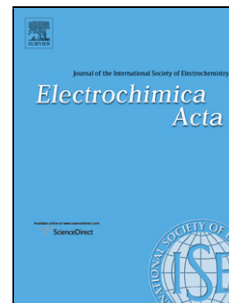


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Authors: Alfonso Sáez, Vicente García-García, José Solla-Gullón, Antonio Aldaz, Vicente Montiel



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## Electrocatalytic hydrogenation of acetophenone using a Polymer Electrolyte Membrane Electrochemical Reactor.

Alfonso Sáez, Vicente García-García, José Solla-Gullón<sup>1</sup>, Antonio Aldaz<sup>1</sup>, Vicente Montiel\*<sup>1</sup>

Instituto de Electroquímica, Universidad de Alicante, Apartado 99, 03080 Alicante, Spain.

### Abstract

The use of a solid polymeric electrolyte, spe, is not commonly found in organic electrosynthesis despite its inherent advantages such as the possible elimination of the electrolyte entailing simpler purification processes, a smaller sized reactor and lower energetic costs. In order to test if it were possible to use a spe in industrial organic electrosynthesis, we studied the synthesis of 1-phenylethanol through the electrochemical hydrogenation of acetophenone using Pd/C 30% wt with different loadings as cathode and a hydrogen gas diffusion anode. A Polymer Electrolyte Membrane Electrochemical Reactor, PEMER, with a fuel cell structure was chosen to carry out electrochemical reduction with a view to simplifying an industrial scale-up of the electrochemical process. We studied the influence of current density and cathode catalyst loading on this electroorganic synthesis. Selectivity for 1-phenylethanol was around 90% with only ethylbenzene and hydrogen detected as by-products.

### Keywords:

Polymer Electrolyte Membrane Electrochemical Reactor, electrocatalytic hydrogenation, acetophenone, 1-phenylethanol,

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\* Corresponding author

Email address: [vicente.montiel@ua.es](mailto:vicente.montiel@ua.es) (Vicente Montiel)

Phone: +34-965903400 (2263)

Fax: +34-965903536

<sup>1</sup> ISE member

## 1. Introduction

1  
2 Electrochemical hydrogenation is an alternative route to catalytic hydrogenation.  
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4 It is performed under more benign conditions (room temperature and atmospheric  
5  
6 pressure) and has been carried out since the beginning of the last century. However, at  
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8 industrial scale, this process has never been as successful as catalytic hydrogenation.  
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12 As far as we know, all the electrochemical reactors employed so far, for  
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14 electrocatalytic hydrogenation processes, are conventional electrochemical reactors with  
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16 or without the separation of compartments and with a liquid supporting electrolyte. In  
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18 the last few decades [1] and at laboratory scale, several electrosynthetic processes have  
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20 been developed using a solid polymer electrolyte, spe, as supporting electrolyte.  
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24 Nowadays, improvements in the fabrication of nanostructured materials  
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26 supported on conductive materials, together with the use of polymeric solid exchange  
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28 membranes for fabricating Membrane Electrode Assemblies (MEA), have led to  
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30 important advances in the field of Polymer Electrolyte Membrane Fuel Cells [2,3].  
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32 Today, there are large-sized fuel cells on the market which can be employed as reactors  
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34 for the industrial electrosynthesis of pharmaceutical and fine chemical products. In our  
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36 laboratory, we have coined the term PEMER (Polymer Electrolyte Membrane  
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38 Electrochemical Reactor) for this type of electrochemical reactor [4]. For these reasons,  
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40 a successful scale-up to industrial level of a synthesis using a spe looks more promising  
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42 than ever.  
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49 According to the literature [5–10], the overall mechanism of the electrocatalytic  
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51 hydrogenation of an unsaturated organic molecule,  $Z=Y$ , on a metal/carbon supported  
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53 electrode involved three steps: the formation of adsorbed hydrogen,  $MH_{ads}$ , on the  
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55 metal, the adsorption of the organic molecule on carbon, and the catalytic hydrogenation  
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57 of the adsorbed organic molecule by the adsorbed hydrogen.  
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In order to test the use of a spe in an electrochemical reactor with a fuel-cell structure, we chose the electrocatalytic hydrogenation of an aromatic ketone, acetophenone, with a Pd/C cathode as test reaction. 1-phenylethanol (two-electron reduction) is the main product of this reduction, and thus of much interest to the fine chemical, pharmaceutical and cosmetic industries [11-15].

The type and composition of the products obtained from the reduction of acetophenone depend on several factors, such as the type of supporting electrolyte, the use of a protic or no-protic medium, pH, the nature and morphology of the electrode, etc. [16-24]. A most careful analysis of the products and of their distribution for the macro-reduction of acetophenone was carried out by L.J.J. Janssen using a graphite cathode [25], DL-pinacol and meso-pinacol being the main products. A very low yield of phenylethanol was also obtained. The main product of the reduction of metal/carbon doped cathodes is 1-phenylethanol if low hydrogen overvoltage metals such as nickel [19], platinum [26] or palladium [27, 28] are used. Polcaro et al. [28] have studied the electrochemical reduction of acetophenone (several concentrations) in acidic and alkaline water-alcohol solutions, using carbon felt catalyzed by electrodeposited Pd as cathode. They obtained 1-phenylethanol with very high selectivity (around 90%) and current efficiencies of 40-50%. The experimental conditions under which these data were obtained have been chosen by us as the basis for our research.

The competitive reaction in electrochemical hydrogenation is the evolution of hydrogen and this frequently prevents the use of high current densities. This is why we decided to use the oxidation of this hydrogen in a gas diffusion electrode as anodic reaction with a view to decreasing the influence of current efficiency on the viability of the synthesis of 1-phenylethanol. The potential applied for the synthesis drops as also

1 the energy cost. Obviously, some hydrogen gas coming from other sources must be  
2 added to the hydrogen that feeds the gas diffusion anode.  
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4 To sum up, the aim of this work is: i) to study the electrocatalytic hydrogenation  
5 of acetophenone for the synthesis of 1-phenylethanol by using Pd nanoparticles  
6 supported on carbon as electrocatalyst ii) to demonstrate that it is possible to use  
7 hydrogen oxidation as the anodic reaction for harnessing the hydrogen evolved at the  
8 cathode during electrochemical hydrogenation; iii) to demonstrate that it is possible to  
9 use a Polymer Electrolyte Membrane Electrochemical Reactor with a similar structure  
10 to that of an organic/air fuel cell for this type of process .  
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## 24 **2. Experimental**

### 25 **2.1. Synthesis of Pd nanoparticles supported on Vulcan XC-72.**

26 Pd nanoparticles were prepared by reducing  $K_2PdCl_4$  with  $NaBH_4$  using a water-  
27 in-oil (w/o) microemulsion consisting of water (3%)/polyethylene glycol dodecyl ether  
28 (BRIJ@30) (16.5%)/n-heptane (80.5%) using the methodology previously used in our  
29 laboratory [29, 30]. The palladium nanoparticles were supported on Vulcan XC-72 to  
30 obtain a nominal loading of 30% wt. The sample has been characterized by  
31 Transmission Electron Microscopy (TEM) to study its morphology, dispersion and  
32 particle size. The equipment used was a transmission electron microscope JEOL mod.  
33 JEM-2010 operating at 300 kV.  
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### 51 **2.2. Manufacture of the cathode.**

52 The cathodes were manufactured by air-brushing a catalytic ink onto a  
53 carbonaceous support (Toray Paper TGPH-90). The catalytic ink was made by  
54 dispersing Pd/C 30% wt in isopropanol as vehicle and a Nafion solution 5% wt as  
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1 binder. For all electrodes, the ratio Pd/C : Nafion in the catalytic layer was always 60:40  
2 with a Pd catalyst loading of 0.2, 0.1, 0.05 and 0.025 mg cm<sup>-2</sup>. Physical characterization  
3 of these electrodes was performed using Scanning Electron Microscopy (SEM)  
4 micrographs obtained with a scanning electron microscope Hitachi S-3000N operating  
5 at 20 kV.  
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11 The current was normalized as current density using the geometric area of the  
12 electrode.  
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### 17 18 19 **2.3. Voltammetric studies.** 20

21 The electrochemical behaviour of the different electrodes in ethanol 96% / water  
22 (90/10 v/v) and 0.1 mol dm<sup>-3</sup> H<sub>2</sub>SO<sub>4</sub> solutions with different concentrations of  
23 acetophenone (from 0 to 0.5 mol dm<sup>-3</sup>) was studied by cyclic voltammetry using a three-  
24 electrode cell. Portions of the fabricated cathodes (0.5 cm x 1.0 cm) were used as  
25 working electrodes. The voltammetric behaviour of 1-phenylethanol and ethylbenzene  
26 was also studied. The electrode potential was controlled using a PGSTAT30 Autolab  
27 system. The counter electrode was a platinum wire. All potentials were measured versus  
28 an Ag/AgCl, KCl (3 mol dm<sup>-3</sup>) reference electrode connected to the electrochemical cell  
29 through a Luggin capillary. The scan rate was 10 mV s<sup>-1</sup>. Acetophenone, 1-  
30 phenylethanol and ethylbenzene solutions were prepared using water type II > 5 MΩ  
31 and ethanol 96%. All reactants were p.a. grade. Finally, experiences were carried out at  
32 room temperature.  
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## 2.4. Electrosynthesis using a Polymer Electrolyte Membrane Electrochemical Reactor.

The electrochemical reactor was a 25 cm<sup>2</sup> PEM single cell fuel cell (mod. EFC-25-01 ElectroChem), with column flow pattern. The cell consisted of a cathode made by air-brushing the catalytic ink on a Toray paper TGPH-90 and an ETEK gas diffusion-type EFGC (Pt catalytic loading of 2.0 mg cm<sup>-2</sup>) as anode. A Nafion 117 membrane was used between cathode and anode as solid polymer electrolyte. These three components were pressed between two carbon plates which act as current collectors (fig. 1) The catholyte starting solutions (volume 60 mL) for the synthesis were: i) 0.5 mol dm<sup>-3</sup> acetophenone in ethanol 96% / water (90/10 v/v) and 0.1 mol dm<sup>-3</sup> H<sub>2</sub>SO<sub>4</sub>, ii) pure acetophenone, iii) 0.5 mol dm<sup>-3</sup> acetophenone in ethanol 96% / water (90/10 v/v) and iv) 0.5 mol dm<sup>-3</sup> acetophenone in ethanol 96%. A peristaltic pump Ismatel Reglo DIG MS/CA 2-8C provided a catholyte flow of 12 mL min<sup>-1</sup>. The anodic reaction was the oxidation of hydrogen (Praxair, purity: 99.999%) that was fed to the anode at 1 atm (ambient pressure) with or without humidification and with a flow of 50 mL min<sup>-1</sup> measured with the MTS-module A-150 of the ElectroChem system. The gas diffusion anode was pressed on the membrane using the current collector. Electrocatalytic hydrogenation was carried out at room temperature and at constant current using an EA-PS 2032-050 power supply.

The catholyte was analyzed by HPLC using a high-resolution liquid chromatograph Agilent 1200 with a Hypersil ODS column 4 x 250 mm, 5 μm (Agilent Technologies). As eluent a mixture of acetonitrile / water (1/1 v/v) (acetonitrile isocratic HPLC grade from Panreac, water type II, >5 MΩ cm, Elix 3 from Millipore) was used. The eluent flow was 1 mL min<sup>-1</sup>, the injection volume was 100 μL, the detection was carried out at 220 nm and the response was linear with a linearity range between 20 -

100 ppm with standards prepared from samples supplied by Sigma-Aldrich. The test temperature was 303 K. The results of the synthesis are expressed as the fractional conversion of acetophenone ( $X_R$ ), product yield ( $\eta$ ) and selectivity ( $\zeta$ ).

### 3. Results and discussion

#### 3.1. Physical characterization of the electrocatalyst and the electrodes.

As previously mentioned, TEM images were obtained to characterize the electrocatalyst. As shown in figure 2, a good dispersion of spherically shaped nanoparticles of 5 nm in size was obtained. On the other hand, figure 3 shows the micrographs of the cathodes prepared with different Pd loadings.

#### 3.2. Products of the electrochemical hydrogenation of acetophenone.

In order to define the experimental conditions for the electrochemical hydrogenation of acetophenone in a divided PEMER, the first experiences were carried out using a liquid catholyte composed of the solvent (ethanol 96% / water 90/10 v/v), 0.1 mol dm<sup>-3</sup> sulphuric acid as supporting electrolyte and 0.5 mol dm<sup>-3</sup> acetophenone. The Pd catalyst loading of the cathode was 0.1 mg cm<sup>-2</sup>. The synthesis was carried out at a constant current density of 10 mA cm<sup>-2</sup>, the total charge passed was 2 F. The products obtained were 1-phenylethanol and ethylbenzene and hydrogen as by-products. Figure 4 shows the fractional conversion of acetophenone and product yield for various charges. For a charge of 2 F the fractional conversion was 0.70. The selectivity for 1-phenylethanol was 90%.



### 3.3. Voltammetric study.

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Cyclic voltammetry curves were recorded for each one of the manufactured cathodes with Pd catalyst loadings of 0.2, 0.1, 0.05, 0.025 mg cm<sup>-2</sup> and without Pd. Curves were also recorded for a bead of bulk palladium (diameter 5 mm) and for different concentrations of acetophenone, from 0 to 0.5 mol dm<sup>-3</sup>. The working electrodes were slices of 0.5 cm x 1 cm of the manufactured cathodes. The voltammetric curves, recorded in absence of acetophenone, show hydrogen evolution at negative potentials, and no other process was observed during the negative or positive scans. The acetophenone can be directly reduced on uncatalyzed cathode surface (curve not shown) at not very high cathodic potential (-1.67 V vs. Ag/AgCl). The pinacol, one of the products of the direct reduction, can be observed as a small anodic peak during the positive going sweep, as reported by Vilar and Navarro [31].

Figure 5 shows the voltammetric curves for Pd/C electrode with a Pd catalyst loading of 0.025 mg cm<sup>-2</sup> for different acetophenone concentrations. The voltammetric profile (with and without acetophenone) is characterized by H<sub>2</sub> evolution and an anodic peak that plausibly could be ascribed to H<sub>2</sub> oxidation. Addition of acetophenone produces a decrease in the rate of oxidation of hydrogen for all Pd/C electrodes studied. In agreement with Ménard and his group [5-9], a plausible explanation of these results is that the mechanism of the electrocatalytic hydrogenation of acetophenone goes through the reaction between the atomic hydrogen adsorbed on the surface of Pd and the acetophenone adsorbed on the carbonaceous support. Finally, the current density of these processes increases with the Pd catalyst loading from 0.025 to 0.2 mg cm<sup>-2</sup> (curves not shown).

The only products detected in the electrocatalytic hydrogenation of acetophenone were 1-phenylethanol, ethylbenzene and hydrogen. For this reason, cyclic

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voltammetry of these two organic compounds was carried out using a working electrode with a Pd catalyst loading of  $0.05 \text{ mg cm}^{-2}$  (not shown). The presence of 1-phenylethanol in the solution also causes a decrease in the rate of oxidation of hydrogen but this effect does not appear if only ethylbenzene is present in the medium. Therefore, it seems that 1-phenylethanol generated by electrocatalytic hydrogenation of acetophenone can also be hydrogenated to ethylbenzene. Under these conditions hydrogenation of the benzene ring is not observed.

### 3.4. Electrocatalytic hydrogenation of acetophenone.

The electrocatalytic hydrogenation of acetophenone was carried out in an electrochemical reactor type PEMER with  $25 \text{ cm}^2$  of electrode area [12]. The counter-reaction was the oxidation of hydrogen that was continuously fed to the anodic compartment without overpressure. The influence on the synthesis of both, catalytic loading and current density, was analyzed. The results have been expressed as fractional conversion, product yield and selectivity.

#### 3.4.1. Influence of current density

The influence of current density on the electrosynthesis was studied using a cathode with a Pd catalyst loading of  $0.1 \text{ mg cm}^{-2}$ . Current densities of 10, 15 and 20  $\text{mA cm}^{-2}$  were tested. The same maximum electric charge of 2 F was passed for each one of the current densities. Other starting conditions were the same as defined above. Table 1 shows the data for fractional conversion, product yield and selectivity for different values of the charge passed, and the mean values of the applied potential. For the lowest current density, a fractional conversion of 0.70 (2 F) compared to values of 0.2 - 0.3 for the other two current densities was obtained. This higher fractional

1 conversion was also noted for each percentage of the total charge. A plausible  
2 explanation of this fact is that hydrogen evolution is faster than electrocatalytic  
3 hydrogenation. The influence of the current density on 1-phenylethanol selectivity is  
4 small (88 %, 91 % and 95 % for 20 mA cm<sup>-2</sup>, 15 mA cm<sup>-2</sup> and 10 mA cm<sup>-2</sup>). Finally, the  
5 differences of potential for the synthesis at 10, 15 and 20 mA cm<sup>-2</sup> were 0.2 V, 0.3 V  
6 and 0.5 V respectively. These very low potentials are obviously due to the use of the  
7 hydrogen oxidation as anodic reaction. Finally, the electrical resistance of the reactor  
8 was approximately 30 Ω cm<sup>2</sup>.  
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### 22 **3.4.2. Influence of the catalyst loading.**

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24 The influence of Pd catalyst loading was studied for loadings of 0.025, 0.05, 0.1  
25 and 0.2 mg cm<sup>-2</sup>. It should be pointed out that a cathode with a Pd catalyst loading of  
26 0.4 mg cm<sup>-2</sup> was also manufactured but the results were dismissed because the electrode  
27 was unstable. It seems that the medium ethanol-water and hydrodynamic conditions  
28 cause loss of cohesion of the catalytic layer.  
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36 Initially, a current density of 10 mA cm<sup>-2</sup> was applied for each one of the  
37 catalytic loadings. In figure 6, the fractional conversion versus the charge passed for  
38 each one of the catalytic loadings is shown. Two conclusions can be drawn from figure  
39 6. On the one hand, in the absence of Pd no significant conversion of acetophenone is  
40 observed and on the other hand, fractional conversion slightly increases with catalyst  
41 loading. Nevertheless, for the different percentages of the charge passed, this  
42 improvement is not proportional to the increase in catalyst loading. Selectivity for 1-  
43 phenylethanol was about 96% and does not depend on the catalytic loading (data not  
44 shown in the figure). For higher current densities, 15 and 20 mA cm<sup>-2</sup>, lower fractional  
45 conversions (around 0.20 and 0.30 for 2 F) were obtained respectively. However,  
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1 similar selectivity for 1-phenylethanol (around 91 % and 88 % for 15 and 20 mA cm<sup>-2</sup>  
2 respectively) was obtained.  
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### 7 **3.4.3. Catalytic hydrogenation without supporting electrolyte.**

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10 Once the possibility of synthesizing 1-phenylethanol from the electrochemical  
11 hydrogenation of acetophenone using a hydrogen diffusion anode and a PEMER was  
12 demonstrated, we tested the possible elimination of the solvent and liquid supporting  
13 electrolyte or at least the supporting electrolyte. So, for these experiments, the  
14 composition of the different catholytes was: 1) only acetophenone, 2) 0.5 mol dm<sup>-3</sup>  
15 acetophenone in ethanol 96%, 3) 0.5 mol dm<sup>-3</sup> acetophenone in ethanol 96% / water  
16 (90/10 v/v). For all cases, the Pd catalyst loading of the cathode was 0.1 mg cm<sup>-2</sup> and  
17 the current density 10 mA cm<sup>-2</sup>. The charge passed was 2 F.  
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29 For the first case, acetophenone only, the applied potential for maintaining the  
30 current density increased very quickly with time if dry hydrogen for feeding the anode  
31 was employed. This increase is caused by an increase in the membrane resistance, due  
32 to the drying of the previously hydrated membrane, most likely caused by the  
33 electroosmotic drag of the water of the membrane caused by the proton transport. When  
34 humidified hydrogen (70%) was used, this potential increase does not appear, but the  
35 catalytic layer of the cathode was gradually destroyed; water micelles appear in the  
36 catholyte due to the electroosmotic drag of the water from the anode caused by the  
37 proton transport. Thus, the use of only acetophenone was excluded.  
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51 In Table II, the results obtained for the fractional conversion of acetophenone,  
52 product yield and selectivity at different charges passed are shown for 0.5 mol dm<sup>-3</sup>  
53 acetophenone in ethanol 96 % and for 0.5 mol dm<sup>-3</sup> acetophenone in ethanol 96 % /  
54 water (90/10 v/v) and for a current density of 10 mA cm<sup>-2</sup> and a catalyst loading of 0.1  
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1 mg cm<sup>-2</sup>. For these initial experiments, the fractional conversions are lower than in the  
2 presence of sulphuric acid. The selectivity is independent of the type of electrolysis. In  
3  
4 any case, these results demonstrate that the electrochemical hydrogenation of  
5 acetophenone can be carried out without a supporting electrolyte. More work is in  
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7 progress for optimizing these results and for increasing the size of the reactor to 100  
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9 cm<sup>2</sup>.  
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#### 17 **4.- Conclusions**

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19 The results show that it is possible to carry out the electrocatalytic  
20 hydrogenation of acetophenone dissolved in ethanol or in ethanol/water using a spe and  
21 providing the protons required for the reaction using a hydrogen diffusion anode. The  
22 main product was 1-phenylethanol that was obtained with a selectivity of approximately  
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24 90% at a fractional conversion of acetophenone of 0.70 (in ethanol/water medium) and  
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26 0.35 (in ethanol medium) for 2 F charge passed. As by-products ethylbenzene and  
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28 hydrogen were obtained. The use of a hydrogen diffusion anode decreases the applied  
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30 potential of the synthesis and opens up the possibility of the use of the hydrogen  
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32 evolved at the cathode to partially feed the hydrogen anode decreasing in this way the  
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34 importance of the current efficiency of electrochemical hydrogenation. More work is in  
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36 progress for optimizing these results and increasing the size of the reactor to 100 cm<sup>2</sup>.  
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**Figure captions**

Figure 1. Scheme of Polymer Electrolyte Membrane Electrochemical Reactor (PEMER).

Figure 2. TEM micrograph of Pd/C 30% wt.

Figure 3. SEM micrographies of the electrodes for each Pd catalyst loading.

Figure 4. Fractional conversion of acetophenone and product yield of 1-phenylethanol and ethylbenzene as a function of the charge passed. Starting solution:  $0.5 \text{ mol dm}^{-3}$  acetophenone in ethanol 96% / water (90/10 v/v) +  $0.1 \text{ mol dm}^{-3}$   $\text{H}_2\text{SO}_4$ . Pd catalyst loading:  $0.1 \text{ mg cm}^{-2}$ . Current density:  $10 \text{ mA cm}^{-2}$ .

Figure 5. Cyclic voltammetry in ethanol 96% / water (90/10 v/v) +  $0.1 \text{ mol dm}^{-3}$   $\text{H}_2\text{SO}_4$  with different concentrations of acetophenone. Pd catalyst loading:  $0.025 \text{ mg cm}^{-2}$ . Scan rate:  $10 \text{ mV s}^{-1}$

Figure 6. Influence of Pd catalyst loading. Pd catalyst loading: — 0, — 0.025, — 0.05, — 0.1, — 0.2  $\text{mg cm}^{-2}$ . Current density  $10 \text{ mA cm}^{-2}$ .



## Tables

Table 1. Fractional conversion ( $X_R$ ), product yield for 1-phenylethanol ( $\eta_{\text{PhCHOHMe}}$ ) and ethylbenzene ( $\eta_{\text{PhEt}}$ ), selectivity for 1-phenylethanol ( $\zeta_{\text{PhCHOHMe}}$ ) versus current density [1] 10, [2] 15 and [3] 20 mA cm<sup>-2</sup> for different charge passed. Pd catalyst loading: 0.1 mg cm<sup>-2</sup>. Starting solution: 0.5 mol dm<sup>-3</sup> acetophenone in ethanol 96% / water (90/10 v/v) + 0.1 mol dm<sup>-3</sup> H<sub>2</sub>SO<sub>4</sub>.

Entry	Parameters studied	Charge (F)				$V_{\text{cell}}$ (V)
		0.5	1.0	1.5	2.0	
1	$X_R$	0.27	0.43	0.56	0.71	0.2
	$\eta_{\text{PhCHOHMe}}$	0.25	0.42	0.55	0.69	
	$\eta_{\text{PhEt}}$	0.01	0.02	0.02	0.02	
	$\zeta_{\text{PhCHOHMe}}$ (%)	95	95	96	96	
2	$X_R$	0.10	0.18	0.24	0.30	0.3
	$\eta_{\text{PhCHOHMe}}$	0.09	0.15	0.21	0.28	
	$\eta_{\text{PhEt}}$	0.01	0.02	0.02	0.02	
	$\zeta_{\text{PhCHOHMe}}$ (%)	91	91	91	92	
3	$X_R$	0.07	0.13	0.18	0.23	0.5
	$\eta_{\text{PhCHOHMe}}$	0.06	0.11	0.15	0.20	
	$\eta_{\text{PhEt}}$	0.01	0.01	0.02	0.02	
	$\zeta_{\text{PhCHOHMe}}$ (%)	87	88	88	89	

Table 2. Fractional conversion ( $X_R$ ), product yield for 1-phenylethanol ( $\eta_{\text{PhCHOHMe}}$ ) and ethylbenzene ( $\eta_{\text{PhEt}}$ ), selectivity for 1-phenylethanol ( $\zeta_{\text{PhCHOHMe}}$ ) for different charge passed. Starting solutions: [1] 0.5 mol dm<sup>-3</sup> acetophenone in ethanol 96%, [2] 0.5 mol dm<sup>-3</sup> acetophenone in ethanol 96% / water (90/10 v/v). Pd catalyst loading: 0.1 mg cm<sup>-2</sup>. Current density: 10 mA cm<sup>-2</sup>.

Entry	Parameters studied	Charge (F)			
		0.5	1.0	1.5	2.0
1	$X_R$	0.09	0.16	0.26	0.31
	$\eta_{\text{PhCHOHMe}}$	0.11	0.17	0.21	0.27
	$\eta_{\text{PhEt}}$	0.01	0.02	0.02	0.03
	$\zeta_{\text{PhCHOHMe}} (\%)$	88	90	89	91
2	$X_R$	0.13	0.17	0.27	0.35
	$\eta_{\text{PhCHOHMe}}$	0.12	0.17	0.24	0.30
	$\eta_{\text{PhEt}}$	0.01	0.02	0.02	0.03
	$\zeta_{\text{PhCHOHMe}} (\%)$	91	89	92	92

## Figures

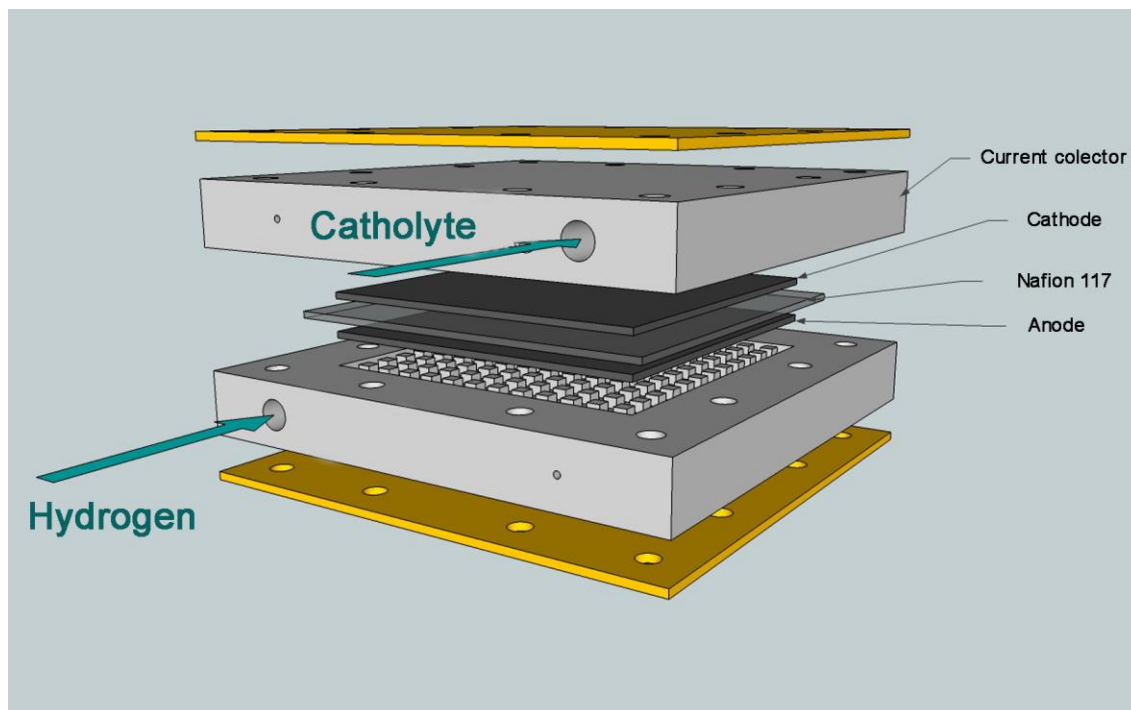


Figure 1

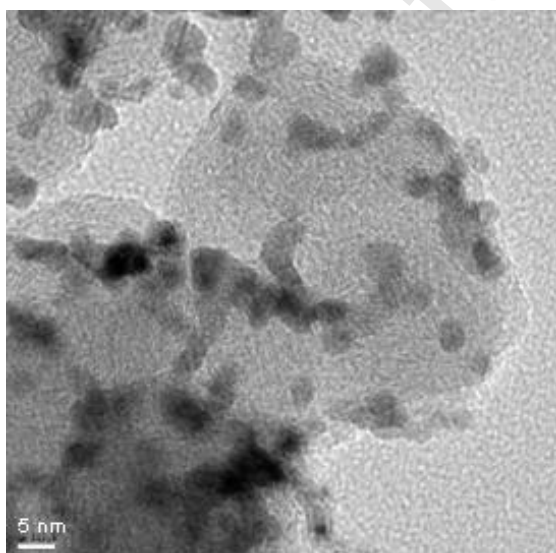


Figure 2

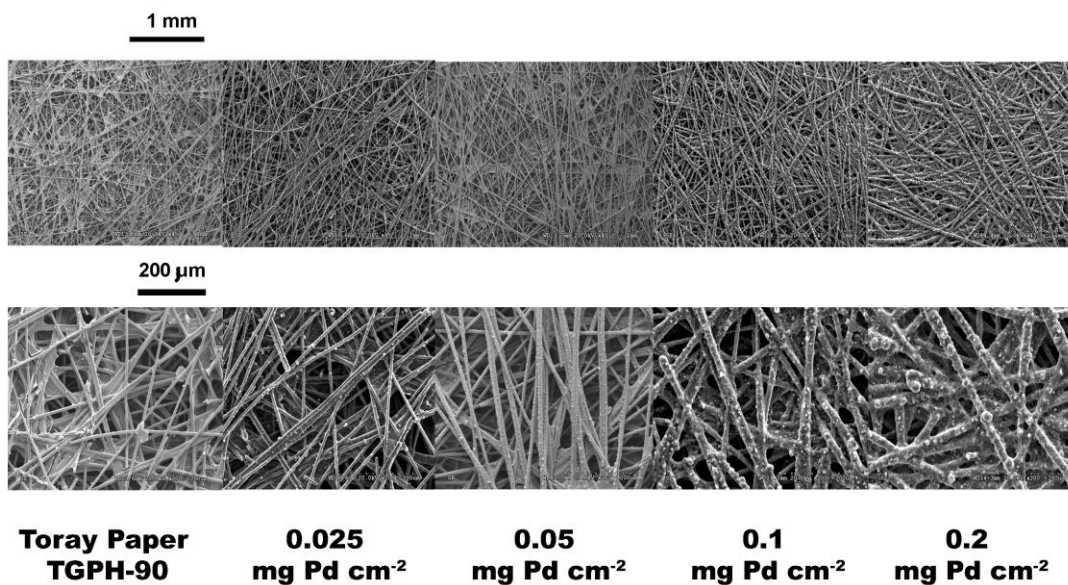


Figure 3

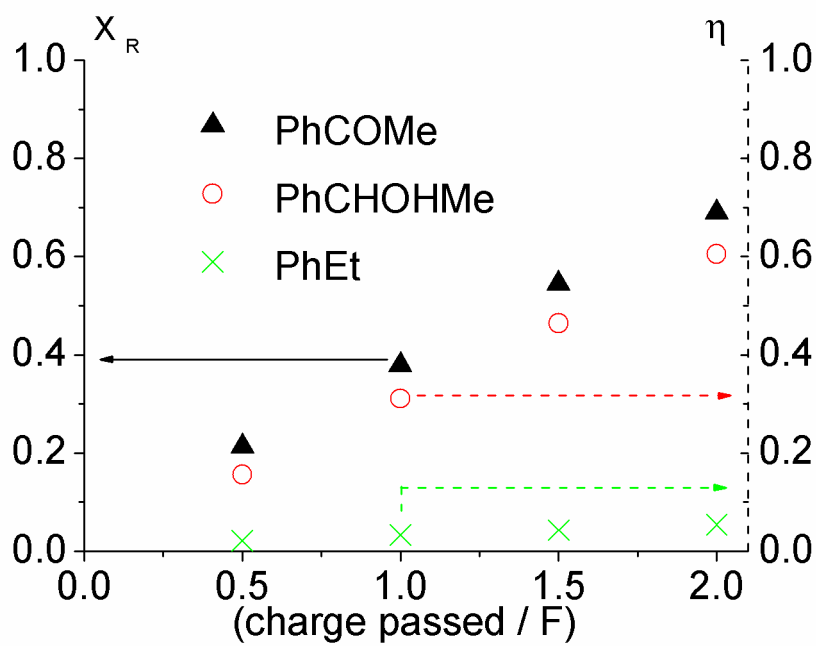


Figure 4

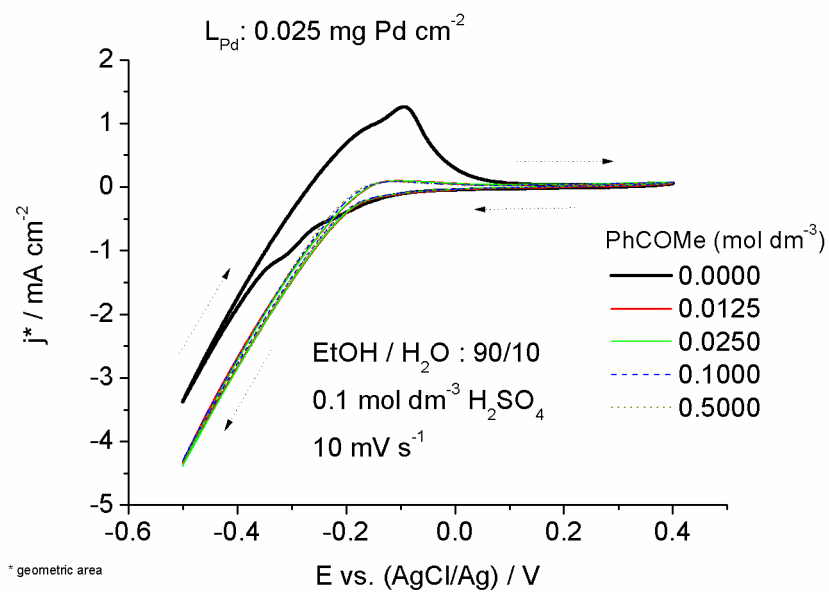


Figure 5.

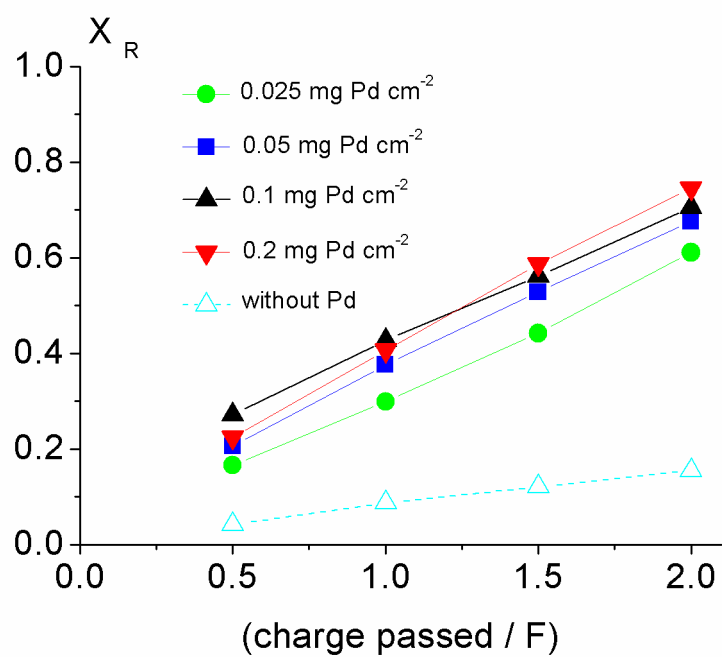


Figure 6.