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PERFORMANCE ASSESSMENT OF A POLYMER ELECTROLYTE MEMBRANE
ELECTROCHEMICAL REACTOR UNDER ALKALINE CONDITIONS: A CASE
STUDY WITH THE ELECTROOXIDATION OF ALCOHOLS

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**ON THE PERFORMANCE OF A POLYMER ELECTROLYTE MEMBRANE
ELECTROCHEMICAL REACTOR FOR ELECTROSYNTHESIS OF
CARBOXYLIC ACIDS IN ALKALINE MEDIA**

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Abstract

A novel polymer electrolyte membrane electrochemical reactor (PEMER) configuration has been employed for the direct electrooxidation of propargyl alcohol (PGA), a model primary alcohol, towards its carboxylic acid derivatives in alkaline medium. The PEMER configuration comprised of an anode and cathode based on nanoparticulate Ni and Pt electrocatalysts, respectively, supported on carbonaceous substrates. The electrooxidation of PGA was performed in 1.0 M NaOH, where a cathode based on a gas diffusion electrode was manufactured for the reduction of oxygen in alkaline conditions. The performance of a novel alkaline anionic exchange membrane based on Chitosan (CS) and Poly(vinyl) alcohol (PVA) in a 50:50 composition ratio doped with a 5 wt.% of poly (4-vinylpyridine) organic ionomer cross-linked, methyl chloride quaternary salt resin (4VP) was assessed as solid polymer electrolyte. The influence of 4VP anionic ionomer loading of 7, 12 and 20 wt.% incorporated into the electrocatalytic layers was examined by SEM and cyclic voltammetry (CV) upon the optimisation of the electroactive area, the mechanical stability and cohesion of the catalytic ink onto the carbonaceous substrate for both electrodes. The performance of the 4VP/CS:PVA membrane was compared with the commercial alkaline anionic exchange membrane FAA –a membrane generally used in alkaline fuel cells- in terms of polarisation plots in alkaline conditions. Furthermore, preparative electrolyses of the electrooxidation of PGA was performed under alkaline conditions of 1 M NaOH at constant current density of 20 mA cm⁻² using a PEMER configuration to provide proof of the principle of the feasibility of the electrooxidation of other alcohols in alkaline media. Conversion the PGA from the electrosynthetic process to Z isomers of 3-(2-propynoxy)-2-propenoic acid (PPA), 0.74 and

0.77 for FAA and 4VP/CS:PVA membrane respectively, and alkaline stability of the membranes within the PEMER configuration was finally evaluated.

Keywords: PEMER configuration, Anionic alkaline exchange membrane, Anionic ionomer, Chitosan/poly vinyl alcohol membrane, alcohol electrooxidation.

1. Introduction

The use of the electrochemical technology in organic synthetic processes to obtain high added-value products is a relevant alternative against conventional chemical procedures in terms of a more environmentally friendly technology [1, 2]. The development of solid polymer electrolyte (SPE) technology [3], and more specifically, direct alcohol fuel cells applications [4] has been introduced into the field of organic electrosynthesis. In this regard, the concept of Polymer Electrolyte Membrane Electrochemical Reactor (PEMER) has been recently introduced in organic electrosynthesis, e.g. for the N-acetyl-L-cysteine production from the electroreduction of N,N-diacetyl-L-cysteine [5] and the synthesis of 1-phenylethanol from the electroreduction of acetophenone [6, 7] under acidic conditions. Moreover, pioneering work performed by Ogumi on the electrochemical hydrogenation of olefinic double bonds [8] and the reduction of nitrobenzene [9] was used a Nafion membrane-based SPE, within a similar configuration to PEMER where the product purification operations were then reduced. To the best of our knowledge and from a

synthetic point of view, there are few works dealing with the electrooxidation of alcohols within a configuration similar to PEMER and/or filter-press electrochemical cell under alkaline conditions [10], [11], [12]. Benefits from the electrooxidation of alcohols in alkaline media is based on the more favourable electroorganic process, e.g., the electrooxidation of primary alcohols to its carboxylic acids requires lower anode potentials with a lower cost of electrocatalysts [13,14].

A PEMER configuration has the same structure of a polymer electrolyte membrane (PEM) fuel cell, and its manufacture involves the design and preparation of nanoparticulate electrocatalysts as well as gas diffusion layers deposited onto carbonaceous structures, prompting the use of lower metallic electrocatalysts loading. In a PEMER configuration, the supported electrolyte is the SPE, which allows exchange of cations or anions according to the membrane composition. Recently, significant efforts are being focused on the production and characterisation of new alkaline anion exchange membranes (AAEMs) as alternative to acidic media, and the commonly used cationic membrane as SPE in a fuel cell [15,16] or direct alcohol fuel cells [17], to mention only a few examples. The use of AAEMs in alkaline media mainly benefits from the kinetic enhancement of the electrochemical oxygen reduction reaction (ORR); the organic fuels oxidation being favoured at alkaline pH; the utilisation of non-noble metals as electrode materials and the use of membranes without perfluorinated ionomers. Nevertheless, alkaline media also present disadvantages regarding the chemical and mechanical stability of membranes when they are submitted to strong alkaline conditions and elevated temperatures, and the progressive carbonation due mainly to CO₂ coming from atmospheric air or fuel oxidation [15]. Thus, AAEMs are vital elements that govern the highest electrochemical performance of a fuel cell or a PEMER, the latter from an electrosynthetic viewpoint. A vast body of

literature focusses on the synthesis and characterisation of novel AAEMs or hydroxide exchange membranes (HEMs) with different eco-friendly polymers as continuous matrix such as chitosan [18], and poly(vinyl) alcohol [19], doped with fillers of different nature [20] and cross-linker [21], to adapt the polymers low electrical resistance and thermal, mechanical and chemical stability, as well as high permselectivity to PEMER type configuration requirements.

The membrane is not the only limiting element in the performance of a PEM electrochemical reactor, but also the electrocatalytic layers attached to the membrane and the gas diffusion layers. This configuration is called Membrane Electrode Assembly (MEA) and comprises the layers of electrocatalytic materials and membrane intimately bound. With regard to electrocatalytic layer, the functions ionomer which deserve to be highlighted are (i) binding of nano-particulate electrocatalyst to form a 3D structure facilitating the mobility and transfer of OH^- as well as reactants and products, (ii) increase of active electrocatalytic surface and (iii) the enhancement of the MEA mechanical durability [17, 22, 23]. Consequently, the ionomer nature and its composition within electrocatalytic layer play a crucial role during the electrochemical processes occurring inside the electrochemical reactor.

This article aims at the manufacture and performance improvement of a 25 cm^2 PEMER configuration working at controlled current intensity in alkaline media for the electrooxidation of a model alcohol molecule, propargyl alcohol (PGA), toward the synthesis of its carboxylic acid derivatives with interest in industry. In our previous works, we have demonstrated that the electrooxidation of PGA at room temperature leads to the selective formation of Z isomers of 3-(2-propynoxy)-2-propenoic acid (PPA) and propiolic acid (PA) [14, 24] using an electrochemical H-cell type. Both PPA and PA compounds are

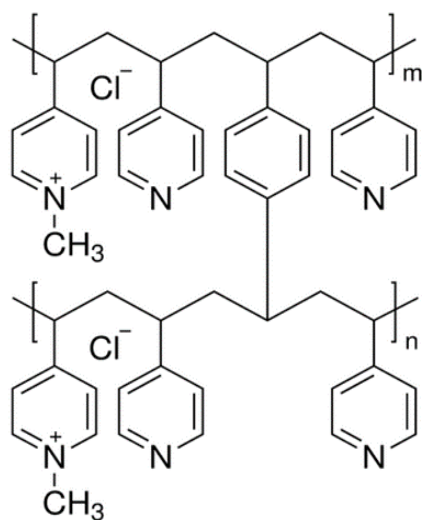
used as (i) polishing agents in electroplating baths to improve metal deposition, (ii) corrosion inhibitors and (iii) intermediates in organic syntheses [25]. For the scale-up of the electrosynthesis process, we have developed and manufactured the three main parts of a PEMER configuration: a nickel based nano-particulate anode for the electrooxidation of PGA, a platinum based nano-particulate cathode for the electrochemical ORR, and the AAEM as a SPE separator. SEM and cyclic voltammetry (CV) have been used for the characterisation of the anode and cathode electrodes. After the assembly of the PEMER, we have examined the conversion of PGA electrooxidation towards the two possible final products expected, PA or PPA.

As alternative membranes to commercial AAEMs, our recent research has demonstrated that membranes based on chitosan (CS) and polyvinyl alcohol (PVA) doped with organic ionomers and layered inorganic fillers exhibit good mechanical properties, thermal and chemical stability, with an improvement of conductivities and reduced alcohol permeability in direct alcohol oxidation in a PEMER configuration [26]. Interestingly, the use of the poly (4-vinylpyridine) cross-linked, methyl chloride quaternary salt resin ionomer binder (4VP), which is employed in numerous works dealing with alkaline fuel cells [27-30], has provided excellent performance for the synthesis of the CS:PVA polymeric blend membrane (4VP/CS:PVA) in terms of ionic conductivity with values over 1.0 mS cm^{-1} . Hence, as an alternative to the commercial AAEMs, this work aims to look into the feasibility of less expensive and biodegradable 4VP/CS:PVA membrane for the electrooxidation of alcohols in alkaline medium using a PEMER configuration.

2. Experimental

2.1 Chemicals and reagents

Propargyl alcohol (PGA) and propiolic acid (PA) were of analytical grade (+ 99% purity, from Alfa Aesar). PGA was purified through distillation before use and its purity was determined by ^1H NMR. Vulcan XC-72R carbon powder was purchased from Cabot Corporation (CAS No 1333-86-4). The ion exchange cross-linked, methyl chloride quaternary poly (4-vinylpyridine) (4VP) salt resin, whose molecular structure is represented in **Scheme 1**, and polytetrafluoroethylene PTFE were purchased from Sigma Aldrich. Commercial FAA membrane was purchased from Fumatech GmbH. The synthesis of the 4VP/CS:PVA membrane has been described in detail elsewhere [26]. All other chemicals were purchased from the highest analytical grade available and were used as received without any further purification. All solutions were prepared using doubly distilled water with a resistivity not less than 18.2 M Ω cm.



Scheme 1. Structure of the methyl chloride quaternary cross-linked poly (4-vinylpyridine) ion exchange ionomer resin.

2.2 Catalytic inks and electrode preparation

Anode and cathode electrodes were prepared by airbrushing technique. The catalytic inks of the anode and the cathode were sprayed onto a 5 x 5 cm² Toray paper (T, TGPH-120) placed on a hot metallic plate at 90 °C to facilitate solvent evaporation, achieving Ni loading of 0.1 mg cm⁻² and Pt loading of 1 mg cm⁻², respectively. The anodic ink consisted of an alcoholic dispersion of nickel nanoparticles supported onto carbon black (Ni/CB) with 20 wt. % metal content in 20 wt. % 4VP ionomer (from a 1.96 wt. % 4VP aqueous solution as mother dispersion) with respect to the total sum of weight of Ni/CB and 4VP. Ni/CB were prepared according to experimental procedure described in previous work [24], in which nickel nanoparticles were synthesised by reducing the NiCl₂·H₂O salt with NaBH₄ in ethanolic sodium hydroxide medium at room temperature under vigorous magnetic stirring.

The gas diffusion electrode (GDE) of the cathode consisted of an electrocatalytic layer made of platinum nanoparticles supported on carbon black (Pt/CB) over a backing layer (a Vulcan carbon to PTFE ratio of 40/60 w/w, and Vulcan XC-72 loading of 2.0 mg cm⁻²), which was supported on a 20 wt. % teflonated Toray Paper TGPH-120. The catalytic ink of the cathode was a Pt/CB powder formed by 7, 12 and 20 wt. % of 4VP ionomer (from a 1.96 wt. % 4VP aqueous solution as mother dispersion). The Pt/CB nanoparticles were prepared according to experimental procedures described in a previous work [31]. Briefly, an equivalent H₂PtCl₄ and sodium citrate solution was reduced by ice-cold sodium borohydride solution. Then, a certain amount of Vulcan carbon was added until a final 20 wt. % of Pt content. Finally, sodium hydroxide pellets were added to precipitated Pt nanoparticles, which are thereafter filtered through nylon membrane filter of 45 μm (Cat

No. MNY045047H, chm by CHMLAB GROUP) and then dried overnight at 70 °C. The anode and cathode were named as follows: 4VP-Ni/CB/T for the anode and 4VP(z)-Pt/CB/GDE/T for the cathode, where z stands for the wt. % of anionic ionomer and T indicates the Toray paper support.

2.3 Electrodes characterisation

Scanning electron microscopy (SEM, HITACHI S-3000N microscope working at 20 kV with X-ray detector Bruker Xflash 3001 for microanalysis.) was employed to analyse the morphology of the electrocatalytic layers of the manufactured electrodes. The electrochemical characterisation of the different electrocatalytic layers was performed in a three-electrode configuration glass cell, using as underlying electrode a polished glassy carbon (GC) surface or a Toray paper where the catalytic inks for the anode and cathode were deposited by dripping or airbrushing techniques, respectively. A gold wire was used as counter electrode and an Ag/AgCl/ (3.5 M KCl) electrode as reference electrode. Solutions consisted of 1.0 or 0.1 M NaOH and were deoxygenated under argon atmosphere. CV experiments were performed using an Autolab III potentiostat/galvanostat (Eco-Chemie). All Ni based anodes were previously pre-treated between -0.5 and +0.6 V versus the Ag/AgCl/ (3.5 M KCl) reference electrode for 100 cycles at a scan rate of 100 mV s⁻¹ to obtain the catalytic form of NiOOH [14, 24, 32, 33] responsible of catalysing the electro-oxidation of alcohols. All CV measurements were performed at 25 ± 2 °C.

2.4 Preparative electrosynthesis

Preparative electrooxidation of PGA was performed using a home-made PEMER configuration that was built by home machining with a flow distributor on two graphite

plates [7]. Figure 1 shows a scheme of the PEMER configuration. The MEA resulted in a 25 cm² projected area. FAA and 4VP/CS:PVA membranes were activated in 1.0 M NaOH for 24 h prior to the experiments and then rinsed, stabilised and stored in deionised water at room temperature. Membranes were placed between the cathode and anode and then the MEA configuration was pressed and assembled between two graphitic column plates that act as anodic and cathodic current intensity collectors. The electrochemical reactor consisted of 4VP-Ni/CB/T as anode and a gas diffusion electrode 4VP(12)-Pt/CB/GDE/T as cathode, both electrodes with a projected area of 25 cm². A peristaltic pump (Ismatel Reglo DIG MS/CA 2–8C) provided a controlled flow rate of the anodic solution. The cathode was fed with synthetic air (99.999 % purity from Air Liquid, Spain) humidified through a distilled water column at atmospheric pressure controlled by a digital mass flow rate controller (Smart-trak 2 Sierra Instruments, Inc.). Current intensity, charge passed and cell potential during the electrosynthesis were controlled and monitored using a Gw instek PSP-2010 power supply as current source. Before starting the electrooxidation of PGA, Ni/CB electrocatalytic layer was activated. To do this, the anode compartment was fed with a 1.0 M NaOH solution and then a current intensity was set to 0.3 A for 16 min to obtain the electrocatalytic NiOOH species. Later, polarisation plots were taken at variable current intensity between 0.020 and 0.500 A, where the current intensity was held for 1 min before recording the cell potential. PGA electrooxidation was carried out at room temperature with a controlled current intensity of 0.5 A, i.e., 20 mA cm⁻² and a charge passed of 2895 C.

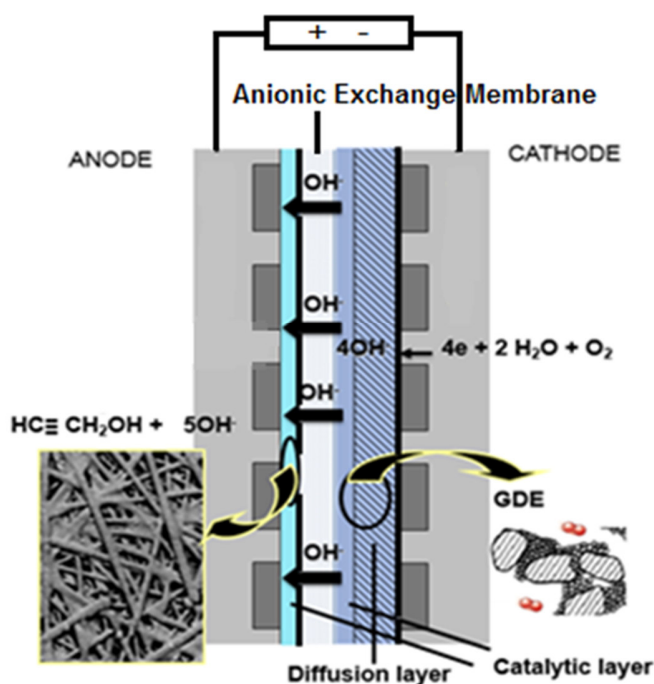


Figure 1. Scheme of a homemade PEMER configuration used for the electro-oxidation of PGA.

For the electrolysis experiments, the conversion of PGA and the formation of the final products from the electrooxidation of PGA were followed by HPLC, according to the experimental procedure described elsewhere [24]. The final products were confirmed by ^1H NMR at 400 MHz for ^1H with a BRUKER AV300 Oxford instrument. For the final workup of the electrooxidative reaction, liquid–liquid extraction of the acidified final anolyte solution was performed in ethyl ether; thereafter the solvent was dried in anhydrous sodium sulphate and finally concentrated *in vacuum* at 40 °C.

3. Results and discussion

3.1. Morphology and electrochemical characterisation of the Pt/CB/GDE/T cathode

We first investigated the influence of the 4VP anionic ionomer concentration on the electrochemical response of platinum nanoparticles (PtNPs) in 0.1 M NaOH aqueous solution. Figure 2 shows the typical response of PtNPs in this medium[34]. Briefly, the peaks of the voltammogram in the potential range between -0.90 and -0.55 V contains the contributions of hydrogen adsorption/desorption. On the other hand, the potential range between -0.35 V and 0.0 V shows the characteristic OH adsorption/desorption region. Therefore, an increase of the 4VP ionomer concentration within the Pt/CB ink preparation leads to the blockage or fouling of the Pt surface. Nonetheless, a key point of this work come up about the counterbalance between the electrocatalytic properties of the PtNPs for the ORR and the adequate catalytic ink formulations to enhancing particles cohesion and therefore the formation of a three dimensional structure. With the aim of shedding light on how the 4VP affects the CV pattern of PtNPs, Figure 2a shows the CVs of Pt/CB varying 4VP wt.% of the ink drop-casted onto the glassy carbon electrode in 0.1 M NaOH. The 4VP content with respect to Pt/CB is examined within a range of 7-20 wt. %. In the absence of 4VP, the CV of Pt/CB nanoparticles depicts well defined the peaks associated with the adsorption/desorption regions of hydrogen and OH [34, 35]. However, the higher the 4VP wt. %, the larger the anionic ionomer adsorption and the blockage of the catalytic surface of the PtNPs, with a consequent reduction of the electroactive area. Hence, a remarkable charge reduction, associated with adsorption/desorption of hydrogen, occurs when 7 wt. % 4VP ionomer are added for the same loading of Pt within the Pt/CB nanoparticles. Not surprising is the fact that an increase in 4VP wt. % from 7 to 12 wt. % is detrimental for the

observation of a clear CV pattern of the Pt/CB nanoparticles in alkaline medium. Moreover, the charge involved on the hydrogen and OH adsorption/desorption in the CV of Figure 2a is similar for both 12 and 20 wt. % 4VP.

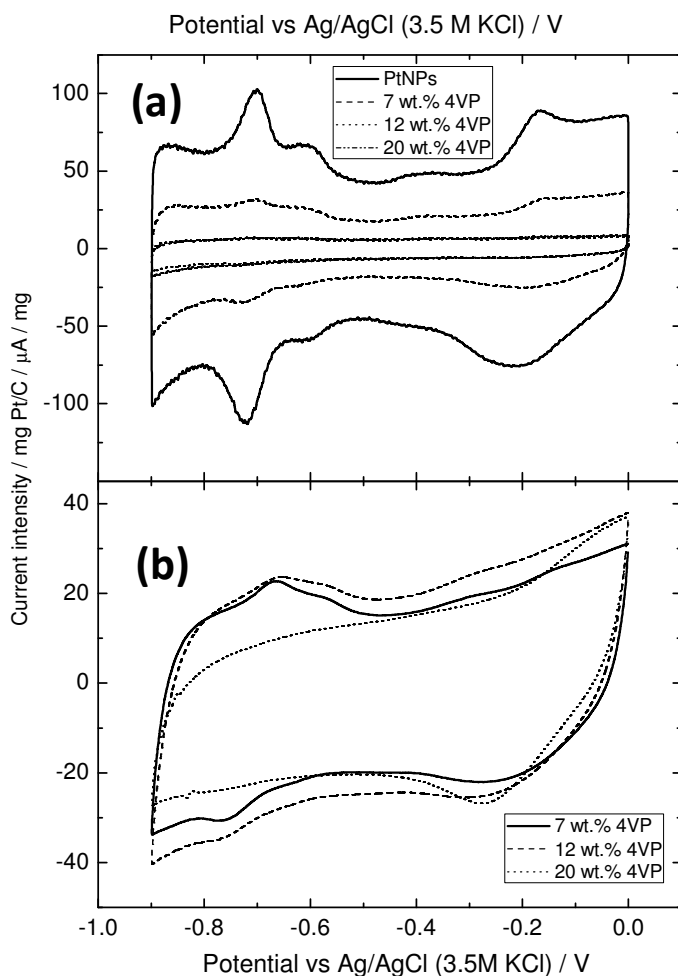


Figure 2. (a) Cyclic voltammetry of the electrochemical response of PtNPs with different content of 4VP casted onto a GC electrode. (b) Cyclic voltammetry of the electrochemical response of 4VP(z)-Pt/CB/GDE/T electrodes. 0.1 M NaOH. Scan rate 10 mV s^{-1} . Fifth scan recorded.

A comparable behaviour is shown in Figure 2b when we assessed the CV response of the cathodic 4VP(z)-Pt/CB/GDE/T electrode, where the Pt catalytic inks have been sprayed onto the carbonaceous gas diffusion layer supported on Toray paper (see the experimental section). Results from Figure 2b reveal that the electrochemical response of 4VP(7)-Pt/C/GDE/T and 4VP(12)-Pt/C/GDE/T in 0.1 M NaOH exhibit still the resolved peaks associated with the adsorption/desorption of hydrogen. As far as the cohesion of the Pt/CB layer is concerned, we found that a percentage of 4VP below 12 wt. % is critically detrimental for the mechanical stability of the Pt/CB layer, leading to leaching of Pt/CB nanoparticles when the 4VP-Pt/CB/GDE/T electrode is immersed in the alkaline solution. On the other hand, ionomer percentages over 20 wt. % resulted in a complete Pt surface blockage by the 4VP molecules, as shown in Figure 2b, even though the adherence and mechanical properties of the 4VP-Pt/CB/GDE/T improved significantly compared to the other percentages. In this regard, Mamlouk et al. [23] and references therein [22, 36-41] have reviewed the importance of ionomer optimisation on the preparation of catalytic inks, and therefore on the electrocatalytic layers of both cathode and anode electrodes towards hydrogen and direct alcohol alkaline fuel cells. Accordingly, the design of the catalytic ink is crucial to obtain electrodes with improved mechanical, thermal stability, electrocatalytic activity and durability performance. Furthermore, other recent studies reported that the optimum percentage of anionic FAA-3 ionomer that leads to the maximum performance of fuel cell was around 25 wt.% when the electrolyte was 1.0 NaOH [28]. On the other hand, Leng et al. [42] performed the electrolysis of water using a MEA configuration, in which the anionic AS4 ionomer amount of the catalytic layer in the anode and cathode was 16 wt. %. It should be noted that an excessive amount of ionomer could lead to higher resistance

mainly ascribed to the hindering of the reactive diffusion or charge transfer and therefore a subsequent inactivation of the Pt electrocatalyst. On the contrary, a low amount of ionomer can involve high resistance and therefore high IR drops and low OH⁻ conductivity through the electrocatalytic layer.

Under the compromised value of 12 wt. % 4VP within the Pt/CB electrocatalytic layer, a highly homogeneous Pt/CB layer was observed in the SEM images of the 4VP(12)-Pt/CB/GDE/T electrode in Figures 3a and 3c. The EDX mapping of the plane section of electrocatalytic layer (Figure 3b), confirms that the Pt/CB nanoparticles were very uniformly dispersed throughout the diffusion layer/Toray paper without agglomeration. The cross-section of the cathode 4VP(12)-Pt/CB/GDE/T was observed in Figure 3c and 3d, depicting Pt nanoparticles onto the top of the electrocatalytic layer.

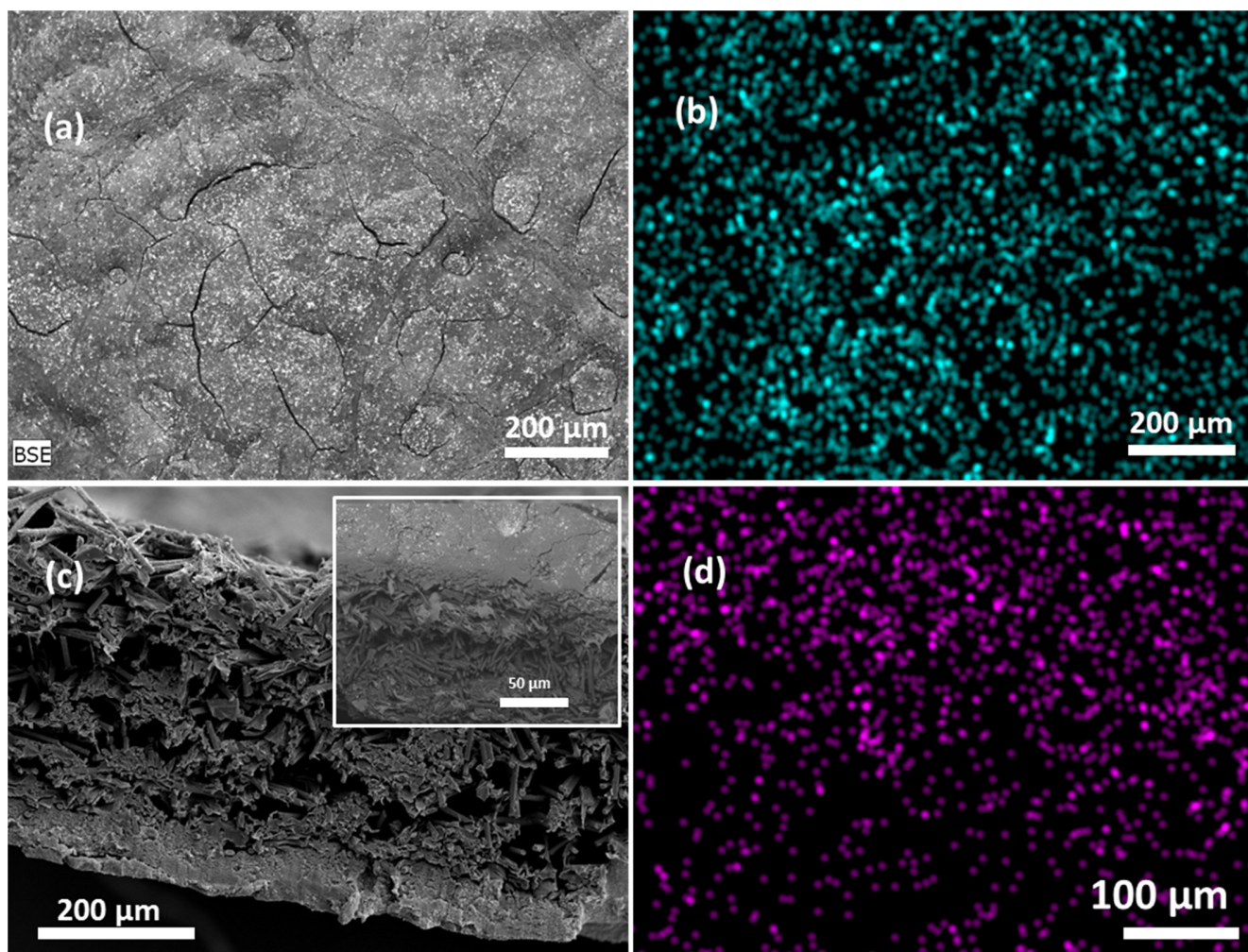


Figure 3. SEM images of (a) plane section of the 4VP(12)-Pt/CB/GDE/T, (b) Pt mapping of the plane section of the 4VP(12)-Pt/CB/GDE/T, (c) cross section of the 4VP(12)-Pt/CB/GDE/T, and (d) Pt mapping of cross section of the 4VP(12)-Pt/CB/GDE/T.

3.2 Morphology and electrochemical characterisation of the 4VP-Ni/CB/T anode.

Figure 4a depicts the cyclic voltammetric response of the electrochemical activation of Ni surface of the 4VP-Ni/CB/T electrode in 1.0 M NaOH. It is worth noting that 20 wt. % 4VP resulted optimum from mechanical property improvement point of view of the

electrocatalytic layer of the Ni/CB. CV behaviour of the 4VP-Ni/CB/T electrode was compared to the same electrode containing a 20 wt. % cationic Nafion ionomer as binder (Figure 4b), i.e. Nafion-Ni/CB/T electrode, characterised in our previous work [24]. The cyclic voltammetric responses demonstrate that both electrodes prepared with different binders exhibited similar voltammetric performance in the absence of PGA. However, it is worth pointing out that the electrochemical responses of 4VP-Ni/CB/T anodes towards the electrooxidation of 0.05 M PGA was slightly higher than when Nafion-Ni/CB/T electrode was used. While the net increase in current intensity associated with the electrooxidation of PGA is 4.0 μA by using the 4VP ionomer, the Nafion-Ni/CB/T showed only an increment of 2.2 μA with respect to the current intensity obtained in the absence of alcohol. Moreover, the peak potential for the electrooxidation of PGA using the 4VP-Ni/CB/T electrode was 0.47 V, lower than the value of 0.54 V obtained for the Nafion-Ni/CB/T electrode. It is difficult to ascribe the slight differences in current intensity or oxidation peak potentials noted above, to the effect of the ionomer nature rather than a higher nickel electroactive area or different resistive components indistinguishably observed for both electrodes. Nevertheless, the anionic ionomer is likely the only species in the electrode assembly that allows hydroxide anions transport through the electrocatalytic layer, thereby enhancing the performance of anode electrode [22].

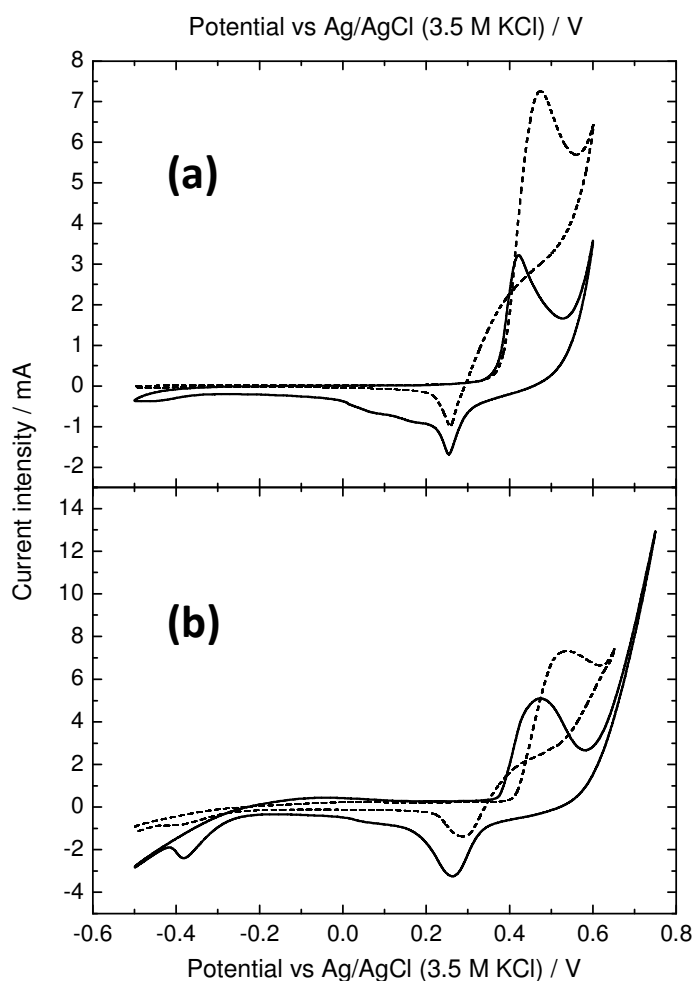


Figure 4. Cyclic voltammetry of the electrochemical response of Ni/CB/T electrode with 20 wt.% of 4VP (a), and Ni/CB/T electrode with 20 wt.% of Nafion (b). 1.0 M NaOH (solid line) and in the presence of 0.05 M PGA (dashed line). Scan rate = 10 mV s^{-1} . Third scan recorded. Geometric area: 0.35 cm^2 .

The surface and cross sections of the 4VP-Ni/CB/T anode are observed in Figure 5. 4VP-Ni/CB layer displayed a homogeneous coverage of the carbon fibres without any

agglomerations. The same results are obtained when Nafion was used as binder [24]. Such a cross section demonstrates that the electrocatalytic layer was deposited onto the tridimensional electrode surface (Figure 5b and 5d).

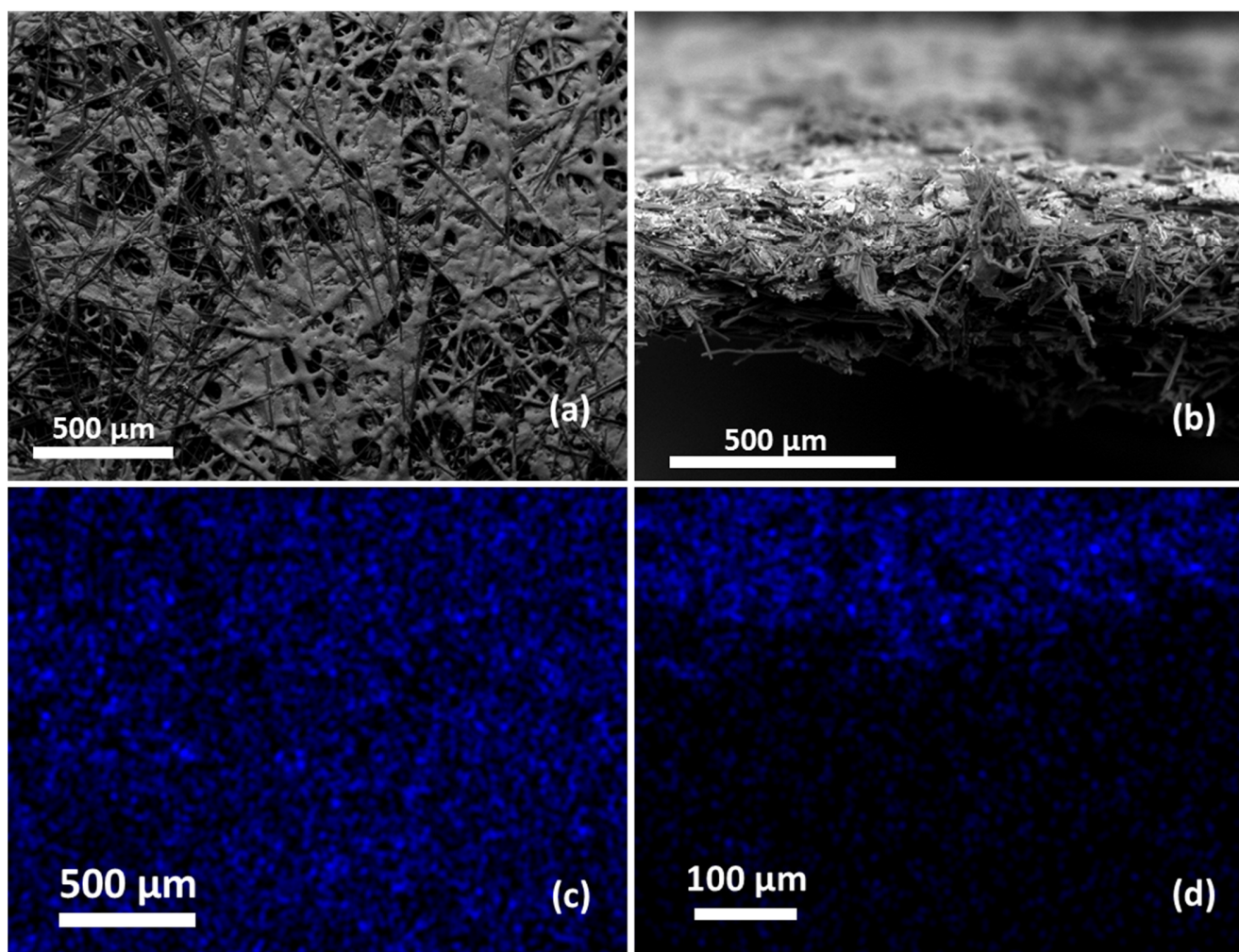


Figure 5. SEM images of Ni/CB/T anode with 20 wt.% of anionic ionomer 4VP of plane section (a) and cross section (b). Ni mapping of plane section (c) and cross section (d).

3.3 Polarisation plots using the PEMER configuration.

A polarisation technique was performed for understanding the electrochemical response of the MEA configuration employed when a current or potential are applied under steady conditions. Figure 6 shows the polarisation plots using the PEMER configuration consisting of a 4VP-Ni/CB/T as anode, a 4VP(12)-Pt/CB/GDE/T as cathode and either 4VP/CS:PVA or FAA membranes using a variable concentration of the NaOH solution. Polarisation experiments were performed in the presence of 0.25 M PGA in NaOH solution.

Figure 6a depicts the polarisation plots for different NaOH concentration in the anodic compartment when the FAA commercial AAEM was used. As expected, the cell potential increased as the NaOH concentration decreased. The increase of almost 200 mV at 0.5 A current intensity in 0.1 M NaOH was mainly associated with effect of the conductivity of NaOH solution. The use of 0.01 M NaOH resulted in a notable increase in the cell potential up to values of 2 V, where the OH⁻ consumed during the electrooxidation of PGA come from the membrane itself. Even though the electrooxidation of PGA is viable with a cell potential near 2 V, the chemical stability of the Ni(OH)₂/NiOOH electrocatalyst redox couple is compromised by the pH reduction of the solution during the electrooxidation.

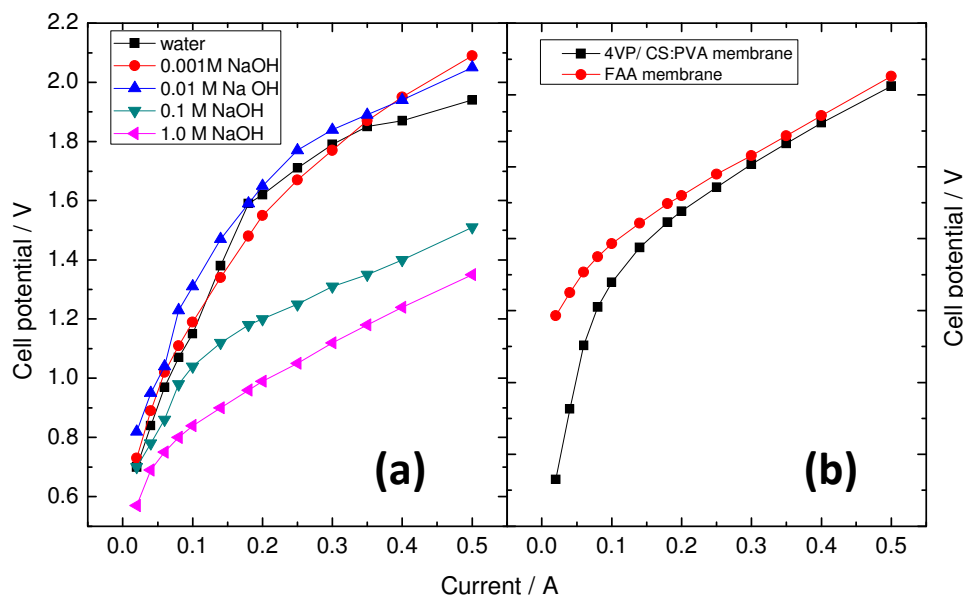


Figure 6. (a) Polarisation plots using a PEMER configuration and the FAA membrane with different NaOH concentration. The range of current intensity is set between 0.020 A and 0.500 A. (b) Polarisation plots using a PEMER configuration as a function of the membrane. 1.0 M NaOH plus 0.250 M PGA. The range of current is varied between 0.020 A to 0.500 A. Flow rate of 12 mL min⁻¹ for the anodic compartment, and 50 mL min⁻¹ for the synthetic air through the cathodic compartment.

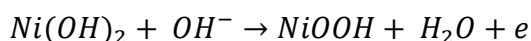
We investigated the influence of the flow rate of the anodic solution through the anode compartment upon the polarisation plots to optimise the cell potential. Within a range of flow rates between 6-20 mL min⁻¹ using a 1.0 M NaOH solution in the anodic compartment no significant differences in terms of cell potential were observed. The only exception occurred when working at higher current intensities, where the oxygen evolution was favoured. Under such conditions, the laminar hydrodynamics dominates in the anodic

compartment, which turns inefficient or influences very slowly the removal of molecular oxygen from this compartment. Hence, the orientation of 4VP-NiCB catalytic layer in contact with the membrane or the graphitic column collector was responsible of the increment or reduction of the cell potential, respectively. When the 4VP-Ni/CB electrocatalytic layer was in contact with the graphitic column collector, the cell potential, at least at higher current intensities, decreased slightly owing likely to an easier evacuation of molecular oxygen bubbles generated from the electrooxidation of water onto the NiOOH electrocatalytic surface. In the case of the influence of air feeding flow rate through the cathodic compartment on the cell potential of the PEMER configuration, no variations of cell potentials were found when feeding air through the 4VP(12)-Pt/CB/GDE/T cathode within a flow rate range between 50 and 200 mL min⁻¹. In view of the above results, we can conclude that a flow rate of 12 mL min⁻¹ for the anodic solution, a 50 mL min⁻¹ flow rate of air through the cathodic compartment and 1.0 M NaOH solution provided the minimum cell potential for the current intensities evaluated. Such experimental conditions were chosen to compare the performance of the novel 4VP/CS:PVA membrane with that of the commercial FAA membrane. Figure 6b depicts the polarisation plots for both AAEMs. Within the current intensity range from 0.02 A to 0.1 A, the cell potential resulted higher for the FAA membrane than the 4VP/CS:PVA membrane. This is due to the different activation of the cathodic process, associated with the ORR, which is a function of the type of membrane used. It is worth noting that the membranes display differences regarding water swelling and alcohol permeation properties [26] that affect the performance of the cathode at low current intensities. Then, after the activation energy for the ORR was reached, the cell potential for the 4VP/CS:PVA membrane increased until values near those for the FAA membrane. On the other hand, the same polarisation plot was also performed

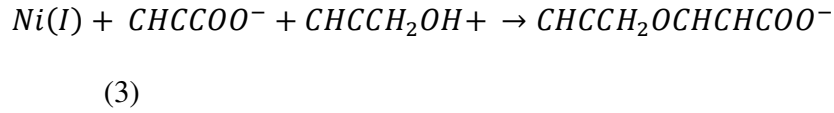
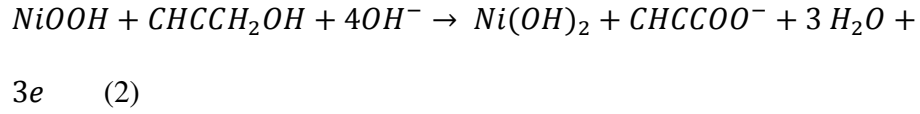
using the Nafion-Pt/CB/GDE/T cathode and the Nafion-Ni/CB/T anode deposited on the graphitic columns, with the FAA commercial membrane (results not shown). This configuration provided a cell potential of around 5.0 V for the highest current intensities tested, demonstrating the detrimental effect of the use of the Nafion ionomer. Moreover, the study of two different PEMER configurations, (i) Nafion-Pt/CB/GDE/T as cathode and 4VP-Ni/CB/T as anode, and (ii) 4VP(12)Pt/CB/GDE/T as cathode and Nafion-Ni/CB/T as anode demonstrated that the highest increase in cell potential was obtained when the Nafion-Pt/CB/GDE/T electrode was used. Hence, it is evident that the use of Nafion as a cationic ionomer for the preparation of the cathode is disadvantageous in alkaline medium under the experimental conditions of this work, precluding the OH⁻ transport through the electrocatalytic layer of the Nafion-Pt/CB/ electrode.

3.4. Preparative electrooxidation of propargyl alcohol

We next turned to the preparative electrooxidation of PGA to the corresponding carboxylic acids derivatives (PA and/or PPA) using the PEMER configuration. Preparative electrolyses were performed either using the FAA or the 4VP/CS:PVA membrane. Anodic, cathodic and the overall electrochemical process reactions as well the overall electrochemical process for the NiOOH species formation are displayed in reactions **1-4** as follows,



(1)



where reactions **2** and **3** denote the formation of PA and PPA, respectively.

Focusing on compartment of anode, it should be pointed out that the electrooxidation of PGA involves the consumption of 5 mole OH^- per mole PGA. With a PGA concentration of 0.250 M within the anodic solution (0.0075 mole of PGA), the mole of OH^- in 1.0 M NaOH anodic solution (0.03 mole of OH^-) is insufficient to carry out the electrooxidative process of 0.0075 mole PGA to PA under the experimental conditions of the present work, according to reaction **1** and **2**. Thus, the ORR under alkaline conditions occurring in the cathode will supply 4 mole of OH^- (0.0017 mole of OH^- for a theoretical charged passed of 30 C) per mole molecular oxygen reacted in the cathode. Hence, ORR provides a continuous flux of OH^- to the anodic compartment needed for the electroregeneration of $NiOOH$ species (reaction **1**) and the electrooxidation of PGA (reactions **2** or **3**).

Table 1. Experimental conditions and results obtained from the preparative electrooxidation of PGA using both FAA and 4VP/CS:PVA membranes.

ELECTROLYSIS CONDITIONS	Initial amount	Anolyte flow rate/ mL min ⁻¹	Catholyte flow rate/ min ⁻¹	j/mL mA cm ⁻²	Temperature/ °C	Final pH	
	PGA/ mole (0.0075 (0.25 M))	12	50		25 ±	14	
RESULTS	Membrane	X _{PGAconversion}	Current efficiency, φ	Products	*Space time yield/k g m ⁻³ day ⁻¹	*Specific electrolytic energy consumption/kW h kg ⁻¹	Average cell potential / V
	FAA	0.74	0.31	Z-PPA	14574	3.32	1.21 ±0.01
	4VP/CS:PVA	0.77	0.33	Z-PPA	15514	3.22	1.25 ±0.04

*Specific electrolytic energy consumption and space time yield were calculated according to references [37] and [38], respectively, where the specific volume V_e has been considered as geometric volume, 25 cm² x thickness of electrode.

Table 1 displays the conditions established for the electrooxidation of PGA and the obtaining of the final products in terms of current intensity and charge passed. The electrolyses performed using the commercial FAA membrane gave rise to a PGA conversion of 0.74. The use of the 4VP/CS:PVA membrane provided a PGA conversion of 0.77 at a current density of 20 mA cm⁻². PPA was the only final product from the

electrooxidation of PGA. Therefore, the viability of the electrooxidation of PGA in alkaline medium using anionic exchange membrane based on low cost and environmentally friendly polymers as SPE in PEMER provides the proof of concept necessary to be extrapolated to a vast variety of alcohol electrooxidation processes that are currently using expensive and environmentally unfriendly commercial membranes, with similar electrochemical performance.

Finally, the stability of the anode and cathode during the electrooxidation of PGA was proved by consecutive electrolyses using both FAA and 4VP/CS:PVA membranes. Cell potentials were found to be very stable during the electrooxidation of PGA and consequently our results were clearly indicative of a proper performance of all parts of the PEMER configuration. Furthermore, the integrity of the membranes was checked by SEM (not shown) after repeated electrolyses, and no physical modifications or deterioration of the membrane materials were observed. In the case of the mechanical stability of the 4VP-Ni/CB/T and 4VP(12)-Pt/CB/GDE/T electrodes, a more profound investigation by SEM of both electrode surfaces revealed no detachment of the electrocatalytic layer as well as a defect-free surface after repetitions consecutive of electrolyses.

4. Conclusions

In this work, we have demonstrated the viability of the electrooxidation of alcohols in alkaline media either using a commercial anionic alkaline exchange membrane or a newly developed Chitosan/poly (vinyl alcohol) CS:PVA-based anion exchange membrane doped with 4VP ionomer in a PEMER configuration. An optimal 12 wt. % 4VP anionic ionomer concentration with respect to Pt/CB electrocatalyst was optimum in terms particles cohesion and electrocatalytic response measured by the adsorption/desorption of hydrogen,

and facilitated an excellent attachment to the carbonaceous substrate (either gas diffusion layer or Toray paper substrates).

The main product obtained from the electrooxidation of PGA in this PEMER configuration under the experimental conditions of current density of 20 mA cm^{-2} and a Ni loading of 0.1 mg cm^{-2} was *Z isomers of 3-(2-propynoxy)-2-propenoic acid*, with a fractional conversion of 0.74-0.77 for 2895 C of charge passed. Furthermore, the performance of the new 4VP/CS:PVA membrane was comparable to that of the FAA commercial membrane in terms of alkaline stability, PGA conversions and cell potentials. Last but not least, the performance and mechanical integrity of both 4VP(12)-Pt/CB/GDE/T and 4VP-Ni/CB/T electrodes were stable at least with repetitive PGA electrooxidations.

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