Electrochemical reforming of ethanol in a membrane-less reactor configuration

Estela Ruiz-López[a], Ernesto Amores[b], Ana Raquel de la Osa[a], Fernando Dorado[a], Antonio de Lucas-Consuegra[a*]

[a] Department of Chemical Engineering, School of Chemical Sciences and Technologies, University of Castilla-La Mancha, Avenida Camilo José Cela 12, 13005 Ciudad Real, Spain

[b] Centro Nacional del Hidrógeno (CNH2), Prolongación Fernando El Santo s/n, 13500 Puertollano, Ciudad Real, Spain

* Corresponding author. Tel.: +34-926295300; Fax: +34-926-295437; E-mail address: Antonio.lconsuegra@uclm.es

Abstract

As a result of the research of a more integrated process for hydrogen production, a new concept of membrane-less electrochemical reformer rises up for single-step hydrogen production in a single chamber reactor. In this system, the solid polymeric electrolyte is replaced by a low concentration liquid KOH solution electrolyte, simplifying its scale up and enhancing the stability of the cell. The viability of the system is studied for electrochemical reforming of ethanol and under an alkaline environment, which avoids the use of Pt-Ru or Pt-Sn high metal loading electrodes. Instead of these catalysts, commercial Pd/C Vulcan and Pt/C black are sprayed over Carbon Paper to be used as anode and cathode catalysts, respectively. In all the experiments carried out, a hydrogen stream with 100 % of faradaic efficiency has been obtained. A temperature of 85 ºC, a 3.5 mm electrodes distance and a fuel feeding solution of 1 mol·L^{-1} EtOH and 4 mol·L^{-1} KOH are the optimised conditions found in the studied range. These optimised conditions lead to current densities above 450 mA·cm^{-2} at lower cell potentials (1.4 V) than required for water electrolysis leading to lower energy consumption values. It is a remarkable result, as this electrocatalytic activity is higher than that obtained in previous studies based on membrane electrode assemblies systems. Finally, the stability of the system has been verified by mild term electrocatalyic experiments coupled with Atomic Absorption Spectrophotometry and X-ray diffraction analysis of fresh and used electrodes.

Keywords: H_2 production; Alcohol Electrolysis; Electrochemical reforming; Single Chamber Electrochemical reactor; Ethanol electro-oxidation

1. Introduction

The increasing demand of worldwide energy joint to the environmental problems which are attached to the use of fossil fuels encourage the development of a sustainable world economy based on the use of clean and renewable energy. The use of hydrogen instead of the present fossil fuels would eliminate many of these problems. In fact, hydrogen produced from renewable sources (such as solar energy) through processes with no carbonaceous species as co-products is an excellent energy carrier via fuel cells utilization [1].

Traditionally, catalytic steam reforming of methane has been the main large-scale process of hydrogen production. However, carbonaceous species such as carbon monoxide and carbon dioxide are produced along with hydrogen, requiring several reaction and purification additional steps. Therefore, in order to achieve a more integrated process, more compact and simple configurations are required for in-situ H_2 production applications [2], being water electrolysis the most established technology to produce pure hydrogen. Although water electrolysis can produce free carbonaceous hydrogen in a single step, it requires high cell voltages which means high energy consumption [3].

In the latest years, electrolysis (or electrochemical reforming) of alcohols has become an attractive alternative due to the high energy contained in these fuels. For this reason, the required external energy is lower, obtaining higher current density values at lower potentials than the one required in water electrolysis [4]. For instance, attending to the Gibbs free energy equation, ethanol electrolysis theoretically starts at 0.08 V [5], compared to water electrolysis, which theoretically starts at 1.23 V [6]. Besides, ethanol, compared to other molecules like methanol or dimethyl ether, offers many favorable features such as safety in storage, handling and transportation, lack of toxicity, lower volatility, high hydrogen content and availability from renewable resources [7, 8].

The operational system of an electrochemical alcohol reformer is similar to a water electrolysis cell. The electro-oxidation of the alcohol is produced on the anodic catalyst, generating in this case electro-oxidised organic products, protons and electrons. The protons are transported to the cathodic chamber (acid media) or the anions to the anodic side (alkaline media) through an electrolyte to produce hydrogen gas. In the last years, different water-alcohol mixtures have been tested as electrochemical reforming feed streams, e.g. methanol [9-13], glycerol [14-18], ethanol [11, 19-21] or even real biomass streams such as bioethanol [4, 22] and lignin [23]. All these previous studies have used different membrane electrode assemblies (MEAs) configurations where the ionic conducting membranes are used as both: an ionic transportation media and a separation barrier between the anodic and cathodic chamber of the reactor. The membranes, e.g. commercially available Nafion (H^+ conductors) or Fumapem (OH^- conductors), are one of the critical components of the electrochemical reformer system. Membranes are the main responsible of both: the high cost of the cells and their limited life-time, which depends on their stability and degradation [24, 25]. Inadequate humidification (that might be caused by high temperatures) or non-uniform pressure between electrodes could also lead to mechanical failures (pinholes, cracking, tearing, blistering), and radicals formed during cell operation that could deteriorate chemically or electrochemically the membrane [26, 27]. In addition, scaling up these alcohol electrochemical reformer units in stacks configuration is also an arduous task. A stack system would imply the addition of a large number of MEAs, with their corresponding inlets and outlets streams for every anodic and cathodic chamber.

In this work, we aim to study for the first time in literature the possible use of a membrane-less electrochemical reformer for hydrogen production in a single chamber reactor configuration. This membrane-less reactor configuration only requires two electrodes and one inlet and one outlet feed streams, simplifying the scale up. In this case, the solid polymer electrolyte will be replaced by a low concentration liquid electrolyte avoiding the previous mentioned barriers. The viability of this system in the electrochemical reforming of ethanol (EtOH) will be studied in alkaline environment, which will additionally avoid the use of high metal loading Pt-Ru or Pt-Sn electrodes. Hence, the influence of the main operational parameters: temperature, composition and electrodes separation distance will be studied in the single chamber electrolysis configuration. In addition, the stability of the system will be investigated through mild-term electrocatalytic reactions experiments in view of the practical application of this technology.

2. Experimental

2.1.Electrodes preparation and characterization

Commercial Pd supported on Carbon Vulcan XC-72 (20% Pd, Alfa Aesar) and commercial Pt on Carbon black (20% Pt/C, Alfa Aesar) were used as the anodic and cathodic catalysts, respectively. Two catalyst inks were prepared in each case by mixing 80 mg of catalyst powder with 50 ml isopropanol (99.9% for HPLC, Sigma Aldrich) as solvent. The corresponding catalyst inks were sprayed on Carbon Paper (Fuel Cell Earth) with an aerograph. The metal loading was controlled by weight measurements after drying the electrodes at 60 ºC. The sequence sprayed / drying / weight measurement was repeated until the final metal loading was 1 $mg\cdot cm^{-2}$ for each electrode. Once the final load was reached, electrodes were dried at 90 ºC overnight.

The mass of Pd and Pt supported on carbon paper was measured before and after electrocatalytic experiments by Atomic Absorption Spectophotometry on a SPECTRA 220FS analyser. The resultant Pd/C and Pt/C film structure was also characterized before and after electrocatalytic experiments by X-Ray Diffraction (XRD) analysis using a Philips PW-1710 instrument with Cu Kα radiation (λ = 1.5404 Å).

2.2.Electrochemical reforming activity measurements

Experimental tests were carried out in an electrolysis cell supplied by ElectroCell Europe A/S with a geometric electrode area of 10.5 cm^2, schemed in Figure 1. The cathode and the anode were introduced between EPDM gaskets and PTFE frames, appropriately designed to ensure sealing between anode and cathode compartments and to avoid short-circuiting of the cell. Graphitic bipolar plates were placed in touch with the cathode and anode serving as current collectors. Cathode and anode compartments were arranged in a single chamber configuration with just one inlet and one outlet stream, unlike conventional electrochemical reforming reactors based on a membrane electrode assembly (MEA) with two inlets and two outlets streams. All elements were finally placed between two external Teflon plates covered with metallic end plates. The entire cell was uniformly tight with nuts and bolts. This commercial cell allows to control the electrodes distance and it is an accurate device that also allows the further scale up by adding additional cells and to have a well fitted system for hydrogen gas measurements: flowrate and composition.

Electrochemical tests were carried out using a Vertex 5A.DC potentiostat-galvanostat electrochemical analyser (Ivium Technologies). The single chamber cell was fed with different aqueous solutions (0-6 $mol\cdot L^{-1}$ KOH or 4 $mol\cdot L^{-1}$ NaOH and 0-2 mol·L^{-1} EtOH) at a constant flow rate of 23 mL·min^{-1} using a peristaltic pump (Pumpdrive 5001, Heidolph). The feeding solution was preheated at a temperature range between 30 to 90 ºC. The gas phase of the outlet stream was separated from the liquid one and measured by a gas volumetric flowmeter and crosschecked via Faraday's Law calculations, based on the cell current. Gas products analysis was also carried out using a gas chromatograph (Bruker 450 GC) in order to check hydrogen quality. The operation mode was batch, i.e., recirculating the liquid phase outlet stream to the feed reservoir with an overall solution volume of 2 L. This volume, compared to the volume of liquid products obtained in a single cell step, is really high, so that the composition change barely affects to the system. Three different types of electrochemical experiments were performed: (a) linear sweep voltammetry measurements at a scan rate of 10 mV·s^{-1} and a 0-1.4 V range, (b) galvanostatic transients from 0.5 to 1 A at 25 ºC, to experimentally measure and crosscheck the hydrogen production rates and (c) chronoamperometry experiments at 85 ºC to check out the stability of the system. On this latter case two kinds of experiments were performed: firstly by applying 1 A for 30 h in a single experiment and secondly by different galvanostatic cycles at 1 A currents held up by open circuit conditions for 10 s with a total overall duration of 37 h.

3. Results and discussion

3.1. Proof of concept experiments of the membrane-less ethanol electrolysis

Due to the novelty of the reactor configuration, preliminary tests were performed in order to check the viability of the system. Linear sweep voltammetry measurements were carried out in a 0-1.4 V range, at a scan rate of 10 mV·s^{-1} and at a constant temperature of 85 ºC, as shown in Figure 2. In this experiment, different composition inlets solutions were fed to the single chamber electrochemical cell: pure water, aqueous

4 mol· L^{-1} KOH solution, aqueous 1 mol·L^{-1} EtOH solution, aqueous 1 mol·L^{-1} EtOH and 4 mol· L^{-1} KOH solution, and aqueous 1 mol·L^{-1} EtOH and 4 mol· L^{-1} NaOH solution. Firstly, it can be observed that no current was obtained when pure water, ethanol or KOH solution were separately fed to the electrochemical cell. For the case of feeding water or KOH solution, under absence of the alcohol molecule, the process is limited by the minimum thermodynamic potential of 1.23 V required for water electrolysis (which including ohmic losses and cell overpotentials typically go above 1.5 V [28]). Otherwise, under feeding 1 mol·L^{-1} EtOH solution and no liquid electrolyte, the ionic conductivity of the aqueous solution (below 15 μS·cm^{-1}) is the limiting factor for OH^- transport in the electrolysis process. Nevertheless, it can be observed that large current densities values were obtained at the explored potential range for the case of the experiments performed under both: 1 mol·L^{-1} EtOH + 4 mol·L^{-1} KOH solution and 1 mol·L^{-1} EtOH + 4 mol·L^{-1} NaOH solution. These results agree with the electro-oxidation thermodynamics of ethanol (84 mV at standard conditions). Hence, the current densities achieved were due to the alcohol electro-oxidation contribution joint to an OH^- transport pathway from the cathode to the anode provided by the liquid electrolyte. On the other hand, concerning the two different tested alkali electrolytes, KOH vs. NaOH, it can be observed that higher current densities were obtained for the former, which can be attributed to its higher ionic conductivity [29].On this basis, KOH solution was chosen as ionic electrolyte for subsequent electrolysis experiments**.** Finally, it is also worth mentioning that a high electrocatalytic activity was obtained on the single chamber electrolysis cell. Thus, the obtained current values (near 400 mA·cm^{-2} at T = 85 ºC and V_{cell} = 1.2 V) were much higher than the typical values observed for ethanol electrochemical reforming based on MEAs. For instance, previous works have shown that using Pt-Ru/C-Nafion-Pt/C MEAs, current densities values

below 100 mA·cm^{-2} were obtained under similar conditions [30]. In the case of a Pt-Sn-Ru/C-Nafion 117-Pt/C MEA, current densities values above 150 mA·cm^{-2} were never obtained [31]. Concerning alkaline media, similar values were obtained in previous works (near 500 mA·cm^{-2} at T = 80ºC and V_{cell} = 1.2V [32]) but using a MEA based on a commercial Tokuyama membrane. These results encourage to continue in this study even if the compared systems present operational differences, due to the advantages of a simplified, membrane-less configuration.

In order to check and measure the obtained hydrogen production rates, galvanostatic transients were carried out from 0.5 to 1 A at room temperature (25 ºC) under 1 mol·L^{-1} EtOH and 4 mol· L^{-1} KOH fuel stream (Figure 3). During each 20-min current application, hydrogen production rates (Q_{H2}) were experimentally measured by a gas-volumetric flowmeter and compared with the ones calculated via Faraday's Law. It can be observed that experimental hydrogen production values were practically identical to the ones calculated via Faraday's Law at each applied current. It demonstrates a 100 % hydrogen Faradaic efficiency value in the single chamber electrolysis cell. In addition, gas chromatography analyses were performed from the gas phase separation unit (Figure 1) in order to evaluate the hydrogen purity. The results of all the gas phase analyses confirmed that 100 % purity hydrogen was obtained in all the cases (an example of the chromatograms is shown in the supporting information, Figure S1). At this point one could envisage that a critical issue in this membrane-less configuration may be the quality of the hydrogen stream produced since cathodic and anodic chambers are not physically separated. However, it has been confirmed that a faradaic pure hydrogen stream was always obtained, not only in the experiments of Figure 3, but also in all the experiments performed in this work. Nevertheless, and in order to clarify the cathode performance, several tests have been carried out in a conventional three electrode system using Pt as counter, an Ag/AgCl electrode as reference electrode and a glassy carbon where the Pt/C ink was deposited as working. As it can be observed in the supplementary information (Figure S2), the addition of ethanol has a negligible effect into the cathodic hydrogen evolution reaction kinetics. These experimental observations are in good agreement with previous studies of ethanol electro-oxidation in alkaline media which have shown a negligible production of total oxidation products such as CO_2 or carbonates [32, 33]. For instance, Monyoncho et al. [33] observed by polarization modulation–infrared reflection absorption spectroscopy that acetate species are the most important ones as a result of ethanol electro-oxidation on Pd. These authors demonstrated that selective supports such as CeO_2 are required for C-C bond breaking. Under alkaline conditions, the anodic reaction pathway suggested in several studies [34, 35] involves the formation of intermediate ethoxy (Eq. 1) and its further stripping and the acetate realising as the main liquid product (Eq. 2-3):

$$CH_3CH_2OH + 3\ OH^- \rightarrow CH_3CO + 3\ H_2O + 3\ e^- \qquad (1)$$

$$CH_3CO + OH^- \rightarrow CH_3COOH + 1\ e^- \qquad (2)$$

$$CH_3COOH + OH^- \rightarrow CH_3COO^- + H_2O \qquad (3)$$

$$CH_3COO^- + 11\ OH^- \rightarrow 2\ CO_3^{2-} + 7\ H_2O + 8\ e^- \qquad (4)$$

According to Liang et al. [34] and de Lucas-Consuegra et al. [32], some traces of carbonates appeared probably due to the further oxidation of acetates (Eq. 4). However, and as mentioned above, the cleavage of the C-C bond is rather difficult on the Pd catalyst, so that acetate remains as the main liquid product. In the cathodic electrode, hydrogen was produced from water as Eq. 5 shows:

$$2\ H_2O + 2\ e^- \rightarrow H_2 + 2\ OH^- \qquad (5)$$

Therefore, hydrogen is the unique gas product stream which can be easily separated from liquid potassium acetate, since no CO or CO_2 was detected at any experiment. At this point, it is also interesting to note that potassium acetate is a product that finds many applications in polymer and food industry.

3.2. Influence of the membrane-less electrolyser experimental conditions.

Once the viability of the proposed system was checked, different operational parameters were studied. Figure 4 shows the effect of the reaction temperature (Figure 4a) and distance between electrodes (Figure 4b). As expected, linear sweep voltammetry experiments showed higher electrocatalytic activity (higher hydrogen production rates) as temperature increased. It can be attributed to two main effects: the increase of the ionic conductivity of the electrolyte and the enhancement of the kinetics of the electrochemical reactions [36, 37]. A similar trend was observed in previous studies using MEA configurations under both: alkaline media [32] and acid media [4, 30, 36]. According to our results using a liquid electrolyte, an optimal temperature of 85 º C was selected for subsequent experiments in order to avoid the boiling point of the solution (≈ 90 ºC). Concerning the effect of electrode distance, the PTFE frame disposed on the cell between cathode and anode (as it is shown in Figure 1) established the chamber width. Three different thickness frames were used, which allowed studying three different distances: 3.5, 5 and 7 mm. As it can be observed in Figure 4 b), when the distance between cathode and anode increased, lower current densities values were obtained. A thinner width of the electrolyte chamber results in a higher conductivity, as the ohmic losses of the system decrease [38, 39]. Considering only this effect, the thinner the chamber width is, the higher current densities will be obtained. However, other factors like short-circuiting or void fraction must be taken into account. Gas bubbles formed as a result of the electrochemical reactions could affect also the ionic conductivity and reduce the electrodes active area, especially at higher current densities [40, 41]. An optimal distance would be the nearest one where the void fraction does not affect to electrodes active area. In all explored distances in this work, current densities obtained showed that electrodes active area was not reduced, i.e., bubbles formed had not a negative effect on the system. Hence, the thinnest frame (chamber width of 3.5 mm) was selected as the optimal one to the studied system and it will be used in further experiments.

In order to check the influence of both ethanol and KOH concentration over the electrochemical behaviour of the system, a series of linear sweep voltammetries was performed (as shown on Figure S3 of supplementary information) at 85 ºC under different fuel compositions (EtOH (0-2 M) and KOH (0-6 M)). Figure 5 summarizes all these experiments, showing the current density values obtained at any case at applied cell voltage of 1.4 V. All these values were fitted in a three-dimensional figure, in order to get an optimal composition taking into account both variables: ethanol and KOH concentration. As the figure shows, a low ethanol concentration (< e.g. 0.5 M) led to low current densities values (< 200 $mA \cdot cm^{-2}$). Under these conditions, it was an insufficient fuel supply limiting the ethanol electro-oxidation reaction. This is in good agreement with previous studies that have shown mass transfer limitations at low ethanol concentrations, leading to a limiting current on the polarization curves [4, 42]. As ethanol concentration increased, higher number of molecules were available for the anodic electro-oxidation reaction, so that the limitations disappeared and current density reached its optimal value at 1 $mol \cdot L^{-1}$ concentration, where current densities values above 450 $mA \cdot cm^{-2}$ were obtained. Nevertheless, as ethanol concentration increased from 1 to 2 $mol \cdot L^{-1}$, the electrocatalytic activity of the system decrease. This decrease in current densities could be attributed to a decrease on the ionic conductivity of the solution at high alcohol concentrations. On the other hand, a high fuel concentration and thus, an excess of unreacted ethanol, could reduce the availability of OH^- ions at catalyst sites contributing also to the observed activity decrease [21]. Regarding the KOH concentration, it is directly related to the ionic conductivity. According to the obtained results the electrochemical reforming activity was probably limited by the ionic conductivity of the fuel solution conductivity at low KOH concentrations. However, high concentrations of KOH solution could result in a large OH^- coverage of the catalyst active sites [15], so that the anodic reaction could be limited by a low coverage of ethanol molecules [21, 39], as it can be observed for concentrations above 4 $mol \cdot L^{-1}$. Besides, a high KOH concentration could increase the viscosity solution, leading to ethanol mass transfer limitations [16]. Hence, an optimal KOH concentration on the alcohol fuel solution of 4 $mol \cdot L^{-1}$ was achieved, where the highest current densities values were obtained. As a result of this study, concentrations of 1 $mol \cdot L^{-1}$ of ethanol and 4 $mol \cdot L^{-1}$ of KOH of the fuel solution were the optimal ones to maximize the electrocatalytic activity of the cell at the explored conditions (1.4 V at 85 ºC, chamber width 3.5 mm). Hence, the optimal current density value obtained was 474 $mA \cdot cm^{-2}$, very close to the value obtained in a previous study under similar conditions (near 500 $mA \cdot cm^{-2}$) using a MEA based on a commercial Tokuyama membrane [32].

3.3. Stability study

Stability and practical viability of the proposed cell were analysed through mild-time electrochemical reforming experiments. Firstly, a constant current of 1 A at T = 85 ºC was applied for 30 h under the previously studied optimal conditions (inlet composition: 1 $mol \cdot L^{-1}$ EtOH and 4 $mol \cdot L^{-1}$ KOH; chamber width = 3.5 mm) as Figures 6 shows.

Although cell potential slightly increased with time, it seemed to reach an almost steady state behaviour after 20 h of working time. The potential increase and therefore, the decline in the cell performance, could be attributed to the poisoning effect of the adsorbed intermediate species on the catalyst surfaces, blocking their active sites due to the dissociative adsorption on ethanol [36]. This effect will be further studied in the following stability test. At this steady state, under an applied current of 1 A and a cell potential of 0.63 V, the electrical energy consumption to produce 1 kg of H_2 was calculated. The value obtained under these conditions was 16.9 $kWh \cdot kg_{H2}^{-1}$, a lower energy consumption value compared to those reported for commercial water PEM electrolysers stacks (50-60 $kWh \cdot kg_{H2}^{-1}$) [43] or commercial water alkaline electrolysers (48-64 $kWh \cdot kg_{H2}^{-1}$). Higher energy consumption values were also obtained under similar working conditions in previous ethanol electrochemical reforming studies with MEAs based configurations. For instance, with a MEA configuration based on Pd/C-Tokuyama-Pt/C or Pd/TNTA-web-Tokuyama-Pt/C, the energy consumption for H_2 production for ethanol electrochemical reforming was in the range of 18.49-30 $kWh \cdot kg_{H2}^{-1}$ [22, 32].

Cycling stability tests were also performed on the same solution under the optimal conditions (inlet composition: 1 $mol \cdot L^{-1}$ EtOH and 4 $mol \cdot L^{-1}$ KOH; chamber width = 3.5 mm, temperature = 85 ºC) and the total volume of hydrogen produced per cycle was measured at different cycles, obtaining the same values in all of the measurements, as it can be observed in the supplementary information (Figure S4 and Table S1).

Additional cyclic stability tests were also carried out under mild conditions (1 $mol \cdot L^{-1}$ EtOH and 1 $mol \cdot L^{-1}$ KOH at T = 85 ºC) by applying a constant current of 1 A. The cycles lasted 12 h each one (except for the last one), and circuit was opened for 10 s between them (OCP). The fed solution was also changed by a fresh one between cycles

2 and 3. As it can be observed in Figure 7, all cycles presented an increase in cell potential, which could be attributed to the poisoning effect of the adsorbed intermediate species, as it was mentioned before. However, it can be observed that the open circuit potential step (OCP) allowed to partially remove the previous adsorbed intermediate species, partly recovering the electrocatalytic activity of the system. Similar behaviour was obtained in previous works [32], where, in fact, the anode solution was changed between cycles.

On the other hand, it is clear that the batch operation mode used also affected to the inlet composition: as time went by, ethanol concentration slightly decreased and the concentration of product species such as potassium acetates increased. These intermediate species in the inlet composition along with adsorbed species on the catalyst surface were responsible for the increase showed in cell potential and therefore, the decline in cell performance. Hence, after two cycles, fresh solution was fed to the system and, as expected, the cell potential obtained was similar to the one obtained at the beginning of cycle 2. Hence, in view of the practical application of this system a feed and bleed operation continuously supplying a flowrate of fresh solution and purging part of the used solution would be convenient in order to stabilise the cell performance.

Finally, in order to evaluate the catalyst structural stability, Pd and Pt metal load was measured by Atomic Absorption spectrophotometry and XRD analysis were performed on both electrodes, before and after all the experiments, here is to say, on fresh and used electrodes. Atomic Absorption spectrophotometry measurements confirmed that there was not any loss of metal from the electrode via dissolution. In Figure 8, it can be observed that both catalysts did not show significance differences in their diffraction peaks before and after the electrochemical performance. In both XRD patterns, the diffraction peaks at around 25° and at 54º are attributed to diffraction at the (0 0 2) and (0 0 4) plane of the hexagonal structure of carbon supports used. In Figure 8 a), where anode XRD patterns were showed, the characteristic peaks at about 40º, 46º, 68º, 82º and 86º are due to the diffraction at the Pd(1 1 1), (2 0 0), (2 2 0), (3 1 1) and (2 2 2) planes, respectively. In the case of cathode XRD patterns (Figure 8 b), the diffraction peaks about 39º, 46º, 68º and 81º are due to diffraction at the Pt(1 1 1), (2 0 0), (2 2 0) and (3 1 1) planes, respectively. These analyses confirmed the good chemical stability of Pd as anode and Pt as cathode catalysts under all the explored reaction conditions in good agreement with the stable electrocatalytic performance and reproducibility experiments shown during the whole study.

4. Conclusions

Different conclusions of great importance can be drawn from this study:

-A hydrogen stream with 100 % of purity and faradaic efficiency can be obtained in a single chamber ethanol electrolysis cell using a liquid alkaline electrolyte. This membrane-less configuration is a simple electrochemical reactor which may simplify the further scale up of an electrochemical reforming process, enhancing the stability of the system due the lack of a polymer electrolyte membrane.

-An optimization study was performed, leading to the following experimental conditions: operation temperature (85 ºC), electrode distance (3.5 mm) and fuel feeding stream (1 mol·L^{-1} EtOH and 4 mol·L^{-1} KOH). Under these optimised conditions, higher electrocatalytic activity (with current density values above 450 mA·cm^{-2} at 1.4 V) was obtained with this novel configuration than that reported in previous studies based on MEAs.

-The values obtained for energy consumption under optimised conditions (16.9 kWh·kg_{H2}^{-1}) were lower than those obtained using commercial water electrolysers or in previous studies on electrochemical reforming of alcohols.

-The system has shown a stable performance under mild working time experiments. The used electrodes have also shown to be stable under the explored working conditions. No changes in the overall metal loading and composition have been confirmed by Atomic Absorption spectrophotometry and XRD analysis performed before and after the electrocatalytic experiments. However, a feed and bleed operation mode is proposed to avoid important modifications of the fuel composition which caused a decrease on the electrocatalytic activity of the system with time.

ACKNOWLEDGMENT

The authors gratefully acknowledge Spanish Ministry of Economy and Competiveness for the financial support of this work.

FUNDING SOURCES

This work was supported by Spanish Ministry of Economy and Competiveness [project CTQ2016-75491-R].

Figure captions

Figure 1. Membrane-less reformer scheme.

Figure 2. Linear sweep voltammetry measurements in a 0-1.4 V range. Scanrate = 10 mV·s^{-1}, T = 85 ºC. Chamber width = 3.5 mm.

Figure 3. Galvanostatic transients: hydrogen production rates vs. current applied. Inlet composition = 1 mol·L^{-1}EtOH and 4 mol·L^{-1} KOH. T = 25 ºC. Chamber width= 3.5 mm.

Figure 4. Linear sweep voltammetry measurements in a 0-1.4 V range. Scanrate = 10 mV·s^{-1}. a) Influence of the temperature. Inlet composition = 1 mol·L^{-1}EtOH and 2 mol·L^{-1} KOH. Chamber width = 3.5 mm. b) Influence of the chamber width. Inlet composition = 1 mol·L^{-1}EtOHand 4 mol·L^{-1} KOH. T = 85 ºC.

Figure 5. Influence of EtOH and KOH concentration vs. current density achieved at $V_{cell} = 1.4$ V. T = 85 ºC. Chamber width = 3.5 mm.

Figure 6. Stability test:chronoamperometry experiment. Current applied = 1 A. Inlet composition = 1 $mol \cdot L^{-1}$EtOH and 4 $mol \cdot L^{-1}$ KOH. T= 85 ºC. Chamber width = 3.5mm.

Figure 7. Stability test: chronoamperometry experiment, galvanostatic cycles. Current applied = 1 A. Inlet composition = 1 $mol \cdot L^{-1}$EtOH and 1 $mol \cdot L^{-1}$ KOH. T = 85 ºC. Chamber width = 3.5mm.

Figure 8. X-ray diffraction patterns of the a) fresh and used Pd/C anode b) fresh and used Pt/C cathode.

References

[1] M. Momirlan, T. Veziroglu, Current status of hydrogen energy, Renewable and sustainable energy reviews 6 (2002) 141-179. https://doi.org/10.1016/S1364-0321(02)00004-7.

[2] A. Nieto-Márquez, D. Sánchez, A. Miranda-Dahdal, F. Dorado, A. de Lucas-Consuegra, J. Valverde, Autothermal reforming and water–gas shift double bed reactor for H2 production from ethanol, Chemical Engineering and Processing: Process Intensification 74 (2013) 14-18. https://doi.org/10.1016/j.cep.2013.10.006.

[3] M. Pagliaro, M. Bellini, J. Filippi, M. Folliero, A. Marchionni, H. Miller, W. Oberhauser, F. Vizza, Hydrogen production from the electrooxidation of methanol and potassium formate in alkaline media on carbon supported Rh and Pd nanoparticles, Inorganica Chimica Acta 470 (2018) 263-269. https://doi.org/10.1016/j.ica.2017.05.055.

[4] A. Caravaca, A. de Lucas-Consuegra, A.B. Calcerrada, J. Lobato, J.L. Valverde, F. Dorado, From biomass to pure hydrogen: Electrochemical reforming of bio-ethanol in a PEM electrolyser, Applied Catalysis B: Environmental 134-135 (2013) 302-309. https://doi.org/10.1016/j.apcatb.2013.01.033.

[5] S.M.M. Ehteshami, S. Vignesh, R. Rasheed, S. Chan, Numerical investigations on ethanol electrolysis for production of pure hydrogen from renewable sources, Applied Energy 170 (2016) 388-393. https://doi.org/10.1016/j.apenergy.2016.03.001.

[6] A. Marshall, R. Haverkamp, Production of hydrogen by the electrochemical reforming of glycerol–water solutions in a PEM electrolysis cell, international journal of hydrogen energy 33 (2008) 4649-4654. https://doi.org/10.1016/j.ijhydene.2008.05.029.

[7] E. Gucciardi, V. Chiodo, S. Freni, S. Cavallaro, A. Galvagno, J.C.J. Bart, Ethanol and dimethyl ether steam reforming on Rh/Al2O3 catalysts for high-temperature fuel-cell feeds, Reaction Kinetics, Mechanisms and Catalysis 104 (2011) 75-87. https://doi.org/10.1007/s11144-011-0335-y.

[8] F. Liu, L. Zhao, H. Wang, X. Bai, Y. Liu, Study on the preparation of Ni–La–Ce oxide catalyst for steam reforming of ethanol, International Journal of Hydrogen Energy 39 (2014) 10454-10466. https://doi.org/10.1016/j.ijhydene.2014.05.036.

[9] A.T. Pham, T. Baba, T. Shudo, Efficient hydrogen production from aqueous methanol in a PEM electrolyzer with porous metal flow field: influence of change in grain diameter and material of porous metal flow field, International Journal of Hydrogen Energy 38 (2013) 9945-9953. https://doi.org/10.1016/j.ijhydene.2013.05.171.

[10] C. Lamy, B. Guenot, M. Cretin, G. Pourcelly, A kinetics analysis of methanol oxidation under electrolysis/fuel cell working conditions, ECS Transactions 66 (2015) 1-12. https://doi.org/10.1149/06629.0001ecst.

[11] F. Sapountzi, M. Tsampas, H. Fredriksson, J. Gracia, J. Niemantsverdriet, Hydrogen from electrochemical reforming of C1–C3 alcohols using proton conducting membranes, International Journal of Hydrogen Energy 42 (2017) 10762-10774. https://doi.org/10.1016/j.ijhydene.2017.02.195.

[12] M. Narreddula, R. Balaji, K. Ramya, K. Dhathathreyan, N. Rajalakshmi, A. Ramachandraiah, Electrochemical methanol reformation (ECMR) using low-cost sulfonated PVDF/ZrP membrane for hydrogen production, Journal of Solid State Electrochemistry (2018) 1-9. https://doi.org/10.1007/s10008-018-3974-3.

[13] K. El-Khatib, R.A. Hameed, R. Amin, A.E. Fetohi, Core-shell structured Pt-transition metals nanoparticles supported on activated carbon for direct methanol fuel cells, Microchemical Journal 145 (2019) 566-577. https://doi.org/10.1016/j.microc.2018.11.020.

[14] S. Kongjao, S. Damronglerd, M. Hunsom, Electrochemical reforming of an acidic aqueous glycerol solution on Pt electrodes, Journal of Applied Electrochemistry 41 (2011) 215-222. https://doi.org/10.1007/s10800-010-0226-3.

[15] J. De Paula, D. Nascimento, J. Linares, Electrochemical reforming of glycerol in alkaline PBI-based PEM reactor for hydrogen production, Chemical Engineering Transactions (2014) 205-210. https://doi.org/10.3303/CET1441035.

[16] J. de Paula, D. Nascimento, J.J. Linares, Influence of the anolyte feed conditions on the performance of an alkaline glycerol electroreforming reactor, Journal of Applied Electrochemistry 45 (2015) 689-700. https://doi.org/10.1007/s10800-015-0848-6.

[17] H. Miller, M. Bellini, F. Vizza, C. Hasenöhrl, R. Tilley, Carbon supported Au–Pd core–shell nanoparticles for hydrogen production by alcohol electroreforming, Catalysis Science & Technology 6 (2016) 6870-6878. https://doi.org/10.1039/C6CY00720A.

[18] M.V. Pagliaro, M. Bellini, M. Bevilacqua, J. Filippi, M.G. Folliero, A. Marchionni, H.A. Miller, W. Oberhauser, S. Caporali, M. Innocenti, Carbon supported Rh nanoparticles for the production of hydrogen and chemicals by the electroreforming of biomass-derived alcohols, RSC Advances 7 (2017) 13971-13978. https://doi.org/10.1039/C7RA00044H.

[19] J. Liu, Z. Luo, J. Li, X. Yu, J. Llorca, D. Nasiou, J. Arbiol, M. Meyns, A. Cabot, Graphene-supported palladium phosphide PdP2 nanocrystals for ethanol electrooxidation, Applied Catalysis B: Environmental 242 (2019) 258-266. https://doi.org/10.1016/j.apcatb.2018.09.105.

[20] L.F. Sallum, A. Mota-Lima, E.R. Gonzalez, Galvano–and Potentio–dynamic studies during ethanol electro-oxidation reaction in acid vs. alkaline media: Energy dissipation and blocking nature of potassium, Electrochimica Acta 293 (2019) 247-259. https://doi.org/10.1016/j.electacta.2018.09.118.

[21] U.K. Gupta, H. Pramanik, Electrooxidation study of pure ethanol/methanol and their mixture for the application in direct alcohol alkaline fuel cells (DAAFCs), International Journal of Hydrogen Energy 44 (2019) 421-435. https://doi.org/10.1016/j.ijhydene.2018.03.008.

[22] Y.X. Chen, A. Lavacchi, H.A. Miller, M. Bevilacqua, J. Filippi, M. Innocenti, A. Marchionni, W. Oberhauser, L. Wang, F. Vizza, Nanotechnology makes biomass electrolysis more energy efficient than water electrolysis, Nature Communications 5 (2014) 4036. https://doi.org/10.1038/ncomms5036

[23] A. Caravaca, W.E. Garcia-Lorefice, S. Gil, A. de Lucas-Consuegra, P. Vernoux, Towards a sustainable technology for H2 production: Direct lignin electrolysis in a continuous-flow Polymer Electrolyte Membrane reactor, Electrochemistry Communications 100 (2019) 43-47. https://doi.org/10.1016/j.elecom.2019.01.016.

[24] D.J. Kim, M.J. Jo, S.Y. Nam, A review of polymer–nanocomposite electrolyte membranes for fuel cell application, Journal of Industrial and Engineering Chemistry 21 (2015) 36-52. https://doi.org/10.1016/j.jiec.2014.04.030.

[25] K.H. Gopi, S.D. Bhat, A.K. Sahu, P. Sridhar, Quaternized poly (phenylene oxide) anion exchange membrane for alkaline direct methanol fuel cells in KOH-free media, Journal of Applied Polymer Science 133 (2016). https://doi.org/10.1002/app.43693.

[26] A. Collier, H. Wang, X.Z. Yuan, J. Zhang, D.P. Wilkinson, Degradation of polymer electrolyte membranes, International Journal of Hydrogen Energy 31 (2006) 1838-1854. https://doi.org/10.1016/j.ijhydene.2006.05.006.

[27] A. B. LaConti, M. Hamdan, R. McDonald, 2010.

[28] E. López-Fernández, J. Gil-Rostra, J.P. Espinós, A.R. González-Elipe, F. Yubero, A. de Lucas-Consuegra, CuxCo3-xO4 ultra-thin film as efficient anodic catalysts for anion exchange membrane water electrolysers, Journal of Power Sources 415 (2019) 136-144. https://doi.org/10.1016/j.jpowsour.2019.01.056.

[29] M.H. Sellami, K. Loudiyi, Electrolytes behavior during hydrogen production by solar energy, Renewable and Sustainable Energy Reviews 70 (2017) 1331-1335. https://doi.org/10.1016/j.rser.2016.12.034.

[30] A.B. Calcerrada, R. Ana, J. Llanos, F. Dorado, A. de Lucas-Consuegra, Hydrogen from electrochemical reforming of ethanol assisted by sulfuric acid addition, Applied Catalysis B: Environmental 231 (2018) 310-316. https://doi.org/10.1016/j.apcatb.2018.03.028.

[31] C. Lamy, T. Jaubert, S. Baranton, C. Coutanceau, Clean hydrogen generation through the electrocatalytic oxidation of ethanol in a Proton Exchange Membrane Electrolysis Cell (PEMEC): Effect of the nature and structure of the catalytic anode, Journal of Power Sources 245 (2014) 927-936. https://doi.org/10.1016/j.jpowsour.2013.07.028.

[32] A. de Lucas-Consuegra, R. Ana, A.B. Calcerrada, J.J. Linares, D. Horwat, A novel sputtered Pd mesh architecture as an advanced electrocatalyst for highly efficient hydrogen production, Journal of Power Sources 321 (2016) 248-256. http://dx.doi.org/10.1016/j.jpowsour.2016.05.004.

[33] E.A. Monyoncho, S. Ntais, N. Brazeau, J.-J. Wu, C.-L. Sun, E.A. Baranova, Role of the Metal-Oxide Support in the Catalytic Activity of Pd Nanoparticles for Ethanol Electrooxidation in Alkaline Media, ChemElectroChem 3 (2016) 218-227. https://doi.org/10.1002/celc.201500432.

[34] Z. Liang, T. Zhao, J. Xu, L. Zhu, Mechanism study of the ethanol oxidation reaction on palladium in alkaline media, Electrochimica Acta 54 (2009) 2203-2208.

[35] S.T. Nguyen, H.M. Law, H.T. Nguyen, N. Kristian, S. Wang, S.H. Chan, X. Wang, Enhancement effect of Ag for Pd/C towards the ethanol electro-oxidation in alkaline media, Applied Catalysis B: Environmental 91 (2009) 507-515.

[36] A. Caravaca, F.M. Sapountzi, A. de Lucas-Consuegra, C. Molina-Mora, F. Dorado, J.L. Valverde, Electrochemical reforming of ethanol–water solutions for pure H2 production in a PEM electrolysis cell, International Journal of Hydrogen Energy 37 (2012) 9504-9513. https://doi.org/10.1016/j.ijhydene.2012.03.062.

[37] M. Miller, A. Bazylak, A review of polymer electrolyte membrane fuel cell stack testing, Journal of Power Sources 196 (2011) 601-613. https://doi.org/10.1016/j.jpowsour.2010.07.072.

[38] N. Nagai, M. Takeuchi, T. Kimura, T. Oka, Existence of optimum space between electrodes on hydrogen production by water electrolysis, International Journal of Hydrogen Energy 28 (2003) 35-41. https://doi.org/10.1016/S0360-3199(02)00027-7.

[39] E. Amores, J. Rodríguez, C. Carreras, Influence of operation parameters in the modeling of alkaline water electrolyzers for hydrogen production, International Journal of Hydrogen Energy 39 (2014) 13063-13078. https://doi.org/10.1016/j.ijhydene.2014.07.001.

[40] M.D. Mat, K. Aldas, O.J. Ilegbusi, A two-phase flow model for hydrogen evolution in an electrochemical cell, International Journal of Hydrogen Energy 29 (2004) 1015-1023. https://doi.org/10.1016/j.ijhydene.2003.11.007.

[41] M. Caspersen, J.B. Kirkegaard, Modelling electrolyte conductivity in a water electrolyzer cell, International Journal of Hydrogen Energy 37 (2012) 7436-7441. https://doi.org/10.1016/j.ijhydene.2012.02.023.

[42] V. Alzate, K. Fatih, H. Wang, Effect of operating parameters and anode diffusion layer on the direct ethanol fuel cell performance, Journal of Power Sources 196 (2011) 10625-10631. https://doi.org/10.1016/j.jpowsour.2011.08.080.

[43] M. Carmo, D.L. Fritz, J. Mergel, D. Stolten, A comprehensive review on PEM water electrolysis, International Journal of Hydrogen Energy 38 (2013) 4901-4934. https://doi.org/10.1016/j.ijhydene.2013.01.151.