2 V at 10 mV s<sup>-1</sup>.

### 1.3. Reference electrode temperature dependence

The potentials reported in the cyclic voltammetry curves reported versus RHE are calculated according to the Ag|AgCl|KCl<sub>sat</sub> electrode temperature dependence as described by Sawyer et al.<sup>[S6]</sup> The potential of silver-silver chloride versus normal hydrogen electrode (NHE) temperature dependence for ranges between 0°C and 95°C is described by:

$$E_{Ag|AgCl|KCl_{sat}} = 199 - 1.01 (T - 25)$$

With T in °C and  $E_{Ag|AgCl|KCl_{sat}}$  in mV.

The reversible hydrogen electrode (RHE) pH correction temperature dependence is described by:

$$E_{RHE} = - \frac{RT}{F} 2.303 pH$$

Where  $E_{RHE}$  is the potential of RHE versus NHE in V, R is the gas constant (8.31 J K<sup>-1</sup> mol<sup>-1</sup>), T is temperature in Kelvin, F is the Faraday constant (96485 C mol<sup>-1</sup>). The correction is applied adding  $E_{Ag|AgCl|KCl_{sat}}$  to the potential referenced versus Ag|AgCl|KCl<sub>sat</sub> to get the potential versus NHE and then subtracting  $E_{RHE}$  in order to get potential versus RHE.

### 3. Supporting literature

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- 3 Seabra J. E. A., Macedo I. C., Chum H. L., Faroni C. E. & Sarto C. A. . Life cycle assessment of Brazilian sugarcane products: GHG emissions and energy use. *Biofuels, Bioproducts and Biorefining* (2011), **5**, 519–532.
- 4 Goldemberg J. Ethanol for a sustainable energy future. *Science* (2007), **315**, 808–810.
- 5 Hall C. A. S., Dale B. E. & Pimentel D. Seeking to understand the reasons for different energy return on investment (EROI) estimates for biofuels. *Sustainability* (2011), **3**, 2413–2432.
- 6 Sawyer D.T., Sobkowiak A., Roberts J., *Electrochemistry for Chemists*, 2nd ed., ISBN-13: 978-0471594680

