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Effect of Distances between Electrodes, Agitation and Chemical Pickling Treatment in a Specific Electrolytic Cell for Alkaline Water Electrolysis

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Abstract: In order to build an alkaline water electrolyzer in the future, in this work we investigated the following aspects: (1) the effect of the presence of a physical diaphragm; (2) distances between electrodes; (3) the use of the same electrode material, stainless steel 316L, without and with a chemical acid treatment; (4) agitation and (5) the addition of a surfactant to the electrolyte. All these parameters were analyzed in a specific electrolytic cell constructed for that purpose. The objective of this experimental work is to establish the optimal operational conditions proposed for alkaline water electrolysis. The results obtained showed that the presence of a physical diaphragm increases resistance but when the electrodes are near (no more than 5 mm) the current density increases. No evidence of bubble resistance was observed in the nearest distances proposed. The chemical pickling proposed did not show an increase in the active area of the electrodes because it decreased the depth of the roughness which is characteristic of the commercial material and it generated porosities or cavities where the bubbles formed were retained. Agitation improved performance when electrodes with a chemical acid treatment were tested because removal of bubbles formed in their tortuous surface is favored.

Key words: Alkaline water electrolyzers, chemical pickling, agitation.

1. Introduction

Hydrogen potential as an energy vector resides in its capacity to be used as an energy source that can be produced in a specific place, stored and transported where it is required. This means that when we refer to hydrogen as an energy vector, it involves its production, storage, transportation and use. Focusing on hydrogen production, it is possible to affirm that about 90 different methods are known. Those methods can be classified into four different categories: Biological, Thermical, Chemical and Electrochemical [1]. As regards the electrochemical method, and in particular, alkaline water electrolysis, we find that this technology offers the following advantages: simplicity, accuracy and it is widely known. Besides, gases obtained as a result of the reaction are highly pure, which makes a further purification stage unnecessary [2]. It is important to mention that the impurity present is mostly water steam, approximately 3 % at 25 ℃ and 1 atmosphere, [3] which does not interfere with the next step: the use of gases in a PEM fuel cell as fuel and comburent. However, using electrical energy for the production of hydrogen is estimated as a disadvantage because a non-renewable energy source (fossil fuels) is being

applied to produce electricity which, at a further stage, will allow to generate hydrogen through electrolysis. There are two steps, one of which (burning of fossil fuels) is highly expensive. On the other hand, the reformed method permits to produce hydrogen in only one step, but clearly the purity of the gases is not as high as that obtained through electrolysis, because the impurity is carbon monoxide which is a poison of the catalyst of the PEM fuel cell. Commercial electrolyzers have an energy consumption of 4.5-5 kWh/Nm^3 hydrogen when conventional sources of energy are used (electrical energy) [4]. Past efforts were mainly focused on improving all the components of electrolyzers in order to reduce energy consumption. Presently, an additional technological challenge is to make them operate appropriately when resorting to intermittent sources of energy like renewable energy sources, which create a more favorable scenario for the use of electrolyzers.

In order to improve the efficiency of this type of systems, several researchers have focused their work on the optimal conditions of operation, such as working at high pressures and temperatures with the purpose of diminishing the potential at which the reactions develop, as well as over-potential [5]. Other researchers focused their work on the current effect, the gap between electrodes and the working temperature [3, 6-7]. However, the tendencies over the last few years have been aimed at the development of electrodes new materials [8], electrocatalyzers, electrolytes, additives and the adequate management of the resulting bubbles [9]. In accordance with the first line of investigation to establish the optimal operating conditions of an electrolyzer prototype developed in our laboratory, the following were studied: (1) the effect of a physical separator in the electrolysis system; (2) the gap between electrodes; (3) the use of the same material for electrodes (stainless steel 316L) with and without the application of pickling treatment with hydrochloric acid; (4) the incorporation of a stirring system and (5) the addition of a surfactant to the electrolyte.

2. Materials and Methods

In order to study the effect that the gap between electrodes has on alkaline water electrolysis, a device consisting of a glass electrolytic cell and an acrylic plate in its base was built. The purposes of that plate were to establish the position of the physical separator through a slot in its center well as to hold the separator, thus ensuring the perpendicular position in relation with the base.

While crystal acrylic was the material used for the physical separator, stainless steel 316L was used for the electrodes. This choice was mainly made because of its high inert chemistry behavior against corrosive environments (like KOH 35% w/w) and its high content of nickel (14%). This allows to obtain a low over-potential in the oxygen evolution reaction and a good performance in the hydrogen evolution reaction in comparison to other steels like 304 an 430 [10].

To increase the gap between electrodes, rectified crystal acrylic blocks were used (90 × 20 × 20 mm), see Fig. 1(a).

An electrolytic solution of KOH 35 % w/w was used for alkaline water electrolysis prepared with bi-distilled water to which a drop of sodium dodecyl sulfate was added with the purpose of decreasing the superficial tension of the solution.

The agitation was made by incorporating a stir bar, placing the device on an electromagnetic stirrer and the bar behind the acrylic plate. Importantly, the plate was raised by 2 centimeters, placing acrylic blocks in the extremes inside the glass electrolytic cell.

As the walls of the glass electrolytic cell have rounded sides, the acrylic plate was not tightly adjusted on its base, which allows the flow of the electrolytic solution from the lower to the upper compartment (where the electrodes are) (Fig. 1(b)).

The electrodes were connected to a power source Agilent N5743A System DC Power Supply (12.5 V/60 A, 750 W) once the device had been assembled. Current

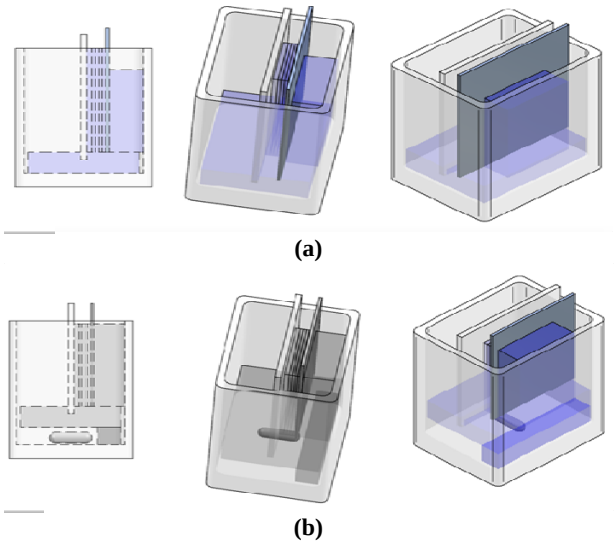


Fig. 1 (a) Device used in the experiences; (b) system of blocks and agitation.

measurements were made at a certain potential between 0.0 and 4.0 V. The operational conditions were room temperature and atmospheric pressure. Current, voltage and temperature were the monitor parameters. They were used to calculate current density, decomposition potential, resistance and resistivity. All experiences were carried out twice.

Two types of stainless steel 316L electrodes were used for the experiences: One was the material in its original condition (after a cleaning treatment which is described later in this paper); another was the same material with a special chemical pickling treatment.

The cleaning treatment that was applied to the electrodes before they were employed consisted of these steps [11-12]:

- Wash the electrodes with distilled water and allow to dry;
- Soak up a filter paper in acetone, and use it to clean the electrode. Then, allow the solvent on the electrode to evaporate;
- Soak up a filter paper in alcohol and use it to clean the electrode. Then, allow the solvent on the electrode to evaporate.

The chemical pickling treatment with hydrochloric acid 1 M (Cicarelli Laboratory, 36.5-38.0 %), applied to the electrodes consisted of these steps [13]:

- Place the samples in a solution of hydrochloric acid 1 M at 70 ℃ during 30 minutes;
- Wash the samples with distilled water and allow to dry;
- Place the samples in a solution of nitric acid 5 % (Cicarelli Laboratory, 65 %) at room temperature;
- Wash the samples with distilled water and allow to dry.

The chemical pickling treatment has the purpose of enhancing the electrode efficiency through the increase of its surface. The objective is to obtain a rough surface that notonly increases the active area of the electrode but also creates a less smooth surface for the generated bubbles to move away. This type of surface allows the bubbles to become detached of the surface more quickly. The additional useful effect is releasing the reaction products of the electrode surface in a shorter time, thus permitting the reaction evolution to obtain a larger amount of products [11].

The studied configurations (systems) are:

- Both electrodes of the material in their original condition, hereinafter called original electrodes;
- Both electrodes with chemical pickling treatment with hydrochloric acid 1 M;
- The negative electrode with chemical pickling treatment and the positive electrode in its original condition;
- The positive electrode with chemical pickling treatment and the negative electrode in its original condition.

The microstructure study of the electrodes was made choosing a representative sample of each electrode, which was cut with a mitre saw. The sizes of the samples were of 10 × 10 × 2 mm with the purpose of analyzing them later under a SEM (Scanning Electron Microscope) Philip SEM 515.

3. Results and Discussion

3.1 Effect of Surfactant Addition

Water electrolysis reaction takes place when the electrolytic solution and the electrode are in contact.

The free surface of the electrode makes this possible. As the products of the reaction are gases, the bubbles formed have to be removed from the surface of the electrode to ensure the electrolytic process is maintained. Consequently, a major problem that this kind of devices presents is how to achieve the fast removal of the bubbles. Generally, the gradual and considerable growth of the bubbles before becoming released from the surface increases the time of permanence on the electrode. This process decreases the active area available for the generation of new products and as a direct consequence, it decreases the device performance.

The behavior of the device was studied (through current density) with or without the addition of surfactant to the electrolyte. Fig. 2 represents the current density as a function of voltage difference. This voltage was applied to the system where the electrodes had a pickling treatment.

In the experiment where the electrolyte solution did not have surfactant, bubbles of considerable size (3-4 mm) were observed on the electrode surface. The fact that the bubbles grow to reach that size means they take longer to be released. The addition of the surfactant prevents the bubbles from reaching that size and therefore, they remain on the electrode surface for a shorter period. The size these bubbles reach is smaller than 0.5 mm. Fig. 2 shows that the system with surfactant presents higher current density than the one without.

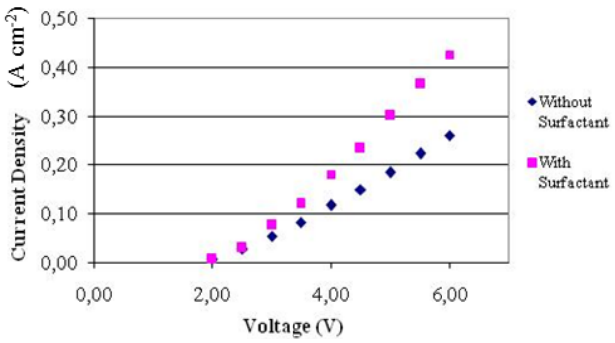


Fig. 2 Graphic representation of current density as a function of voltage differences, applied to the system with pickling treated electrodes. Distance between electrodes 6 mm with or without surfactant.

The addition of surfactant to the electrolytic solution is positive for the system because it decreases the superficial tension, allowing the bubbles to be more easily released, since even the largest size they can reach is smaller than without surfactant.

3.2 Effect of Distance between Electrodes

In Fig. 3, graphic representations were drawn for: current density as a function of applied voltage differences and resistance as a function of distance between electrodes for two different systems: original electrodes and both electrodes with chemical pickling treatment.

The proposed distances between electrodes were 6-10-14-18-22 mm respectively. The experiment was made without agitation.

As expected, in the analyzed systems without agitation, it can be observed that increasing the distance between electrodes decreases the performance of the system as a consequence of the rise in resistance. This is the direct result of applying the equation $R = (\rho\ l)/S$, where R is the resistance, ρ is the resistivity; l is the conductor length and S is the transversal section.

In the work by Nagai, et al., the same results were obtained: electrical resistance increases as the gap between electrodes becomes greater, for current densities between 0.1, 0.5 and with Ni-Cr-Fe (Inconel 600) electrodes. In their research, they analyzed that effect considering that voltage represents the necessary electrical power for the production of certain hydrogen mass flow rate. Therefore, if the same mass flow is obtained at a lower voltage, water electrolysis process is more efficient because it consumes less electrical energy [7]. Mahrous and co-authors, working with stainless steel 316LHS electrodes, observed the same effect regarding electrical resistance and distance between electrodes [3]. In the device used when we studied distance below 6 mm between electrodes, some experimental complications arose, derived from a constant fluctuation in the current determination (its value varied constantly).

In Fig. 3, only two of the four systems under study are

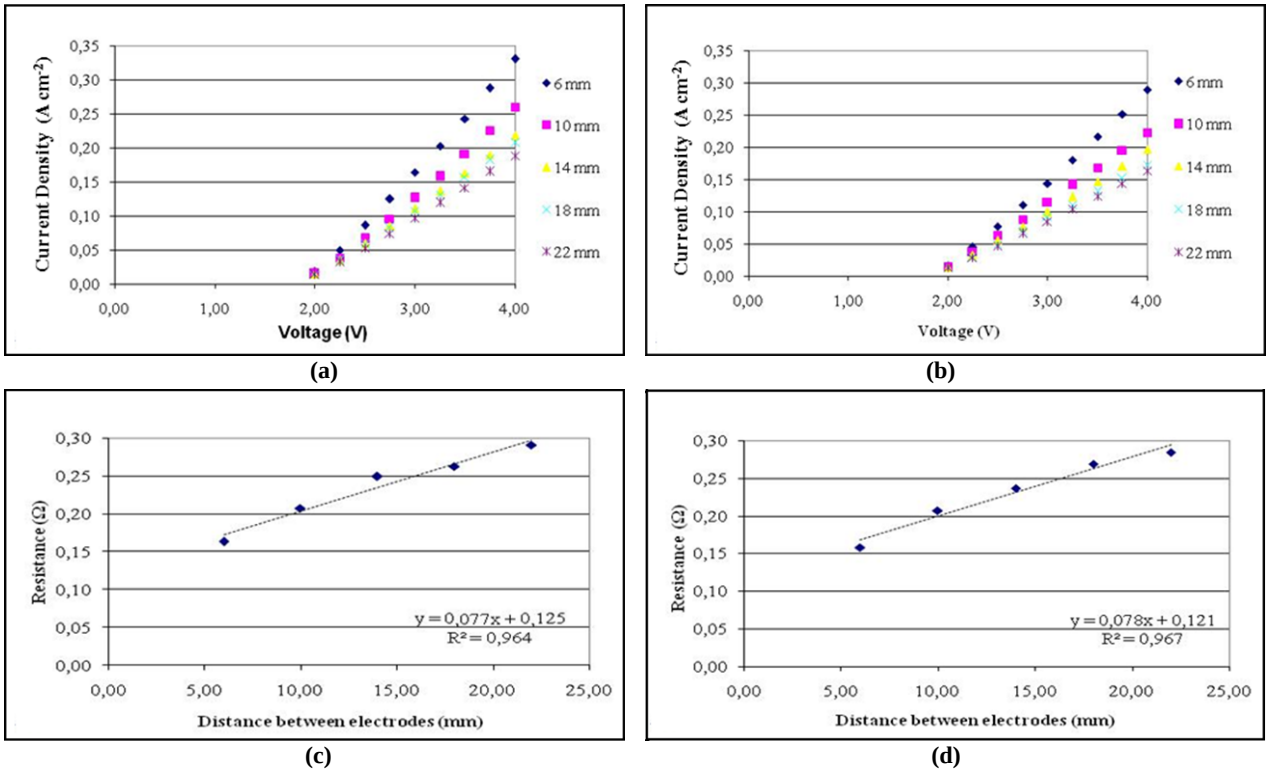


Fig. 3 Graphic representation of (a) and (b): current density as a function of applied voltage differences for the system of original electrodes and for the system of pickling electrodes respectively (both without agitation); (c) and (d): resistance as a function of distance between electrodes for the same systems.

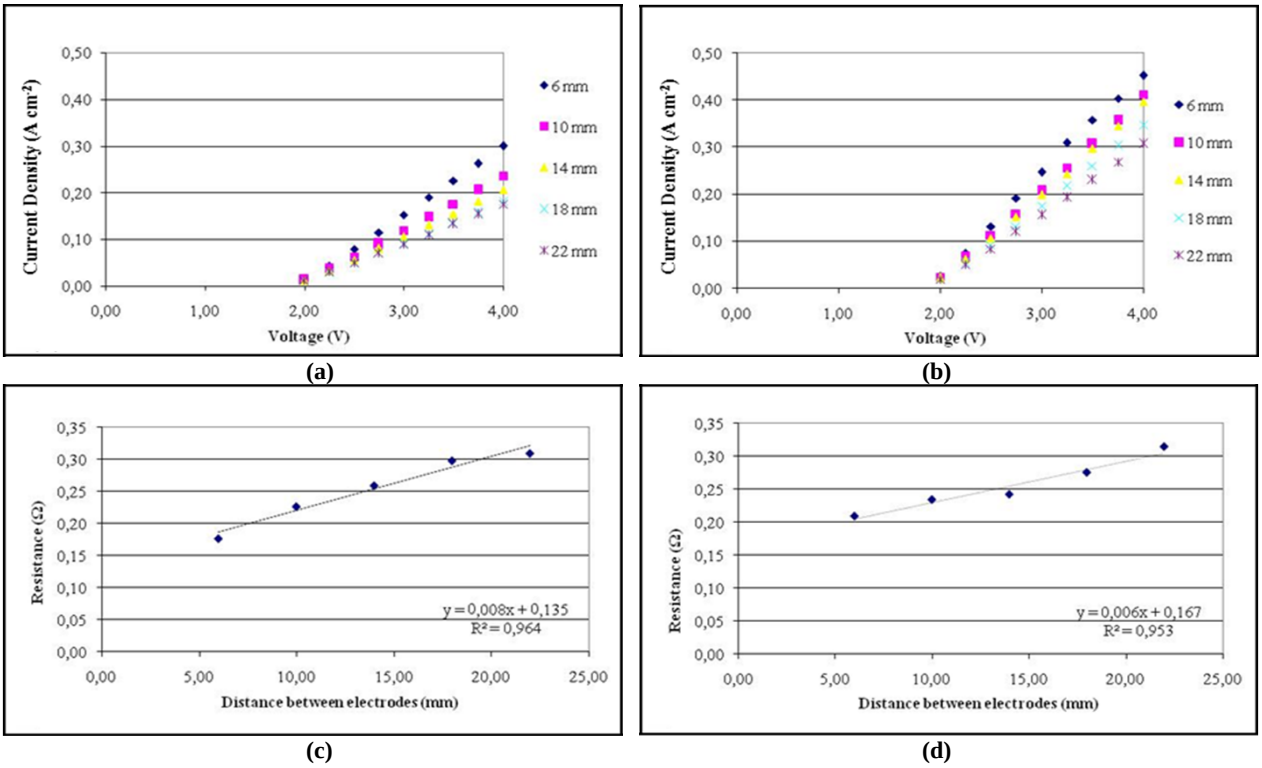


Fig. 4 Graphic representation of (a) and (b): current density as a function of applied voltage differences for the system of original electrodes and for the system of pickling electrodes respectively (both with agitation); (c) and (d): resistance as a function of distance between electrodes for the same systems.

represented, because the behavior shown by the systems presenting chemical pickling in one of their electrodes also reduces the system performance as the distance increases.

Fig. 4 shows the results obtained for the same systems but with the incorporation of agitation.

Agitation did not modify the behavior of the systems in relation to the rise in the resistance as a consequence of the gap increase between electrodes. Likewise, agitation did not improve results in shorter distances where instability was still observed. It may be concluded that for the distances evaluated in our study, 6 mm is the distance presenting the highest current density for both systems.

3.3 Agitation Effect

One aspect to consider is the incorporation of agitation as a tool to improve the performance of the systems under study. For that purpose, we compared the different systems with and without agitation (Fig. 5).

Agitation in the systems where one or both electrodes were treated with hydrochloric acid chemical pickling improved their performance. This is due to the movement generated in the electrolytic solution which allowed the removal of the bubbles that had been formed in the cavities on the electrode surface. This faster removal led to the generation of a greater amount of product as a consequence counting with available surface for the reaction. In the case where the system had original electrodes, no perceptible improvement was observed. The movement generated in the electrolytic solution could be insufficient or just inadequate to accomplish the removal of bubbles from the surface of the electrodes.

For a detailed study of the stirring phenomenon in this type of device, 6 mm distance between electrodes was evaluated for all systems as it was the distance where the greatest amount of products was obtained.

Fig. 6(a) showed the current density of each system as a function of the applied voltage differences. The

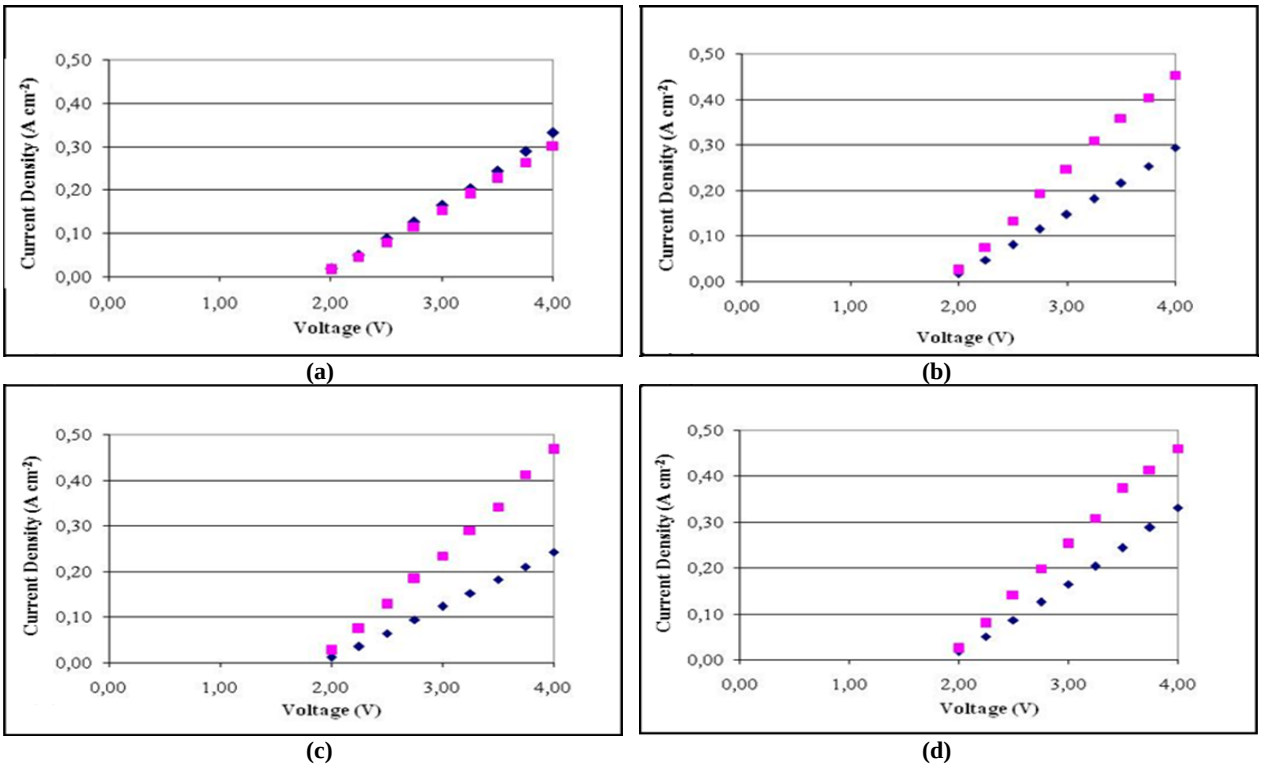
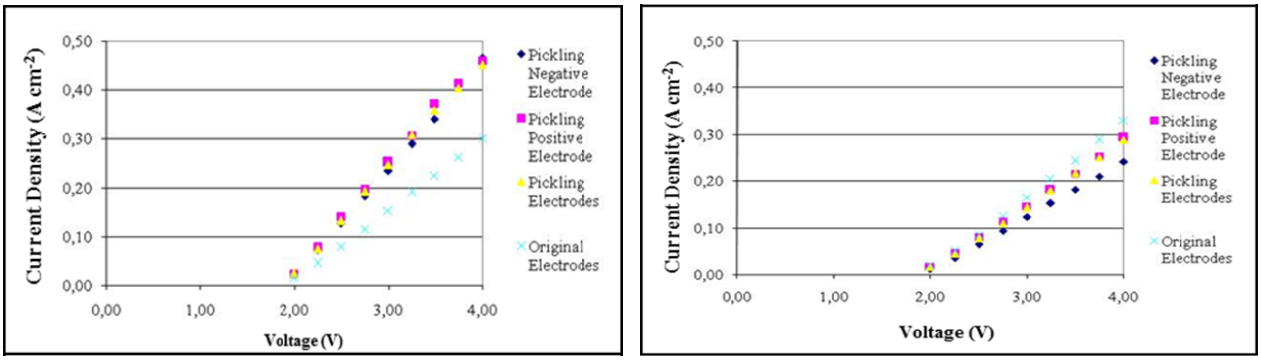


Fig. 5 Graphic representation of the current density as a function of applied voltage difference for the systems with and without agitation: (a) original electrodes; (b) chemical pickling electrodes; (c) chemical pickling negative electrode and (d) chemical pickling positive electrode. Pink squares represent systems with agitation. Blue triangles represent systems without agitation.



(a) (b)

Fig. 6 Graphic representation of the current density as a function of the applied voltage differences, for all the systems under study for a gap of 6 mm between electrodes: (a) with stirring and (b)without stirring.

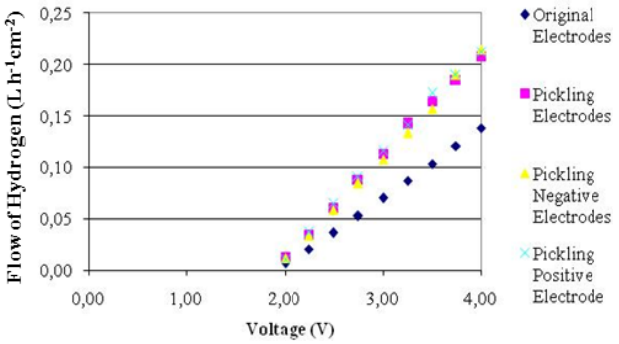


Fig. 7 Flow of hydrogen as a function of applied voltage differences for the studied systems.

systems with chemical pickling electrodes presented a better performance than the system with original electrodes. However, the stirring of the electrolytic solution did not present a noticeable difference between systems with chemical pickling electrodes.

Analyzing the performance of the different systems by the production of hydrogen, Fig. 7 shows the flow of hydrogen obtained for each of the systems studied. The systems with chemical pickling treatment were the one presenting the best performance.

If the system with original electrodes is compared with the others, in absence of stirring, it presents the best performance, but if it is compared with the same systems in stirring conditions, its performance becomes worse.

3.4 Effect of Applying Pickling Chemical Treatment

The results obtained for all the systems with and without stirring were analyzed (without stirring see Fig. 6(a) and with stirring see Fig. 6(b)).

The system without stirring and with original electrodes presented the highest current density. The surface of those electrodes allowed a faster removal of bubbles from the reaction products. This phenomenon was not the same in the systems where one or two of the electrodes had chemical pickling because the bubbles generated were held in the cavities formed by the chemical pickling treatment.

On the other hand if we compare the same systems with stirring, those which had chemical pickling electrodes presented higher current density. The movement generated by stirring the electrolytic solution permits the removal of the bubbles in the cavities, improving the performance of those systems. This fact could be related to the microstructure of the electrode surface which is discussed in the following section.

3.5 Microstructure Study

After water electrolysis, the electrodes microstructure was analyzed as follows (Fig. 8(I)). As it was mentioned above, the system with original electrodes and without stirring presented the best performance, due to the depth of the canals conforming the microstructure. This is probably due to the fact that the active surface exposed was considerably larger. Contrastingly, the electrodes with chemical pickling treatment presented a smaller surface because they lost depth as a result of the treatment which selectively attacked the hills on the surface. It is important to remark

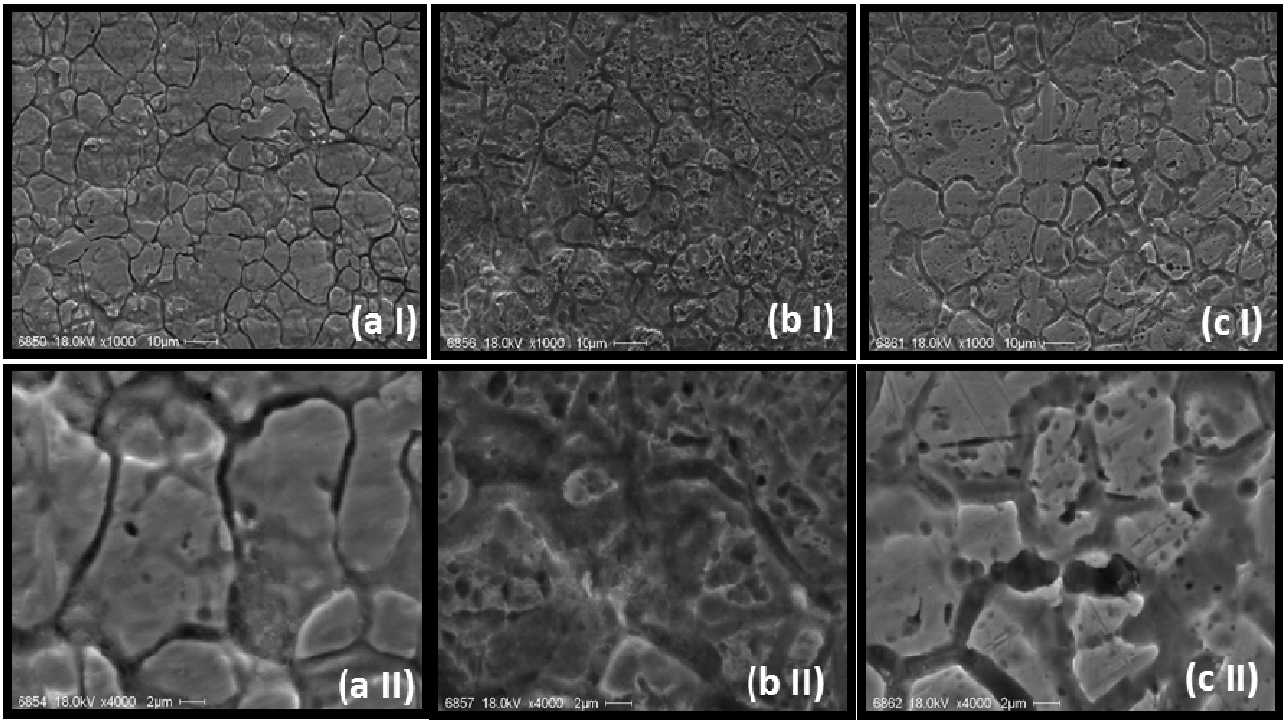


Fig. 8 SEM micrographs I (1000x) and II (4000x), of the electrodes used in the different systems: (a) original electrodes; (b) chemical pickling negative electrode; (c) chemical pickling positive electrode.

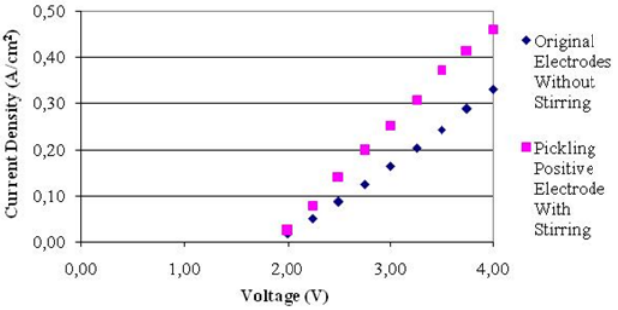


Fig. 9 Graphic representation of current density as a function of the applied voltage differences for the system with original electrodes without stirring and for a system with chemical pickling positive electrode with stirring.

that differences in the performance between the studied systems were not significant because as a result of the pickling treatment, roughness increased. Thus, on the one hand the depth of canals was decreased but on the other hand, erosion caused by the treatment increased the area exposed. As a final result, a reduction of the active area was obtained. Cavities or pores formed did not compensate for the loss in depth and as a consequence, the systems presented a lower performance. An additional reason could be that bubbles stayed in the formed cavities for longer periods of time and did not release the electrodes active area.

Fig. 8(II) shows, with greater detail, that the size of canals increased in chemical pickling positive electrode. This means that it becomes wider than canals in original electrode. A larger number of pores appeared in the chemical pickling negative electrode, thus increasing the surface exposed.

Results allowed to explain the performance of the studied systems with and without stirring. In the systems without stirring, the one with original electrodes obtained a better result in current density because the generated bubbles could easily be released from the surface. This occurred because the surface did not present as much roughness as the other systems.

When stirring was incorporated, the systems with chemical pickling electrodes presented a higher current density as stirring allowed bubbles to be more easily removed from the surface. In absence of stirring, on the contrary, bubbles stay in the cavities for a longer period of time.

Fig. 9 shows the graphic representation of the

current density as a function of the applied voltage differences for two systems: original electrodes without stirring and the system with a chemical pickling positive electrode with stirring. The graphic representation evidenced that the performance of the pickling systems with stirring was better than the one which had the best performance without stirring.

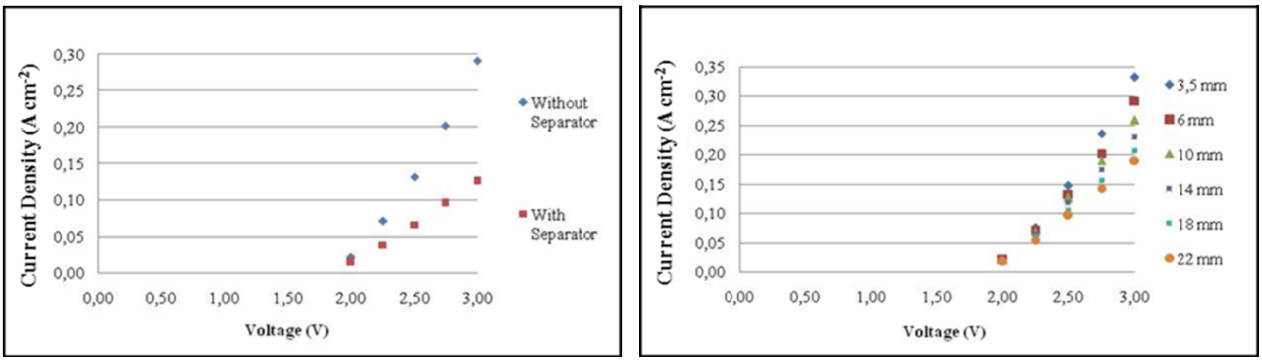
3.6 Effect of the Presence of a Physical Separator

In this case, the system under study is one where no physical separator was used. The behavior of this system with original electrodes was compared with the same system with a separator. The material employed as a separator was a 2 mm-thick crystal acrylic sheet which allowed the electrodes to face each other in an area of 11 cm^2. The results obtained for those systems in the shortest distance (6 mm) were presented in Fig. 10(a). Fig. 10(a) was the graphic representation of the current density as a function of the applied voltage differences for the systems under study.

The first expected result was the decrease of the resistance in the system where no physical separator was present. This fact was reported by Nagai et al., when they showed the same phenomenon with a polyflon filter as separator material [7]. The graphic representation (Fig. 10(a)) showed the different behavior of the systems in relation to the achieved current density. The physical separator presence blocked bubble removal, and impeded the production of new bubbles. The electric resistance increased and as a direct result, the efficiency of the system decreased.

A graphic representation of the behavior, in current density, for the distance between electrodes proposed was presented in Fig. 10(b).

It is important to remark that the phenomenon observed in current determination (fluctuation) did not happen in the shortest distance studied of 3.5 mm. The fluctuation in current determination could be the result of greater affinity of the bubbles with the separator material. The time that the bubbles stay on the separator surface depends on the size and the movement



(a) **(b)**

Fig. 10 Graphic representation of the current density as a function of the applied voltage differences for: (a) the systems with and without crystal acrylic separator for a distance of 6 mm and (b) the studied distances between electrodes.

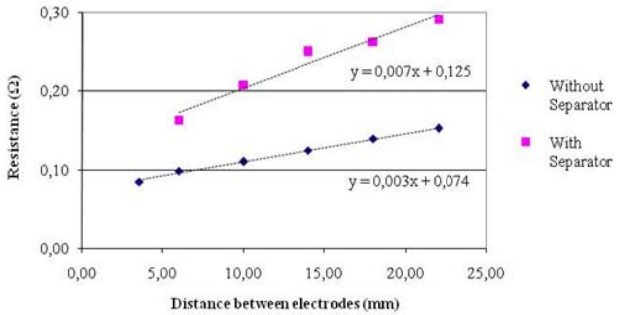


Fig. 11 Graphic representation of resistance as a function of distances between electrodes proposed in this work.

caused in the electrolytic solution by the generation and the removal of the bubbles. Resistance as a function of distance between electrodes for those systems was presented in Fig. 11.

The slope calculated in both systems showed that the resistance obtained for the system with separator was the result of the contribution of the material, distances between electrodes and the electrode current distribution resistances.

4. Conclusions

The addition of surfactant improves bubbles removal because it allows bubbles to decrease their size and the time of permanence on the electrode, as a consequence of decreasing the surface tension of the system.

A larger distance between electrodes increases resistance. This fact is supported by other authors (Nagai and Mahrous) who obtained the same results with other materials as electrodes.

In our experience, the best results were obtained when the distance between electrodes was 6 mm because in shorter distances, the current fluctuates. This effect could be explained by the affinity that the bubbles present with the separator material, in addition to the shorter distance between the separator and the electrode which hinders bubbles removal and presents a current fluctuation.

Stirring only improves the system performance where one or both electrodes are treated with chemical pickling. Chemical pickling affects the surface of the electrodes and allows a faster bubble removal as a result of a honeycomb surface. For the systems without stirring, the pickling treatment proposed with hydrochloric acid did not show an increase in the active area of the electrode because on the one hand it decreases the depth of the roughness which is characteristic of the commercial material and on the other hand, it generates porosities or cavities where the bubbles formed are retained or located. This last phenomenon in addition to the loss of surface due to a reduction of the roughness makes the system with pickling electrodes not to behave in the expected way.

In the experience with stirring, the result is the one expected, because stirring allows the faster removal of the bubbles.

As it was evidenced, the presence of a physical separator in this type of systems increased resistance. The result of this work can be used to compare with different materials to be employed as separators to maintain the products obtained by water electrolysis separated.

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