Hydrogen and electricity at once: An alkaline-acidic ethanol electroreformer

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ABSTRACT

This study presents the results of an alkaline-acidic ethanol electroreformer producing hydrogen and electricity simultaneously. This is due to the pH gradient between an alkaline anolyte/fuel (1 mol/L ethanol and 4 mol/L KOH) and an acidic catholyte/comburent (1 mol/L H_2SO_4), separated by a K^+-pretreated Nafion® 211 membrane to prevent chemical neutralization, resulting in an extra electromotive force. At 70 °C, the electroreformer delivers a maximum power density of 23 mW cm^{-2}. An increase in the flow rate from 0.17 to 1.12 mL min^{-1} is also beneficial due to the mass transport enhancement. Finally, over the stability tests for 3 h at 50 °C and a flow rate of 1.12 mL min^{-1}, it is possible to produce H_2 at an average rate of 0.218 and 0.267 STP m^3 m^{-2}h^{-1}, and an average energy of 0.0877 and 0.0997 kWh m^{-2} in recirculation and single-pass mode, respectively. The worse performance in the recirculation mode seems to be due to the accumulation of the ethanol electro-oxidation products, resulting in the poisoning of the catalyst surface.

1. Introduction

Hydrogen plays a crucial role in transitioning from the fossil-fuel-based energy mix to a much more sustainable matrix based on renewable energies (REN) as an energy vector [1]. Natural gas and carbon steam reforming are the main routes to produce H_2 [2]. Green hydrogen routes from water electrolysis occupy a scarce fraction (<1%), which needs to be reversed to dovetail REN and green H_2 in the future energy panorama.

The growth of green H_2 is hindered by the high production costs of water electrolysis [2]. A notable contribution comes from the electricity consumption due to the high voltages required [3] (in practical terms, cell voltages above 1.5 V are necessary [4]). One alternative to reduce the energy demand is replacing water with an organic molecule in the anode. This approach becomes more attractive if green alcohols, such as ethanol or glycerol, are used. The water oxidation standard potential is 1.23 V *vs* SHE, whereas the standard oxidation potential of any alcohol is close to zero *vs* SHE. A recent approach to reduce the energy demand or even produce electricity is to apply a pH gradient between an alkaline anode and an acidic cathode, converting the chemical neutralization energy into a favorable electromotive force (EMF) [5,6]. This approach

allows producing fuel (hydrogen) and electricity simultaneously.

With this background, this manuscript presents, for the first time, the results of an alkaline-acidic ethanol electroreformer constituted by an alkaline anolyte (ethanol as fuel and KOH as electrolyte), a polymeric electrolyte K^+-pretreated Nafion® 211 membrane (to avoid neutralization), and an acidic catholyte (H_2SO_4 as electrolyte). The influence of the temperature and the fuel flow rate is presented in this study as preliminary results of this innovative system. Finally, a test was applied to verify the system stability for 3 h at a constant voltage.

2. Material and methods

The chemicals potassium hydroxide (85 wt%, P.A.-ACS), sulfuric acid (>95 wt%, P.A.-ACS), and 2-propanol (99.5 %, P.A.-ACS) were acquired from Dinâmica (São Paulo, Brazil). Ethanol (ACS reagent, ≥ 99.5 %) was purchased from Sigma-Aldrich (São Paulo, Brazil). The Nafion® 211 membrane and Nafion® emulsion (5 wt% in a mixture of aliphatic alcohols) were acquired from IonPower (New Castle, DE, USA). The commercial 20 wt% Pt on Vulcan-XC72 carbon black was purchased from Premetek (Cherry Hill, NJ, USA).

The anode was prepared from a 20 wt% Pd on Vulcan XC-72
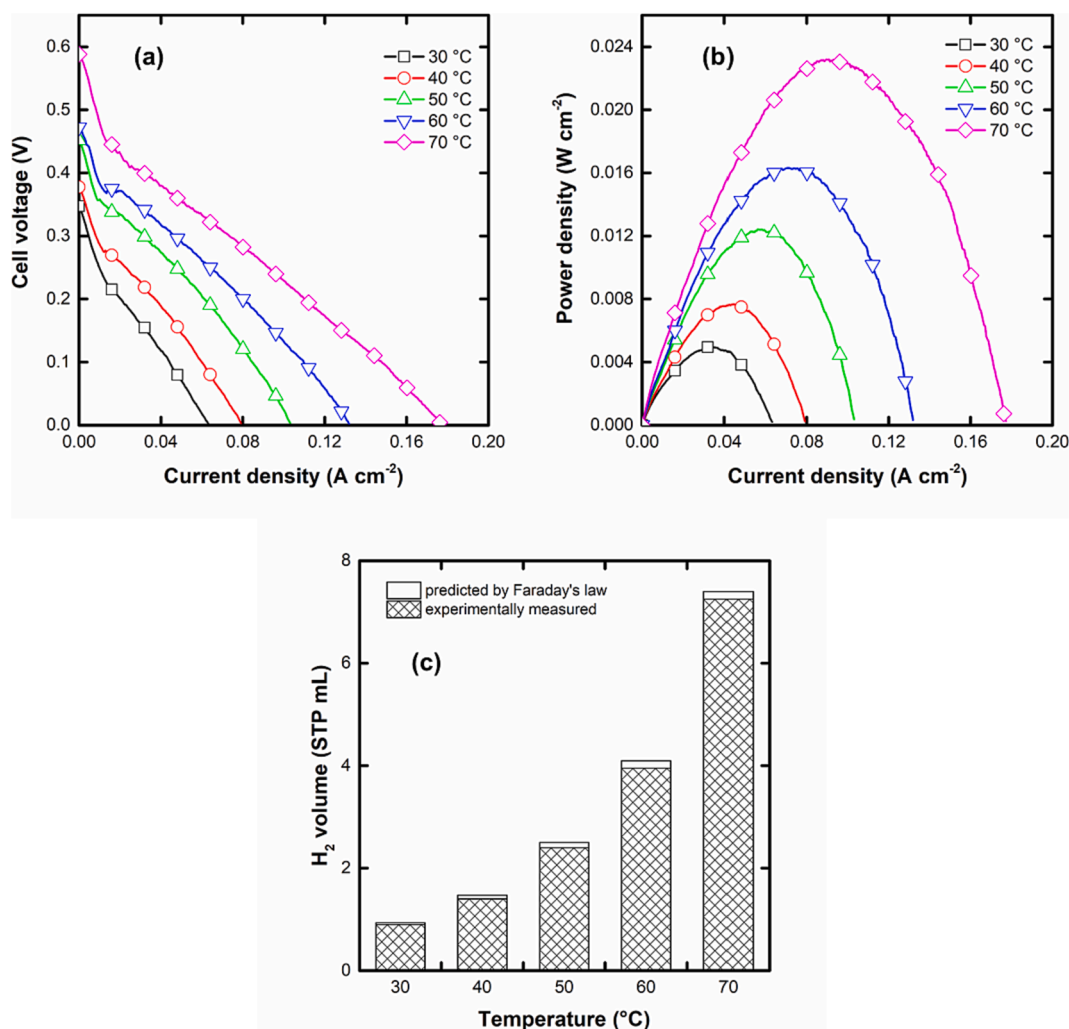
Fig. 1. (a) Polarization curves; (b) Power density curves; and (c) Volume of H$_2$ collected over the polarization curves at different temperatures (anolyte: 4 mol/L KOH, fuel: 1 mol/L ethanol, catholyte: 0.5 mol/L H$_2$SO$_4$; fuel and comburent flow rate of 0.72 mL min^{-1}).

prepared by sodium formate chemical reduction described elsewhere [6]. A catalytic slurry was prepared by mixing the catalyst, the Nafion® emulsion (10 wt% with respect to the total amount of catalyst), and 2-propanol as solvent. The slurry was applied onto a carbon cloth diffusion layer (Zoltek, Bridgeton, MO, USA) to complete a Pd loading of 2 mg cm^{-2}. In the cathode, the procedure was equivalent, except for using the commercial Pt/C (0.5 mg Pt cm^{-2}). The electrodes were dried in an oven for 1 h at 80 °C. The Nafion membrane was pretreated in a 1 mol/L KOH solution for 24 h to exchange H$^+$ by K$^+$ as ionic carriers. The active area of the electrodes was 2 cm^2.

The electroreformer tests were performed in an alkaline-acidic membrane single-cell. A peristaltic pump (Marte model MC-32, Brazil) adapted for two channels pumped the alkaline fuel and the acid comburent. The applied flow rate was 0.72 mL min^{-1} in the studies of the influence of the temperature. For the effect of the flow rate, values of 0.17, 0.72, and 1.12 mL min^{-1} were fixed at 50 °C. The electrochemical measurements were carried out with an AUTOLAB PGSTAT 302 N potentiostat/galvanostat (Metrohm Autolab BV, The Netherlands). The polarization curves were carried out in linear sweep galvanometry (LSG) from open circuit voltage up to the current in which the cell voltage is 0 V at a scan rate of 1 mA s^{-1}. The stability tests were carried out at the cell voltage where the maximum power density was achieved for 3 h, at 50 °C and 1.12 mL min^{-1}. Two operating modes were used, total recirculation, in which the anolyte and catholyte were returned to the feed reservoir, and single-pass, in which the exhausts did not return to

the feed reservoirs. The amount of hydrogen produced was measured with a laboratory gasometer. The experimental volumes were compared to the theoretical ones (V$_{th}$) estimated from Faraday's law (Eq. (1)), where I is the applied current, t is the time, F is the Faraday constant (96485C mol^{-1}), and 22711 mL of H$_2$ per mol in STP conditions. In the recirculation mode, the volumes of anolyte and catholyte used were 40 mL.

$$V_{th} = \frac{\int_0^t I(t)dt}{2F} 22711 \left(\frac{mL}{mol\ H_2} \right) \tag{1}$$

3. Results and discussion

Fig. 1 shows the polarization and power density curves, the experimental STP volume of H$_2$ collected, and the theoretical one from Faraday's law (over the polarization curves) at different temperatures. As seen in Fig. 1a, it is possible to produce electricity, in addition to hydrogen, thanks to the favorable pH gradient between the alkaline anode and the acidic cathode. Regarding the influence of the temperature, higher temperatures allow the electroreformer to achieve higher current and power densities (PD), up to a maximum PD of 23.1 mW cm^{-2} at 70 °C. This improvement is due to the promoted kinetics of the ethanol electro-oxidation and hydrogen evolution reactions and the higher ionic conductivity. In addition, the open circuit voltage (OCV) increases with the temperature. At higher values, the formation of the
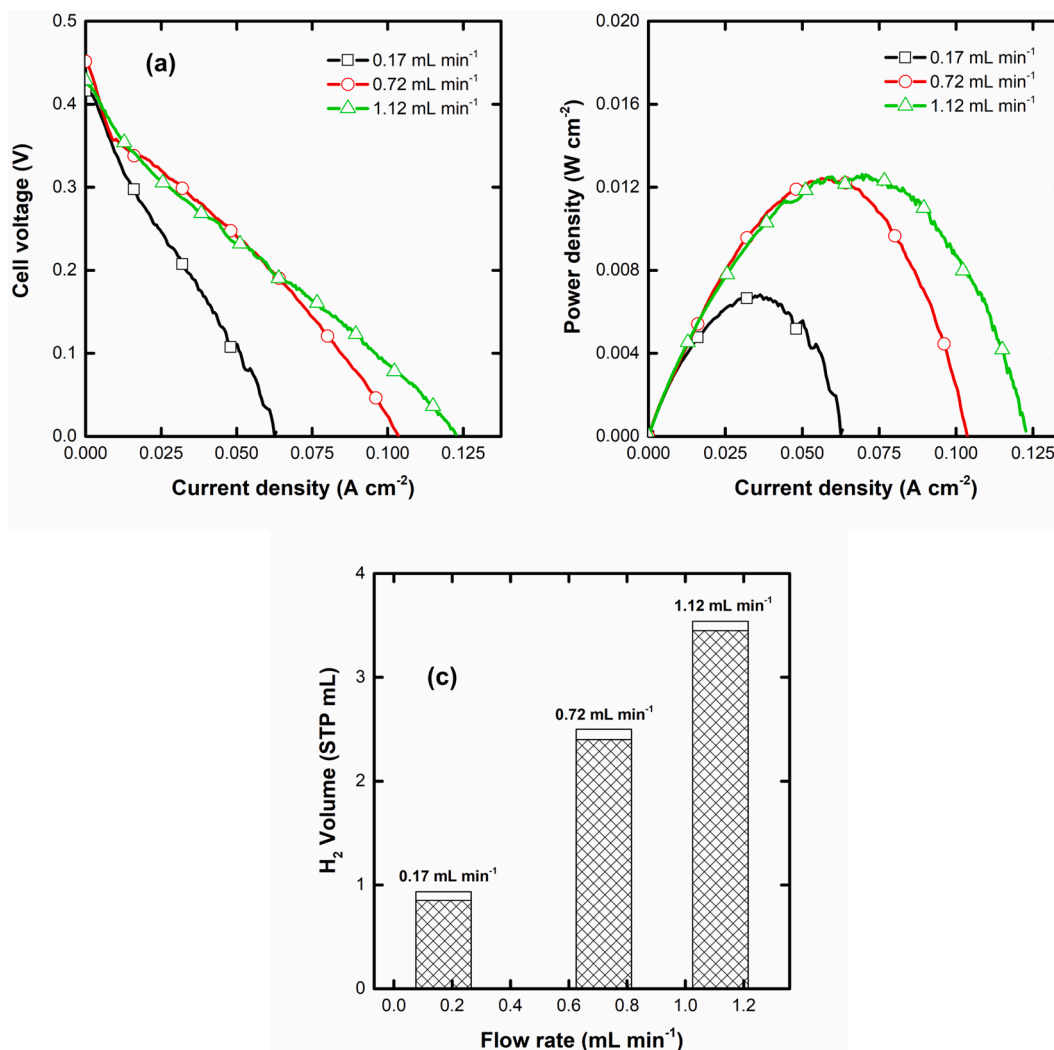
Fig. 2. (a) Polarization curves; (b) Power density curves; and (c) Volume of H_2 collected over the polarization curves at different temperatures (anolyte: 4 mol/L KOH, fuel: 1 mol/L ethanol, catholyte: 0.5 mol/L H_2SO_4; cell temperature of 50 °C).
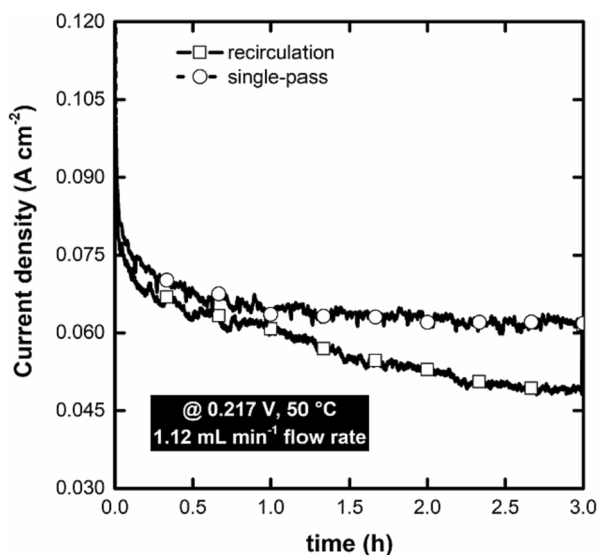

Fig. 3. Stability test for 3 h at 0.217 V, 50 °C and a flow rate of 1.12 mL min^{-1} in the recirculation and single-pass configuration (anolyte: 4 mol/L KOH, fuel: 1 mol/L ethanol, catholyte: 0.5 mol/L H_2SO_4; cell temperature of 50 °C).

OH_{ads}-species onto the surface of the catalyst, required for the ethanol electro-oxidation proceeds, occurs at lower potentials, reducing its onset potential and, by extension, the OCV [7]. Finally, in agreement with the improvement in the performance of the electrolyzer, the volume of H_2 produced increases with the temperature. Furthermore, the measured volumes are very close to those predicted by Faraday's law, indicating no crossover to the anode.

Fig. 2 shows the influence of the anode flow rate on the electroreformer current and power densities, the hydrogen produced, and its comparison to that predicted by Faraday's law. As the flow rate increases, there is a notable enhancement in the performance, especially in the transition of 0.17 to 0.72 mL min^{-1} and, to a lower extent, when the flow rate is increased from 0.72 to 1.12 mL min^{-1}. In this latter sequence, the increase in the cell performance is in the high current density region due to the promotion of the mass transport phenomena [8,9]. In the case of the 0.17 – 0.72 mL min^{-1} sequence, the cell performance enhances in the entire range of current density, including the low current density region where the kinetic of the ethanol electro-oxidation and the water reduction control the cell performance. As Alzate et al. [10] stated, the more difficult removal of the ethanol oxidation products and the slower mass transportation can be responsible for poorer cell performance. This also reflects in the lower power densities and the volume of STP hydrogen produced. These latter volumes are very close to those predicted values from Faraday's law.

Table 1

Hydrogen flux produced, energy produced over 3 h of operations, and variations in the pH in the anolyte and catholyte compartments in the single-pass (final pH measured in the exhaust compartments not recirculated) in the stability tests.

Parameter	Single-pass	Recirculation
H_2 flux (STP m^3 $m^{-2}h^{-1}$)	0.267	0.218
Energy produced (kWh m^{-2})	0.0997	0.0877
Initial pH – anolyte	14.8	
Final pH – anolyte	14.7	14.6
Initial pH – catholyte	-0.3	
Final pH – catholyte	-0.3	0.0

The performances shown are relatively lower than Direct Ethanol Fuel Cells (DEFC) [11]. Nevertheless, the electrochemical reactions and the environments differ, resulting in a smaller OCV, 0.74 V for this alkaline-acidic electrolyzer *vs* 1.14 V for DEFC). A possible reason is the high ohmic contribution of the cation exchange membrane in an environment in which other species than H^+ are transported (K^+ and OH^- species), as well as the water-splitting process that occurs in the alkaline-acidic electrolyzer [12]. Bipolar membranes may be more suitable for this application. Also, the authors are exploring other catalyst formulations to enhance the activity of ethanol electro-oxidation. Nevertheless, if we consider the energy available from the hydrogen produced (lower heating value of 59.98 kJ mol^{-1}), for instance, at the maximum power at 70 °C (23.1 mW cm^{-2} at a current density of 0.091 A cm^{-2}, corresponding to a theoretical molar flow of H_2 of 0.471 μmol of H_2 cm^{-2} s^{-1}) an extra power of approximately 28 mW cm^{-2} (increase of 122 % with respect to the electricity produced) could be drawn from the electrolyzer. The combination of the electricity produced with the energy coming from hydrogen makes this technology more attractive.

Long-term operation stability is another critical aspect of the electrolyzer. The electrocatalyst can undergo deactivation during ethanol electro-oxidation due to the accumulation of ethanolic residues on the surface. Furthermore, proton crossover can also occur, reducing the ΔpH electromotive force and, thus, the spontaneity. Fig. 3 shows the current density evolution for 3 h in a potentiostatic test recorded at the cell voltage where the maximum power density was achieved at 50 °C (0.217 V) and a flow rate of 1.12 mL min^{-1} for the recirculation and single-pass model.

As can be observed, the performance in the recirculation and single-pass modes differs. In the recirculation mode, there is a monotonous decrease in the current density at an average rate of 6.6 mA $cm^{-2}h^{-1}$, whereas the decline is 1.6 mA $cm^{-2}h^{-1}$ in the single pass-mode. A possible explanation for this could lie in the accumulation of oxidation products. Acetaldehyde can be formed and dimerized in an alkaline medium, favoring the blockage of the Pd active sites [13]. Also, acetate, the main oxidation product [14], accumulates and can get adsorbed onto the Pd surface, resulting in severe Pd surface deactivation [15]. Given the relatively short time for the stability test, we do not attribute the performance decay in the recirculation mode to the decrease in the ethanol concentration from its consumption in the electrochemical reaction (from Faraday's law, considering acetate as the main oxidation product, the final ethanol concentration is approximately 0.85 mol/L, $CH_3CH_2OH + 5 OH^- \rightarrow CH_3COO^- + 4 H_2O + 4 e^-$). On the other hand, in the single-pass mode, oxidation products accumulate to a lower extent due to the continuous feed with a fresh ethanol solution. Despite the apparent benefit of operating in a single-pass mode, we must consider that the ethanol utilization would be lower than in the recirculation mode. This would demand a subsequent purification system to recycle the non-reacted ethanol and KOH and extract the oxidation products.

Table 1 collects the H_2 flux for the stability tests, the energy produced, and the pH at the beginning and end of the stability measurements. The results confirm the possibility of simultaneously having hydrogen and electricity for extended periods. Also, they corroborate the negative impact of the accumulation of oxidation products on the system performance. Finally, an interesting analysis is the variations in the pH of the anolyte and catholyte over the stability tests to assess the crossover of H^+ from the cathode to the anode compartment with the consequent ineffective chemical neutralization. From the application of Faraday's law, considering acetate as the ethanol electro-oxidation product, the expected ΔpH is 0.1 for the anolyte and 0.2 for the catholyte in the recirculation mode. The change in the single-pass manner is expected to be imperceptible. The observed values are very close to the predicted ones, which can be an indication of a reduced crossover of H^+ through the polymeric electrolyte. From the practical point of view, the occurrence of a low proton crossover is crucial to maintaining the spontaneous capacity of the alkaline-acidic electrolyzer.

4. Conclusions

Hydrogen and electricity can be simultaneously produced thanks to the combination of the ethanol electroreforming and a favorable pH gradient between an alkaline anode and an acidic cathode. Increasing the temperature and the flow rate renders higher current and power densities, thus producing more electricity and hydrogen (experimental H_2 volumes close to the predicted from Faraday's law). The enhancement in the kinetics of the electrochemical reaction, ion transportation and mass transfer of the reactants and products explains these improvements. In terms of electroreformer stability, the operation in a single-pass mode is beneficial as the accumulation of oxidation products is avoided, reducing the current density decay. Finally, the chemical neutralization from the proton crossover scarcely contributes to the loss of system performance.

As seen throughout the study, this electrolyzer presents a solid strength based on simultaneous hydrogen and electricity generation, which should stimulate further studies to overcome some of the weaknesses observed. In this sense, some suggestions for future studies include using bipolar membranes, which are more suitable for large pH gradients. Furthermore, more active electrocatalysts than Pd/C could also be explored to increase the electrolyzer performance.

CRediT authorship contribution statement

Fernando M. de L. Amorim: Conceptualization, Methodology, Investigation, Data curation, Formal analysis, Writing – original draft. **Rudy Crisafulli:** Conceptualization, Formal analysis, Writing – original draft, Writing – review & editing, Supervision, Project administration, Funding acquisition. **José J. Linares:** Conceptualization, Formal analysis, Writing – original draft, Writing – review & editing, Supervision, Project administration, Funding acquisition.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Data availability

Data will be made available on request.

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