Influence of the GDL and assembly mode of a PEM cell on the ethanol revalorization into chemicals

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Abstract

This work reports the influence of the gas diffusion layer (GDL) and cell assembly mode on the ethanol revalorization through the electro-reforming process, focusing on hydrogen and value-added organics (acetaldehyde, ethyl acetate and acetic acid) products distribution. All essays were conducted in a Proton Exchange Membrane (PEM) Electrolysis Cell of 5 cm^2 at mild conditions (80 ºC and 1 atm) on commercial Pt/C (cathode) and PtRu/C (anode) catalysts. In this scenario the selection of a proper GDL and way of assembly proves to be a critical step influencing the electrochemical performance. Carbon paper-based configurations exhibited the best profiles in terms of electro-catalytic activity, reaching high current density values (600-720 mA·cm^{-2} at 1.4 V of cell potential), which are close to those obtained in alkaline media. Conversely, that based on porous titanium showed a lower efficiency (less than a half) due to the mass transfer limitations of reactants and products through the GDL, as confirmed by the electrochemical impedance spectroscopy essays. Regarding organic product distribution, non-assembled carbon paper-based configuration displayed the best results, increasing the production of value-added organics and shifting the acetic acid generation to lower cell potential values (close to 0.7 V). This was attributed to the direct deposition of the catalytic layers over the membrane instead of over the carbon GDL, which enhances the

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1   reactants and ions transport, improving the electrochemical activity. In addition, this

2   configuration showed quite lower energy requirements for H_2 production (<20

3   kWh·kgH$_2^{-1}$ at 0.8 V) in comparison with a PEM water electrolyzer stack.

4   **Keywords:** Ethanol electro-reforming; PEM cell architecture; GDL; assembly mode;

5   hydrogen; value-added organic production.

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7   1. Introduction

8   The world total population has not stopped to increase since the middle of the 20th century

9   which has caused a serious raise in the energy consumption. This fact, joined with the

10   exhaustion of fossil fuels reserves, has led the scientific community the challenge of

11   searching new and cleaner alternative ways of energy [1-3]. In this context, bioethanol

12   has attracted great interest as fuel, due to its numerous advantages: it is nontoxic, safe,

13   easy to transport (liquid compound) and has a higher energy density (8 kWh·kg^{-1}) than

14   other compounds such as methanol [4]. Also, it can be produced from biomass feedstock

15   (energy crops, grain, corn…) becoming a renewable fuel as the total balance of carbon

16   remains constant. It is widely used in gasoline (mainly in USA), and can be used more

17   efficiently in fuel cells (DEFC), being one of the best substitutes to the internal

18   combustion engines due to its low emission of pollutants [5]. Alternatively, bioethanol

19   can be electro-oxidized in a proton exchange membrane (PEM) ethanol electrolysis cell

20   (EEC) to produce hydrogen, which is considered an interesting energy vector in the last

21   decades [6]. The viability of hydrogen generation from light alcohols is well developed

22   in the current literature [7-13], requiring lower energy consumption (25-30 kWh·kgH$_2^{-1}$)

23   than water electro-reforming systems (50 kWh·kgH$_2^{-1}$), which constitutes an attractive

24   process from an industrial point of view [14]. In an EEC, ethanol is electro-oxidized at

the anodic side of a PEM cell, leading to the formation of carbon dioxide, protons and electrons (Eq. S1 from the supplementary information (SI), $n = 12$ transferred electrons). The external circuit provides the electrical potential to drive the reaction, while protons migrate through the proton exchange membrane to the cathode side, where they recombine with electrons generating high purity hydrogen (Eq. S2). However, in the practice, low yields towards CO_2 have been generally reported due to the high energy requirements to break the C-C bond. This results in a partial ethanol electro-oxidation with the formation of different organic compounds such as acetaldehyde (Eq. S3-S5), and in a less concentration, acetic acid (Ec. S6-S8) [15]. In this scenario, different authors have focused on the study of anodic electro-catalysts with the purpose of improving the reaction kinetic of ethanol oxidation. Thus, bimetallic catalysts such as Pt-Ru/C and Pt-Sn/C, among others, have proved to be a suitable option promoting the electrochemical process [16-21]. However, this is not the only important parameter to consider of this technology since the cell architecture could play a key role in the electro-reforming process. In general terms, a typical PEM cell unit includes a membrane electrode assembly (MEA) sandwiched between the flow field plates (FFPs) of the anode and cathode, into which flow channels are grooved. The MEA is the most important part of the cell, containing two gas diffusion and catalyst layers (GDLs and CLs) on the anode and cathode side respectively, and a proton exchange membrane in between [22]. The GDL plays a very important role in the performance of these devices, allowing an efficient transfer of the reactants to the catalytic layer and a correct evacuation of the produced compounds. Also the mass transport in the diffusion layer seems to have a strong effect on the PEM cell behaviour, being able to decrease the efficiency of the process [23]. Parameters such as thickness and porosity of the layers, permeability, or conductivity, along with suitable compression conditions and reaction area position in the catalyst

layers must be considered [24-28]. In this context, different authors have studied the GDL type and MEA architecture testing different materials [22, 23, 29-33] and modifying the pressure conditions of MEA assembly [34]. However, these studies deal with the management of generated water in the cathode side of a PEMFCs in order to avoid the flooding or dehydration processes [35], limiting the mass transport of oxygen to the catalyst. In this sense, most of the available current literature is related to the fuel cells field, while papers which deal with the influence of the MEA architectures on the alcohol electro-reforming performance are scarce [36]. Therefore, in order to reach a compromise between both performance for alcohol electro-reforming and cost requirements, the structural, electrochemical and transport parameters that characterize the GDL and assembly conditions in the PEM cell need to be optimized.

Other point to highlight is the product distribution obtained from ethanol electro-oxidation. Most of the authors have exclusively focused on the hydrogen production rates on the cathode. However, the anodic co-production of value-added organics such as acetaldehyde, acetic acid or ethyl acetate would be more advantageous from an economical point of view. Therefore, the overall obtained profit of the process could be increased from the simultaneous production of all those compounds, mainly if the selectivity toward acetic acid is high. In this sense, the electro-catalytic pathway is presented as a promising alternative to the traditional systems, since it is possible to simultaneously co-produce hydrogen and value-added organic compounds in an only reaction step, directly separated into two compartments (anode and cathode chambers). Furthermore, the use of a PEM cell reactor brings several advantages such as potential energy savings and reduction of the environmental impact, compared with those coming from the acetaldehyde (Wacker process) [37], hydrogen (natural gas steam reforming) and acetic acid (methanol carbonylation) conventional production processes. In addition,

it is a compact device easily to scale by modulation and it is possible to couple with renewable energy systems.

Taking all into account, the aim and contribution of the present work is to evaluate the influence of different MEA architectures (varying the GDL type, catalyst layer support and way of assembly) on the ethanol electro-reforming process, focusing on the product distribution (hydrogen and organic compounds) in order to accomplish a better ethanol revalorization.

2. Material and methods

2.1 Membrane electrode assembly (MEA) preparation using different configuration

In this paper three configurations of membrane electrode assembly (MEA) named *a*, *b* and *c* were tested in order to study the influence of the gas diffusion layer (GDL) and assembly mode on the ethanol electro-oxidation, focusing not only on the activity but also on the product distribution.

Bimetallic commercial catalysts of Pt-Ru (Ru-40% Pt-20% PtRu/C-Alfa Aesar) and Pt supported on carbon (20% Pt/C-Alfa Aesar) were used as the anode and cathode, respectively, and for all configurations. Coating inks containing proper amounts of each electrocatalyst were prepared to obtain a loading of 1.5 mg/cm^2 for the anode and 0.5 mg/cm^2 for the cathode electrode. To this purpose, catalysts in powder form were dispersed in a solution of Nafion ionomer (5 wt. %, Sigma- Aldrich) and 2-propanol with a binder/catalyst weight ratio of 3.64. Then, ink solutions were sonicated for 2 h using an ultrasonic bath (110 W/50-60 Hz, Selecta) before deposition.

On the other hand, a proton conducting Nafion membrane of 180 μm thickness (supplied by Hydrogen Works) was used as the electrolyte. As described in other studies [9, 38],

prior to use, the polymeric membrane was pretreated through successive immersion in H_2O_2 and H_2SO_4 solutions (100 ºC for 3 h) and finally in deionized water.

So-called configuration *a* corresponds to the conventional configuration used by many authors [39-41] and served as standard. It was formed by a GDL of carbon paper TGP-H90 (0.25 mm, supplied by Fuel Cells Earth), which also worked as a support for the metal active catalytic layer. Inks were thus deposited on carbon paper substrates by spry at 80 ºC in order to evaporate the 2-propanol present in the solution, obtaining the metal loading specified above. Finally, different hot-pressing steps were conducted at different levels of temperatures from 30 ºC to 120 ºC at intervals of 10 ºC. Each level was kept for 1 min and in the last step 1 metric ton was applied for 3 min.

Configuration *b* uses two porous titanium plates (0.5 mm) as GDLs instead of carbon paper. In this case, inks deposition was carried out directly on both sides of the polymeric membrane, which worked as a support instead of the GDL. This resulted in a fine catalytic layer which could reduce ohmic resistance of the process (related to the mechanical part of the cell). Moreover, in this case, there was no need for a heating-pressure assembly step but the simply sandwich of the membrane (with the catalytic layer) and porous titanium plates with the rest of components of the cell in the montage step.

Finally, configuration *c* combines both previous configurations. This way, the GDL employed here was carbon paper (same specifications as for configuration *a*) and the deposition of the inks was carried out directly on the membrane sides (as for configuration *b*), avoiding the high-pressure assembly stage.

Figure 1 shows a scheme of the three proposed MEA configurations.

2.2 Electrochemical reforming of ethanol in a proton exchange membrane reactor

Experimental tests were carried out in a PEM electrolysis cell SQUAREPARK 5 (purchased from Pragma Industries) with a geometric surface area of 5 cm^2. The MEA was introduced between two Teflon gaskets designed to avoid short-circuiting of the cell. Graphitic bipolar plates of 5 mm thickness and 25 cm^2 of area were placed on both sides of the MEA. The plates present parallel indentations, with 1 mm x 1 mm of depth and a total volume of 3.51 cm^3. Also these components count with a hole of 1.5 mm of diameter to introduce a thermocouple to control the temperature of the process. In order to ensure the sealing between anode and cathode compartments various o-ring were placed in the graphite plates. These latter are in contact with two gold-plated copper alloy electrical collectors, which allow the transmission of the electrical current to the graphite plates. Finally, all the above items were placed between two external compression plates of steel (16 mm of thickness and 64 cm^2 area) applying a par of 1 Nm with a torque wrench.

The anode compartment of the cell was supplied with a 4 M water/ethanol solution, while deionized water was fed to the cathode, in order to keep a suitable humidity on the membrane. Both streams were preheated at 80 ºC and flow rates were regulated using a peristaltic multichannel pump (Heidolph 5001), fixing the value in 2 mL·min^{-1} for the anode and cathode respectively, according to previous works [42]. The anodic chamber of the PEM reactor operated in continuous mode, while the deionized water was recirculated in the cathode. In addition, a cooling condensation column was installed (- 6 ºC) with the purpose of avoiding ethanol evaporation in the feeding reservoir. Electrochemical measurements were carried out using a potentiostat/galvanostat VERTEX 5V (Ivium technology) controlled by a Research Electrochemistry software. Polarization curves were conducted at a potential range between 0-1.4 V and 20 mV·s^{-1} scan rate in order to study the electro-catalytic performance related to each configuration.

Then, an electrochemical impedance spectroscopy essay (0.1-10000 Hz and 1 mV of amplitude) was carried out in the range of 0.5 to 0.9 V with the aim to determine the different resistances involved in the process. Moreover, chronopotentiometry essays were carried out to determine the as-derived product distribution (organic compounds and hydrogen). To that purpose, different levels of constant current, ranging from 0.2 to 0.8 A at intervals of 0.2 A, were applied. Each level was kept for 500 s. The organic value-added liquid production was then analyzed offline (every 15 min), in an Agilent Technologies 8220A gas chromatograph equipped with a FID detector and a capillary column (Agilent DB-WAS UI, 30 m x 0.250 mm x 0.25 μm), using helium as a carrier gas. Hydrogen production flow rate from the cathodic compartment was measured by a high-precision flowmeter (supplied by Mervilab) and compared with the theoretical one via Faraday's Law. In order to check the stability of the system, a mild-term electrochemical reforming experiment was carried out for 2 h operating under 0.5 A constant current density (0.1 A·cm^{-2}). Finally, for configuration b, this technique was also conducted applying OCV cycles of 30 s every 30 min.

3. Results and discussion

In order to study the electro-catalytic performance for the three proposed configurations, a linear sweep voltammetry test was performed. First, the applied potential was verified to be invested in the alcohol electro-reforming process excluding water electrolysis contribution. For that purpose, a separate experiment with only deionized water was conducted at 80 ºC and room pressure screening a potential range between 0 to 2.5 V at 20 mV·s^{-1} of scan rate. Figure 1S from the SI (supplementary information) shows the comparison between these results with the profile obtained for 4 M ethanol/water mixture recorded at the same conditions (within an interval of 0-1.4 V) using the configuration a. Note that hydrogen production is only attributed to the alcohol electro-oxidation, since

no current density was obtained at this potential range (0-1.4 V) with the deionized water experiment, checking the onset potential for water electrolysis close to 1.4 V. After proving the viability of the system, a comparative study among the different configurations was accomplished. Figure 2 depicts the comparative between the linear sweeps for the three configurations at 2 ml·min^{-1}, 80 ºC, room pressure and 4 M ethanol/water solution. In general terms, a typical trend was obtained: current density and hence hydrogen production rate increased as along with the applied potential, which is attributed to the enhanced kinetic of the electrochemical reaction by increasing the driving force. At low polarization levels the process is governed by kinetic limitations, showing the onset potential for ethanol electro-reforming close to 0.4 V (although partial ethanol electro-reforming is thermodynamically favoured at a potential higher 0.08 V [43]). In this sense, non-important activity toward H_2 and organic liquids was observed for this potential range, since no current density was registered. This suggest that in this potential range there are some kinetic limitations (activation energy,) requiring an increase in the driving strength and consequently, a rise in the overpotential. At an intermediate potential range (0.5-1 V), the system follows an ohmic behaviour being able to adjust to a straight line. It can be observed that the slopes for both carbon paper configurations (*a* and *c*) were considerably higher than that obtained for configuration b, using porous titanium as GDL, which showed lower values of current density. Finally, at high polarization levels, the system starts to be limited by the mass transfer resistance, especially when the electro-catalytic activity is high, reaching a final current density of 600 mA·cm^{-2}, 250 mA·cm^{-2} and 725 mA·cm^{-2} for configurations *a*, *b* and *c* respectively at 1.4 V. Accordingly, the worst result in terms of electro-catalytic activity was obtained for configuration *b*, where mass transfer limitations seemed to take place at lower potentials values (from 0.8 V) than those for configurations *a* and *c*, preventing from a proper electro-catalytic performance.

This fact can be attributed to the properties and characteristics of the material employed as a GDL. The porous titanium thickness is twice that of carbon paper, which could derive in a higher resistance to mass transfer for reactants and products involved in the electrochemical reactions, and even for the ions transported through the GDL. It can be also observed that between the two configurations which used carbon paper as a GDL, configuration c is highlighted. Note that a maximum current density of 720 mA·cm^{-2} was reached at the end of the explored interval, which is very promising compared with previous works on ethanol electro-reforming carried out under the same operation conditions (200 mA·cm^{-2} at 1.1 V, close to 4 times lower than that presented in this work) [9, 11] and very similar to those obtained in basic media (theoretically more efficient) [44]. For this configuration, the mass transfer resistance took place at the end of the potential range (from 1.3 V) compared to the configuration a, where the efficiency loss in the current density starts to be appreciable from 1 V of applied potential. This phenomenon could be explained attending to differences in the electrode preparation and the assembly mode of the MEA. In case of configuration a, inks deposition was carried out over the carbon paper requiring a high pressure-temperature assembly step to conform the MEA. However, for configuration c, inks were deposited directly on both sides of the membrane. This results in the formation of a more homogenous catalytic layer on the membrane surface, which could enhance the reactants and ions transport, shifting mass transfer limitations to higher potential values. Moreover, this configuration seemed to allow a better GDL-membrane contact without an assembly step, which would avoid possible damages in the GDL surface during the preparation (breakages, pore blockage). In order to better support the proposed hypothesis, electrochemical impedance spectroscopy essays were conducted. This technique allows quantifying the different resistances involved in the electro-reforming process. First, the influence of the potential

in the total resistance was evaluated for each configuration. Essays were performed at 80 ºC for 4 M of ethanol/water solution and 2 ml·min^{-1} varying the cell potential from 0.5 to 0.9 V. Also, the frequency range was fixed between 0.1-10000 Hz with 1 mV of amplitude. Experimental data were fitted to an equivalent electrical circuit formed by 3 resistors (*R1*, *R2* and *R3*) and 2 capacitors (*C1* and *C2*) as summarized in Table 1. *R1* is associated with the resistance of the MEA, while the sets *R2-C1* and *R3-C2* are associated with the anode and cathode resistances, respectively. Figure 3.a shows the Nyquist diagram for configuration *a* (rest of configuration are not shown since the behaviour is analogous). In general terms, an increase in the applied potential causes a decrease in the offered resistance toward the ethanol oxidation reaction, and hence an enhancement in the electro-catalytic activity due to a rise in the kinetics of the process. This decline in the resistance values are clearly visible at low potential range (0.5-0.7 V) where *R2* varies from 0.813 to 0.515 ohm and *R3* from 0.099 to 0.056 ohm. At higher potential range (0.7-0.9 V), the differences start to be lower reaching very similar resistance values (see Table 1). This fact is attributed to the mass transfer limitations that take place at high potential levels (as corroborated in the LSV tests, Figure 2), which correspond to a maximum in the EOR kinetics, and therefore, to the obtention of minimum resistance values close to 0.44 and 0.06 ohm for *R2* and *R3*, respectively. Note that *R3* value for the last potential step (0.9 V) is lightly increased from 0.056 to 0.062 ohm. Considering the experimental error in the mathematical fitting model process (up to 5%), these small differences would be within the limits of the standard deviation, and then, the last three cathodic resistances values (*R3*) can be considered practically constant. Even with this, it is important to highlight that despite of this slight variation in the *R3* parameter, the total impedance value (sum of *R1*, *R2* and *R3* contribution) decreases with the increase in the potential for the last interval of study (check the x-axis cutting point at 0.8-0.9 V, Figure 3.a). Also, it

can be observed that $R1$ remains practically constant in the whole potential range, which proves that the MEA resistance is independent of the applied potential. Note that $R2$ values (anode) are always higher than $R3$ values (cathode). Therefore, the rate determining step of the electro-reforming process seems to be caused by the anodic reaction (ethanol rupture) more than by protons and electrons recombination for hydrogen production in the cathodic chamber. Once the potential influence in the total impedance was accomplished, a comparative between the impedance values obtained for each configuration is showed in Figure 3.b at 0.5 V of cell potential. In general terms, porous titanium-based configuration exhibited the highest z", which is reflected in the fitted parameters summarized in Table 2. It can be observed that all the architectures studied presented low $R1$ values compared with the rest of parameters, being the MEA contribution negligible in the total cell impedance. Resistances associated with anode and cathode were considerably higher for porous titanium configuration compared with carbon paper-based ones. This effect can be sharply appreciated for $R2$ parameter, reaching values of 3.41, 0.81 and 0.77 ohm for the configurations *b*, *a* and *c* respectively. In this sense, porous titanium architecture offers a higher anodic and cathodic charge transfer resistance, limiting the transport for reactants and products through the GDL. This is in consonance with the results obtained in the linear sweeps voltammetry tests detailed above, where the configuration *b* exhibited the lowest electro-catalytic performance.

However, small differences were found for the carbon paper configurations. Anyway, the anodic and cathodic resistances ($R2$ and $R3$) were slightly lower for configuration *c*, which may improve the performance of the system. This corroborates the hypothesis proposed in this work, where the new membrane-electrode-assembly set formed by a

catalytic layer deposited directly over the membrane leads to an enhancement of mass

transport, which increases the activity of the ethanol electro-reforming process.

Chronopotentiometry measurements were then carried out for a 4 M water/ethanol

solution at 80 ºC and different current steps (i.e. 0.2, 0.4, 0.6 and 0.8 A, which correspond

to 40, 80, 120 and 160 mA·cm^{-2} of current density, respectively) for 500 s. The purpose

was to evaluate the product distribution (organic compounds and hydrogen) and energy

requirements related to each level of applied current. Figure 4 shows the potential vs. time

profile for each of the three configurations at four different applied current values. An

increase in the potential with the current was registered for all architectures, as it

corresponds to the behaviour of this type of systems. For the same current, the lowest

potential values were attained with the carbon paper configurations (*a* and *c*), fact that

significantly influences on the total cell energy consumption. In addition, these

configurations showed a stable potential profile vs. time on stream for each current step,

as a steady state was always reached at the beginning of each polarization. On the other

hand, configuration *b* shows very unstable profiles mainly from the third applied current

step (0.6 A, 120 mA·cm^{-2}). At this level, a considerably increase in the potential was

registered, exceeding the 1.4 V range, indicating that water and ethanol electro-reforming

processes simultaneously occurred (as demonstrated in Figure 1S, SI). In this sense, the

mass transfer limitations associated to the porous titanium GDL cause an increase in the

driving force in order to keep the kinetics imposed at this level of applied current

(demanded hydrogen production), shifting the potential to more positive values and

consequence, reaching the water electrolysis region. Note that despite of the mass transfer

limitations take place from the third step of fixed current, the effect caused by the porous

titanium GDL was also noticeable at low current levels (0.2-0.4 A). At this range, the

potential values registered for configuration b (0.62-0.8 V) were higher than those

Regarding the total product generation, hydrogen production was measured and compared with the theoretical one expected. As an example, results for the configuration *a* are displayed in Figure S2 (SI). The rest of layouts presented an identical profile. Note that experimental hydrogen rates obtained for each applied current step are similar to those calculated via Faraday's law, confirming that there are not faradaic losses related to the hydrogen production. In addition, from experimental hydrogen flow rate data and the potential-current profile depicted in Figure 4, it was possible to calculate the corresponding energy requirements, expressed in $kWh \cdot kgH_2^{-1}$, for the three configurations at each current level. Note that an average potential (V_m) was used in all calculations, since the steady-state regime was quickly reached, mainly for carbon paper configuration. All data were collected in Table 3. As expected, the required power (W) and total energy consumption ($kWh \cdot kgH_2^{-1}$) increases proportionally to the applied current, as the proportion with that the required power increases is higher than the rise in the hydrogen flow rate production. The lowest energy requirements were obtained for configurations *a* and *c* (14-22 $kWh \cdot kgH_2^{-1}$ at 40-160 $mA \cdot cm^{-2}$), which showed a quite similar profile. Configuration *b* exhibited higher potential ranges, demanding twice the power to produce the same amount of hydrogen, especially at the last two current steps,

where very high potential values (0.9 V to 1.8 V) were reached resulting in a consumption range comprised between 35.2-44.6 $kWh \cdot kgH_2^{-1}$. Note that these energy requirements are closer to the consumption of a PEM water stack (50 $kWh \cdot kgH_2^{-1}$) [9], as part of the total energy is being invested in the water electrolysis process, decreasing the cell energetic efficiency.

Along with H_2 production, in order to study the influence of the proposed configurations on the organic product distribution and, hence, the viability of ethanol valorization towards other value-added compounds, the anodic effluent was also analyzed. Figure 5 shows the organic production flow rates obtained for each layout at the different current steps. It can be observed that, regardless of the configuration, the main anodic product was acetaldehyde, followed by ethyl acetate and acetic acid, whose production was strongly related to the cell potential. H. Li et al. [45] suggested that, under the application of low cell potentials, adsorption and dissociation of ethanol take place mainly on Pt sites, producing acetaldehyde (Eq. S3-S5, SI). The subsequent oxidation of this molecule would generate reaction intermediates (CH_3CHO^- species) which remain strongly chemisorbed on the Pt active sites, leading to the poisoning of the anodic catalyst, thus inhibiting the electro-reforming process. On the other hand, under the application of higher cell potentials, water molecules could be activated in order to produce active OH^- species that are adsorbed on the Ru surface [45, 46] (Eq. S9, SI), which can further oxidize the adsorbed acetaldehyde leading to the formation of acetic acid (Eq. S6-S8, SI). Although in general the onset potential associated to each organic compounds obtained in this work are in consonance with those reported in the literature, the MEA architecture was found to modify the liquid product distribution, as explained below.

As expected, acetaldehyde was generated for the whole intensity range of study (0.2-0.8 A) from 0.5 V steady-state cell potential, since according to the ethanol reaction

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mechanism it is kinetically favored (0.082 V of theoretical potential). Carbon paper-based configurations (Figures 5.a and 5.c) exhibited similar ranges of acetaldehyde production, which were comprised between $1.6 \cdot 10^{-3}$-$6 \cdot 10^{-3}$ g·min^{-1} and $2.3 \cdot 10^{-3}$-$6.3 \cdot 10^{-3}$ g·min^{-1} for configurations a and c, respectively. Also, the overall production rate increases with the applied current, which corresponds with a higher level of cell potential and, therefore, a further progress in the electro-oxidation reaction mechanism. However, this trend was not fulfilled in configuration b (Figure 5.b), mainly from the third current step (0.6 A, 120 mA·cm^{-2}) to the end of the range. In this case, a decrease in the production rate was registered at higher cell potential values, which can be attributed to the simultaneous water electro-reforming process, as already commented above. In this sense, under these conditions, a competition between oxygen evolution and ethanol oxidation reactions seems to take place in the anodic compartment. Therefore, not all the applied energy is invested in the alcohol electro-reforming process and much of the total hydrogen is produced from water electrolysis, causing efficiency losses in terms of organic compounds generation.

Ethyl acetate begins to be produced from the second current level (0.4 A, 80 mA·cm^{-2}) at cell potential values close to 0.6 V (for the three configurations) but it is generated in a much smaller proportion than acetaldehyde ($1.7 \cdot 10^{-4}$ - $5.6 \cdot 10^{-4}$ g·min^{-1}), being around 8 wt. % of the total organic liquid production.

Acetic acid production occurred at different potentials levels depending on the configuration being tested. Thus, configuration a exhibited a low acetic acid production close to $1.22 \cdot 10^{-4}$ g·min^{-1}, which only occurred from the last current step at 0.8 V. However, configuration c seemed to enhance the generation of this compound since its production is shifted to a lower cell potential (0.7 V) from de second current step. Also, the range of production associated with configuration c was higher, approximately four

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times ($1.3 \cdot 10^{-4}$-$4 \cdot 10^{-4}$ $g \cdot min^{-1}$) than that obtained by configuration *a*. This is attributed to

the morphology and thickness of the catalytic layer depending on the material used as

support. Therefore, the direct deposition of both electrodes over the membrane surface

appeared to enhance the transport mechanism, increasing not only the electro-catalytic

activity but also the selectivity toward acetic acid. On the other hand, despite of the mass

resistance limitations offered by configuration *b* (demonstrated in the impedance study,

Figure 3), porous titanium architecture exhibited an acetic acid production slightly higher

($2 \cdot 10^{-4}$-$5 \cdot 10^{-4}$ $g \cdot min^{-1}$) than that of configuration *c*. However, note that the potential range

was considerably higher for this configuration (0.8-1.66 V) obtaining consumption values

per kg of acetic acid close to 44 $kWh \cdot kgC_2O_2H_4^{-1}$, a low competitive result compared to

that obtained for configuration *c* (26 $kWh \cdot kgC_2O_2H_4^{-1}$).

Furthermore, it is important to mention that the formation of other reaction products such

CO_2 was not detected. This compound is strongly limited in these systems, as the Pt-Ru

has a poor activity toward the scission of C-C bonds under low temperature conditions

(temperatures below 100 ºC). In order to check the possible generation of this compound

a chronopotentiometry was carried out at 0.5 A for 3 h (not shown in this study), where

approximately less than 1% in mole fraction of CO_2 was obtained working even in recycle

mode of operation.

Once studied the ethanol electro-reforming to different value-added ethanol-derived

compounds, and with the purpose of demonstrating the stability of each configuration for

future practical applications, a mild-term galvanostatic essay was conducted at 0.5 A (100

$mA \cdot cm^{-2}$) and 80 ºC for 2 h by feeding a 4 M water/ethanol solution (2 $ml \cdot min^{-1}$). The

selection of this applied current level was due to comparative purposes with the existing

data from the literature. Different authors have studied the stability of the EOR process

at these current values (0.5 A, 100 $mA \cdot cm^{-2}$) in both electrolysis [9, 11, 47, 48] and fuel

cell modes [49]. In this sense, to run this essay at the same operating conditions is essential to avoid errors in the comparison of system efficiencies since the consumption values hardly depends on the applied current. Figure 6.a depicts the variation of the cell potential with time on stream for the three configurations under study. An increase in the potential was observed during the first minutes of operation. However, after that period, the system seemed to achieve a steady-state potential (mainly for carbon paper configuration), which led to a stable operation during the rest of the interval. This loss of efficiency has been reported in other works [9, 49] and can be assigned to several reasons. Many authors hold the idea that the deterioration of the system is related to either the higher swelling degree of the polymer membrane [50-53] or to the poisoning of the catalyst at higher concentrated alcohol solutions. Another option is the accumulation of reaction intermediates derived from the partial electro-oxidation of ethanol, which could be chemisorbed on the Pt active centers, causing the progressive increase in the potential [54]. In addition, ethanol crossover can play an important role for the stability of these systems, poisoning the cathode chamber [53-56]. Regarding the different configuration tested in this work, *a* and *c* show the best electrochemical behavior, reaching a constant cell potential close to 0.8 V for the applied current. The steady-state value was reached in a short period of time (10-20 min), which supposes very promising values compared to other ethanol electro-reforming studies, where the transition time was estimated in 3 h [9, 11, 44]. Furthermore, the potential increase for the whole recorded range was very low for both configurations, approximately an increment of 0.02 V was registered after 2 h of experiment. This small decrease in the cell efficiency seems to be linked to the poisoning effect of adsorbed species on the catalyst layer instead of the swelling process, which would irreversibly destroy the MEA causing a noticeable increase in the potential.

Configuration *b* showed a different behaviour. The transition period until stabilization was significantly higher, requiring 1.8 V of cell potential to keep a constant applied current of 0.5 A, which is more than twice as much as it takes for carbon paper-based configurations to produce the same quantity of H_2. Taking into account this loss of efficiency, a galvanostatic open circuit potential (OCV) regenerative test was carried out for configuration *b*. This essay was conducted under the same conditions as the previous experiment, but with application of OCV cycles of 30 s every 30 min. In Figure 6.b, both profiles (with and without regeneration) are compared. It can be observed that including OCV steps, the potential is reduced to the half, reaching a steady-state cell potential close to 1 V, which might be associated to the removal of intermediates under fluid circulation without the application of current. The corresponding energy consumption was calculated for all configurations, obtaining values close to 19.3 kW kgH_2^{-1} for configurations *a* and *c*, while configuration *b* demanded 48 kW·kgH_2^{-1} and 26.8 kW·kgH_2^{-1} for the non-regenerative and regenerative tests, respectively. These results are very competitive compared with those energy requirements found in the literature at same operation conditions, which are around 27 kW·kgH_2^{-1} [9].

Taken all into account, the MEA architecture of a PEM cell has proved to be a key variable with a considerably influence on the ethanol electro-reforming process. In this sense, configuration *c* (based on carbon paper as GDL and a catalyst layer directly supported on the membrane without high-temperature and pressure assembly step) showed the best electrochemical performance. This novel layout exhibited high electro-catalytic activity in continuous mode (without recycling) of operation, low energy requirements in terms of hydrogen production and a suitable organic product distribution, shifting the acetic acid generation to lower cell potential values.

4. Conclusions

In summary, the influence of different ways of MEA architectures on the ethanol electro-reforming process for the added-value product generation (organic compounds and hydrogen) has been studied. For that purpose, three different configurations were designed changing the GDL type (carbon paper or porous titanium), the assembly mode (high temperature-pressure assembly or non-assembly step) and the active phase deposition (over GDL/membrane). Carbon paper configurations (*a* and *c*) exhibited the best electrochemical performance, reaching high density current values (600 and 720 mA·cm^{-2}) in the linear sweep voltammetry tests (same order as those obtained for basic medium) and low potential profiles in the chronopotentiometry essays. Conversely, configuration *b* provided lower current density values (300 mA·cm^{-2}) and a sharp increase in the potential for certain current steps, resulting in a low electrochemical activity,

Even more, despite faradaic hydrogen production was obtained for all configuration, the energy requirements were much lower for carbon paper-based configurations compared to that based on a porous titanium architecture, which can be associated to a higher architecture resistance and mass transfer limitations offered by porous titanium. Regarding the value-added compounds production, the organic product distribution was found to vary with the different MEA architectures. Acetaldehyde and ethyl acetate production starts at potentials close to 0.5 V and 0.6 V for all configurations, while acetic acid production was higher for configuration *c*, shifting overpotential to a lower value (0.7 V) compared to the rest of configurations (close to 0.8 V). Finally, electrochemical impedance spectroscopy essays showed the lowest resistance values for carbon paper configurations, being slightly better for configuration *c*. In this sense, the catalytic layer deposited directly over the membrane proved to be more active in electro-catalytic terms, enhancing the mass transfer and the selectivity towards acetic acid.

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1   **Figure captions**

2   Figure 1. Scheme of MEA configurations.

3   Figure 2. Linear sweep voltammetry tests for each configuration at 0-1.4 V potential

4   range. 80ºC, 1 atm and 20 mV·s^{-1} scan rate.

5   Figure 3. Electrochemical impedance spectroscopy essays. a) Nyquist diagram for

6   Configuration *a* at 0.5-0.9 V potential range, b) Comparative for each configuration at

7   0.5 V.

8   Figure 4. Stepped chronopotentiometry for each configuration between 0.2-0.8 A.

9   Figure 5. Liquid products distribution for each configuration from Figure 4. a)

10   Configuration *a*, b) Configuration *b*, c) Configuration *c*. 0.2-0.8 A.

11   Figure 6. Mild-term stability at 0.5 A of applied current. a) Potential profiles for each

12   configuration, b) comparative between standard and OCV mild-term test for

13   Configuration *b*.

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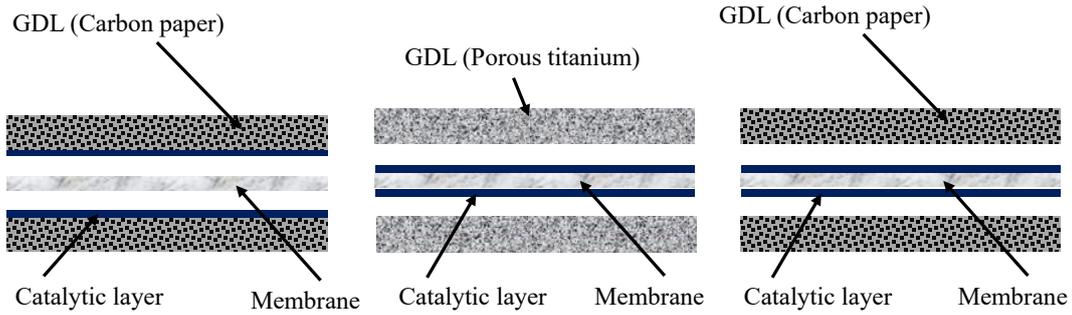
a) Catalytic layer deposited over the carbon paper. GDL: Carbon paper.

b) Catalytic layer deposited over the membrane. GDL: Porous Titanium.

c) Catalytic layer deposited over the membrane. GDL: Carbon paper.
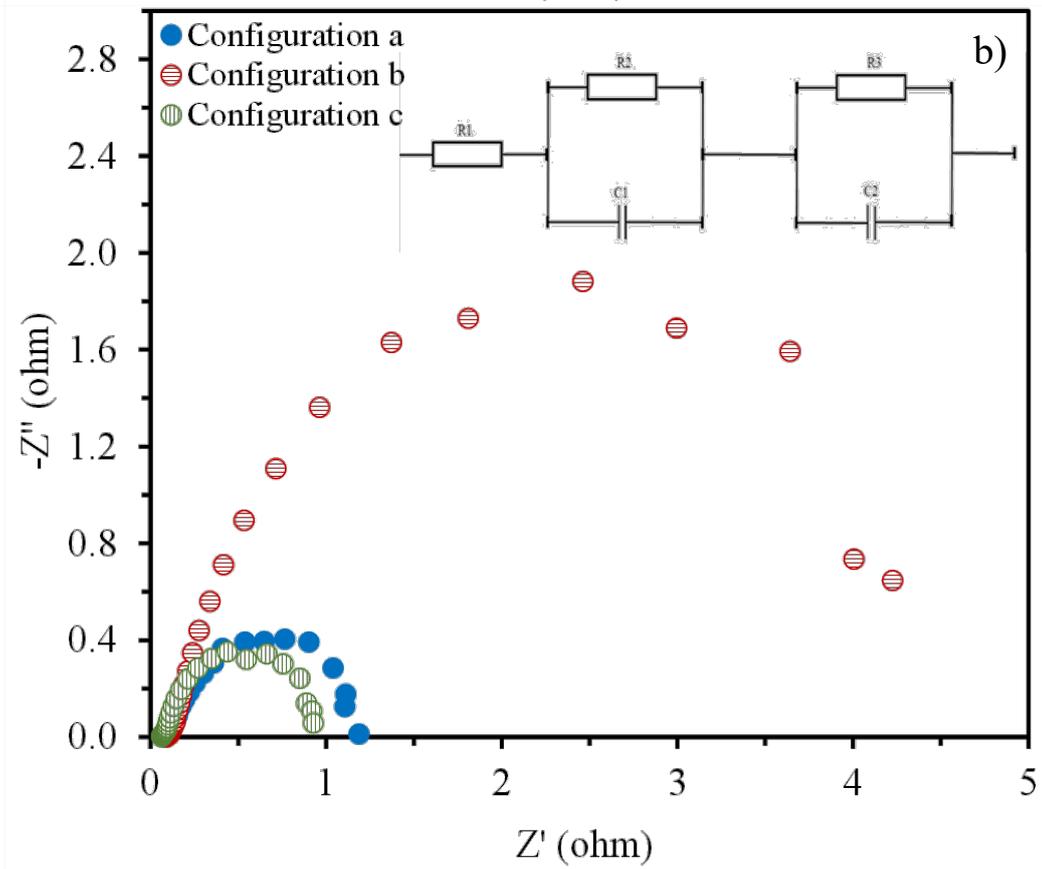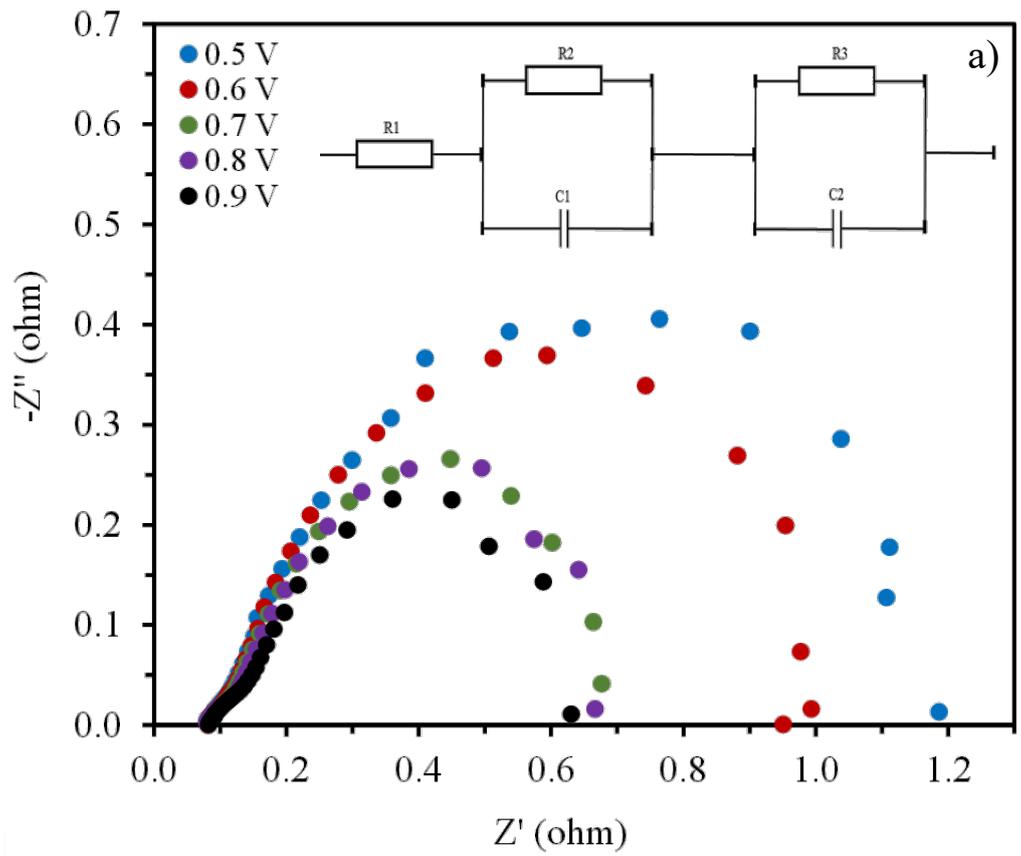
Figure 1.

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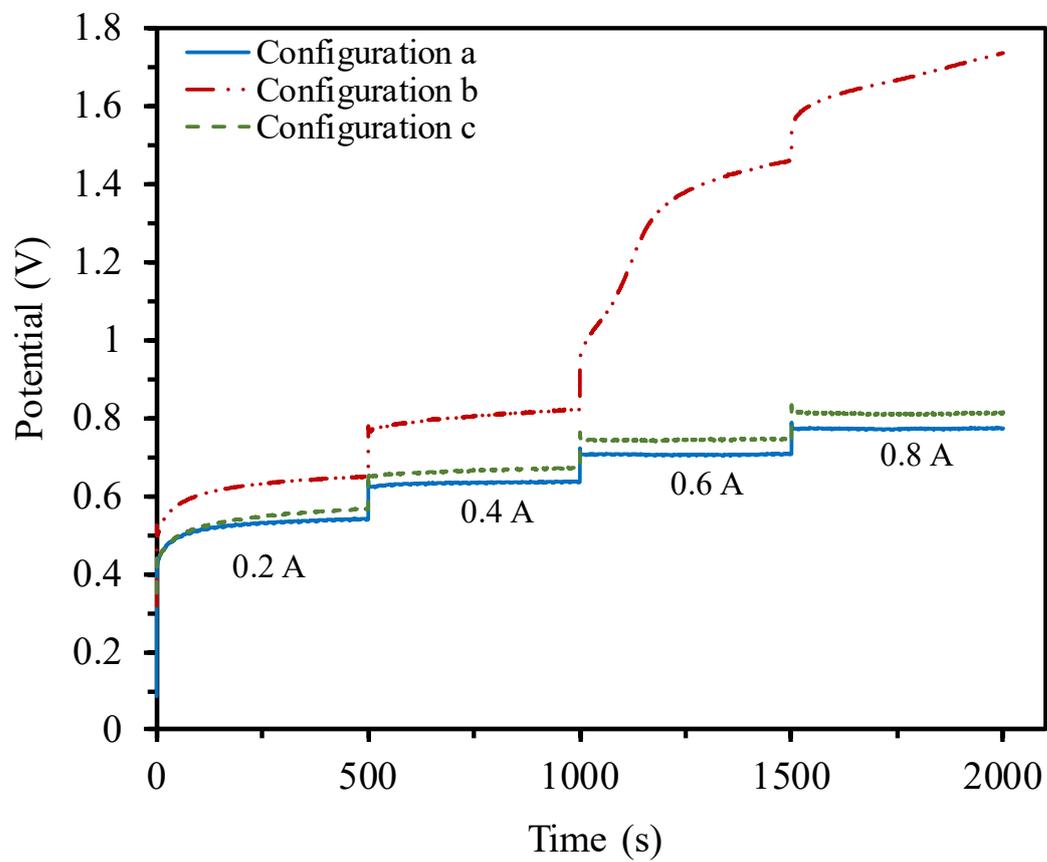15

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Figure 2.

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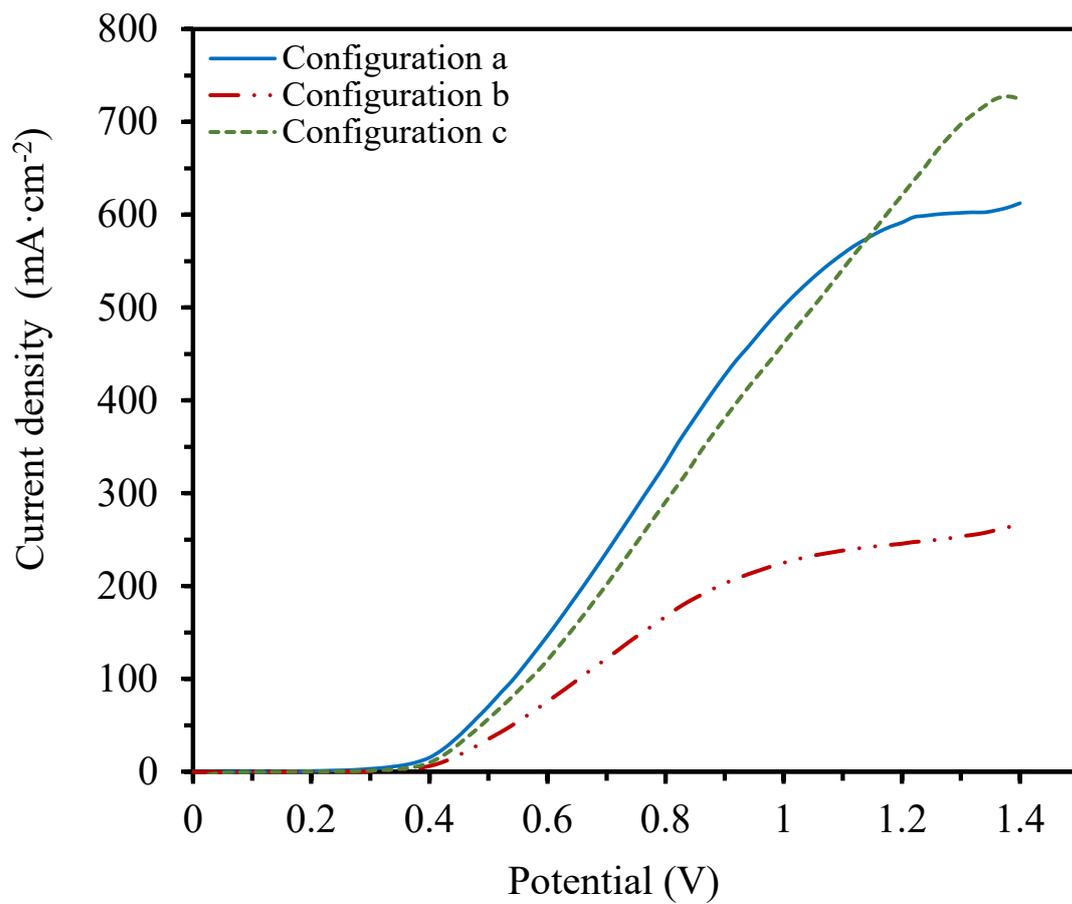
Figure 3.

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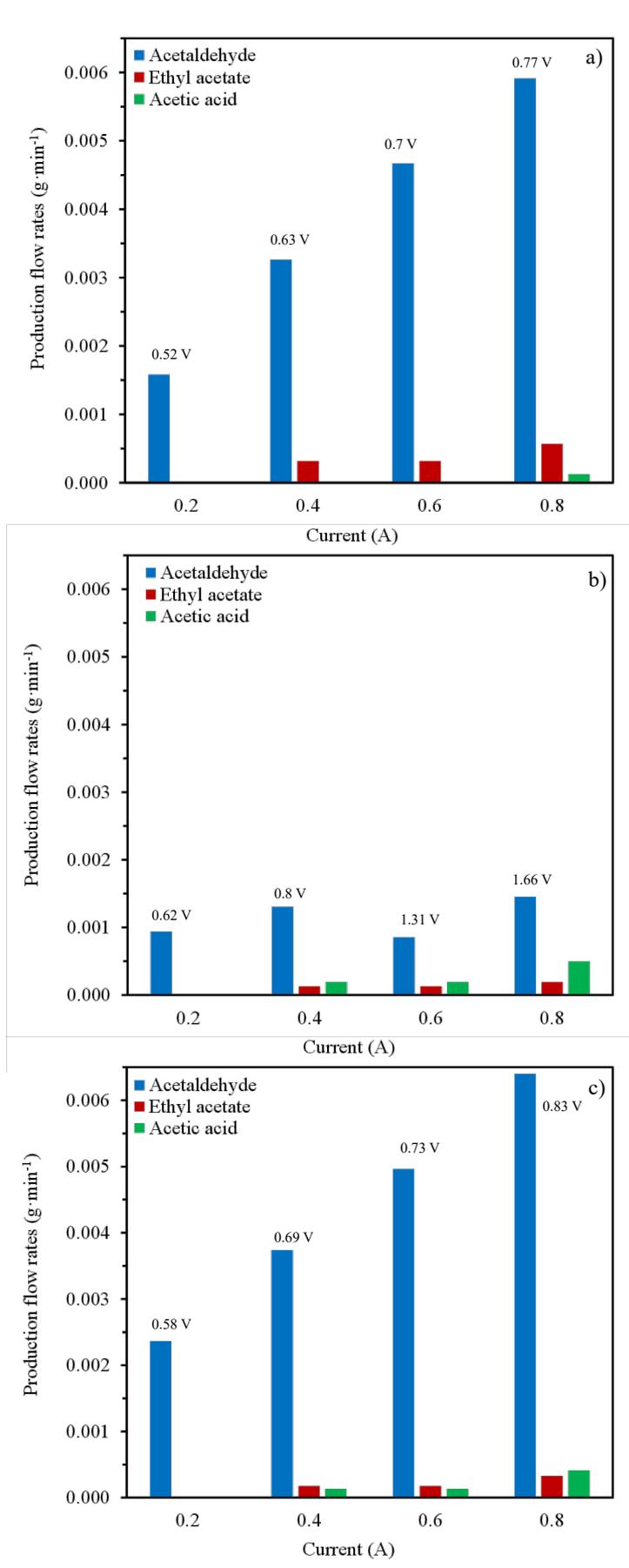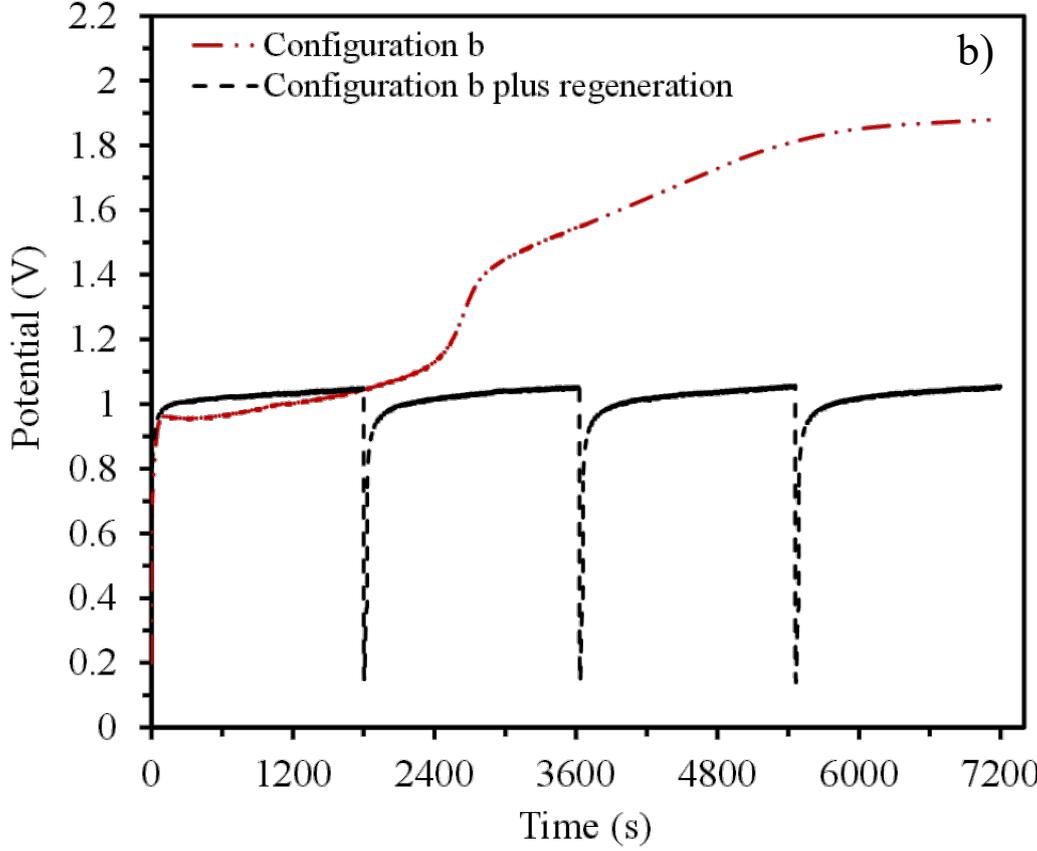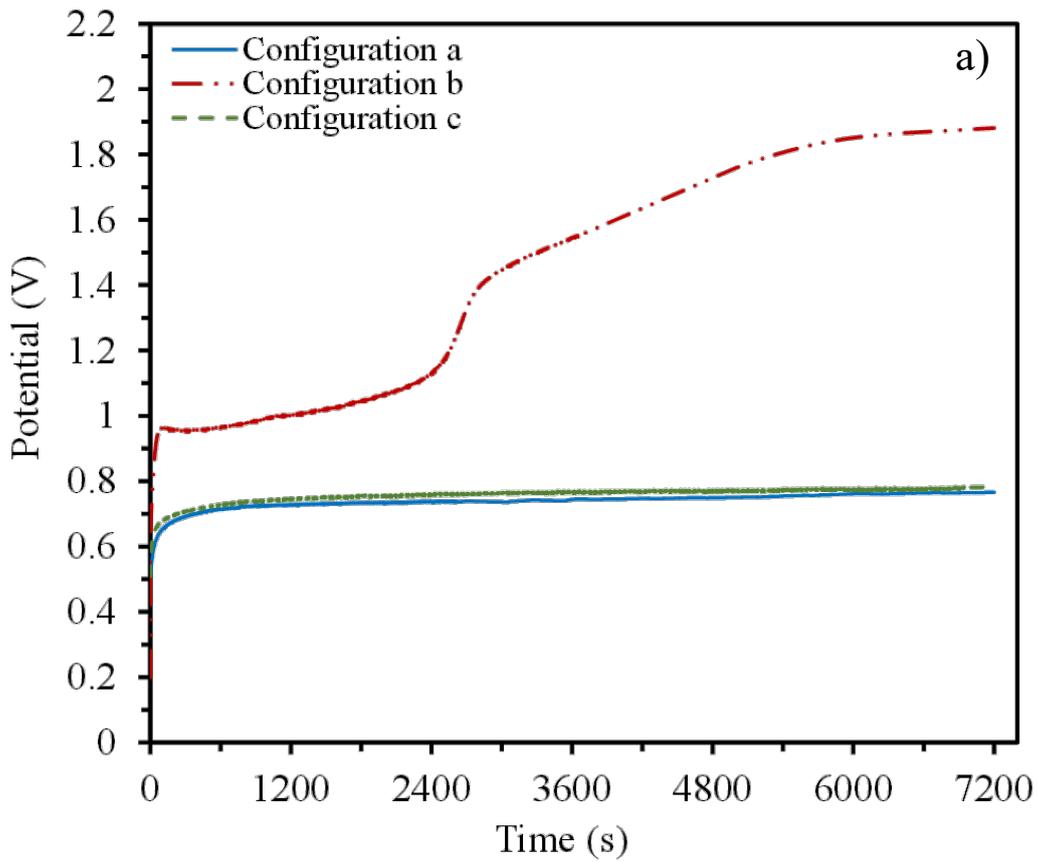3

Figure 4.

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Figure 5.

Figure 6.

1 **Table captions**

2 Table 1. Electrochemical impedance spectroscopy fitted parameters for the potential

3 range of study. Configuration *a*.

4 Table 2. Electrochemical impedance spectroscopy fitted parameters for all configurations

5 at 0.5 V of applied potential.

6 Table 3. Energetic requirements comparison for all configurations at different levels of

7 current.

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Table 1.

Components	Applied potential (V)				
	0.5	0.6	0.7	0.8	0.9
$R1$ (ohm)	0.094	0.092	0.089	0.089	0.092
$R2$ (ohm)	0.813	0.741	0.515	0.507	0.441
$R3$ (ohm)	0.099	0.078	0.056	0.056	0.062
$C1$ (F)	0.131	0.131	0.111	0.098	0.089
$C2$ (F)	0.053	0.046	0.023	0.015	0.013

Table 2.

Components	Configuration a	Configuration b	Configuration c
$R1$ (ohm)	0.094	0.111	0.088
R2 (ohm)	0.813	3.410	0.773
$R3$ (ohm)	0.099	0.134	0.053
$C1$ (F)	0.131	0.051	0.042
$C2$ (F)	0.053	0.045	0.024

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4   Table. 3

Current (A)	Vm (V)			Power (W)			Total energy consumption (kWh·kgH₂⁻¹)		
	Configuration								
	a	b	c	a	b	c	a	b	c
0.2	0.52	0.62	0.58	0.10	0.12	0.12	14.0	16.6	14.4
0.4	0.63	0.80	0.69	0.25	0.32	0.28	16.9	21.5	17.7
0.6	0.7	1.31	0.73	0.42	0.78	0.46	18.9	35.2	19.9
0.8	0.77	1.66	0.83	0.62	1.33	0.66	20.7	44.6	21.7

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