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Water electrolysis with Zirfon® as separator and NaOH as electrolyte

María José Lavorante[a,b,*], Carla Yanina Reynoso[b], Juan Isidro Franco[a]

[a]*Departamento de Investigación y Desarrollo en Energías Renovables (CITEDEF-EST), San Juan Bautista de La Salle 4397, B1603ALO Provincia de Buenos Aires, Argentina, Tel. + 54 11 4709 8100, ext. 1472; emails: mjlavorante@gmail.com (M.J. Lavorante), jfranco@citedef.gob.ar (J.I. Franco)*

[b]*Facultad de Ingeniería del Ejército Nicolás Manuel N. Savio (CITEDEF-EST), Cabildo 15, C1426AAA Ciudad Autónoma de Buenos Aires, Argentina, Tel. +54 11 4779 3300; email: carlayaninareynoso@gmail.com (C.Y. Reynoso)*

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ABSTRACT

Composite membranes are aimed at employing and enhancing some characteristics of the two materials they consist of: organic and inorganic materials. In this research work, a member of the composite membrane family, Zirfon®, was studied. This material consists of a polysulphone matrix and zirconium oxide, in the form of powder. The presence of zirconium oxide improves the wettability of the material, an important issue if the process includes the evolution of gaseous products as in water electrolysis. Zirfon® was tested in a crystal acrylic electrolytic cell with rectified blocks, which established the different distances between electrodes. The material selected for the cathode and the anode was stainless steel 316 L. In this experience, 20% w/w NaOH was used as electrolytic solution at room temperature. The experiment was carried out by applying a range of differential potential to the electrolytic cell. Six different distances between electrodes were studied: 7.5, 6.5, 5.6, 4.45, 4.25 and 3.10 mm. The control parameters were current, voltage and temperature. These parameters allowed us to calculate the following: decomposition voltage, resistance and conductance of the electrolytic solution. Resorting to this data set, the distance between electrodes selected was 3.10 mm, where the best performance of the system is obtained.

Keywords: Zirfon®; Alkaline water electrolysis; Distances between electrodes

1. Introduction

Composite membranes are aimed at employing and enhancing some characteristics of the two materials they consist of: organic and inorganic materials. When analyzing organic materials, the focus is on the easy process to synthesize polymers and the low cost that this process involves; in the case of inorganic materials, the characteristics to be exploited are their mechanical strength and their intrinsic properties.

This type of membrane can be easily adapted to be used in a specific application. The problem at hand is to avoid affecting the membrane physical integrity, finding a balance between the improvement of the

*Corresponding author.

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properties and the formation of defects that may arise from the synthesis process of both materials. For example, if the membrane is intended to be used in water treatment, its selectivity should be previously increased as well as incorporate specific functional groups and improve its thermal, mechanical and chemical stability. To reach high selectivity, micron-sized particles are incorporated to classical membranes and this can add to the base material the characteristic properties of the incorporated material [1].

Inorganic material has influence over the porosity, distribution and increment of the interconnectivity of the pores as well as the mechanical strength. The objective was to produce morphological and mechanical changes to prevent the membrane from becoming more compact, in processes in which gases are separated at high pressure.

Zirfon® is a composite membrane that consists of zirconium oxide powder as inorganic material and polysulphone polymer as organic material. This type of membrane is synthesized by film casting technique [2,3]. The materials that form Zirfon® provide high stability and hydrophilic properties to the membrane to be used in aggressive conditions such as the alkaline solution of KOH 30% w/w which is used as electrolyte.

This membrane was developed to be used in electrochemical systems, mainly as separator in alkaline water electrolysis. The membrane function in this type of systems is separating oxygen and hydrogen gases and closing the electric circuit through the potassium and hydroxide ions migration of the electrolyte [4]. The material used at the beginning of alkaline water electrolysis was asbestos, but in spite of fulfilling its functions of separating the reaction products and carrying the ions satisfactorily, it had operational problems. Corrosion was one of them, which occurred when the operational temperature of the system exceeded 100˚C. The objective of using that temperature was to reduce the cell voltage and as a direct consequence increase the energy efficiency [3,5,6]. An important problem was that asbestos is a carcinogenic material, and for that reason, its use started to be regulated in the mid-eighties, in a progressively restrictive way until its complete prohibition. In this type of electrolytic cells, such as water electrolysis cells, where the production and detachment of bubbles occur, it is necessary to count with the presence of a material with hydrophilic characteristics to compensate to some extent the membrane hydrophobic nature. The gas bubbles tend to become attached to the membrane surface creating hot spots and as a consequence, cause its deterioration. Nowadays, Zirfon® is a common material used as separator in alkaline water electrolysers [3–7]. In the work of Vermieren et al. [6], it was informed that an electrolysis cell that used Zirfon® has a cell voltage of 2.0–2.1 V at 60˚C decreasing towards 1.7–1.8 V when the working temperature is of 120˚C [3]. Zirfon® forms part of an electrode–separator–electrode, a single unit that comprises anode, separator and cathode improving the stack assembly, to be used in space applications. The objective was to produce oxygen from the splits of liquid water for the astronauts in cabins [4].

Zirfon® was used as a replacement of asbestos in alkaline fuel cells, where a special matrix to contain the electrolyte, potassium hydroxide (KOH), was necessary [2]. During the development of Ni–H_2 batteries, the potential of Zirfon® was observed because the life of those devices was limited by membrane degradation. The materials used in those batteries were asbestos, Zircar® (a zirconium oxide cloth) and nylon. Zircar® is a fragile material from the manipulation point of view, for its assembly and in addition, its synthesis is highly expensive. Nylon presents an excellent performance, but it has low stability in time besides its temperature susceptibility [5].

Other important Zirfon®´s applications are as ultrafiltration membrane and in biotechnological developments. As ultrafiltration membrane, it is used in the production of drinking water, desalination and water softening, removal of microcontamination and dye retention; it is also used in wastewater treatment [8,9]. Zirfon has started to be used in microbial fuel cell as separator material. The technology of microbial fuel cells employs the metabolic activity of micro-organisms to perform wastewater treatment and at the same time the production of energy. This device consists of an anode that is composed of micro-organisms, a cathode and a separator. The micro-organisms oxidize organic or inorganic substrates and transfer the electrons to the electrodes. The conventional wastewater treatment has high energy consumption, so this technology could provide the solution to this problem offering the production of energy and the wastewater treatment [10–12]. The investigation work of Sevda et al. [11], compared the performance of Zirfon® and Fumasep® as separator in microbial fuel cells. The results showed that Zirfon® presented more power density and lower resistance than the other separator Fumasep® [11].

In the field of biotechnology, it is used in heavy metal removal in water current by immobilized bacteria [2]. Chemical, paper, lubricant, pharmaceutical and food industry also use Zirfon® membrane.

This work presented the study of alkaline water electrolysis using Zirfon® as separator material, stainless steel 316 L as electrodes and NaOH as electrolyte,

with the purpose to reduce the cost of construction and maintenance of these devices. The cost of Zirfon®, just to mention one, is the fourth part of the cost of Nafion®, another material used as membrane. The use of simple flat electrodes without a catalyst coating on their surface is another reason for cost reduction, but it is necessary to analyze this in depth because it has to take into account the properties of those materials in this type of systems.

In this experimental work, alkaline water electrolysis was tested with six different distances between electrodes (7.5, 6.5, 5.6, 4.45, 4.25 and 3.10 mm) under specific work conditions. Current, voltage, and temperature were the control parameters. The calculated parameters were decomposition voltage, resistance and conductance of the electrolytic solution of NaOH 20% w/w. The data obtained were analyzed to establish the best performance of all the studied systems.

2. Experimental

The objective of this experimental design was to study the six proposed distances between electrodes (7.5, 6.5, 5.6, 4.45, 4.25, and 3.10 mm), using a special electrolytic cell with Zirfon® as separator material, an electrolytic solution of NaOH 20% w/w and electrodes of stainless steel 316 L. The electrolytic cell, which has been described in detail in Lavorante et al. [13], consists of a cubic container, two guide brackets, two mobile locks, four screws and a set of six different gauges. In Fig. 1, the isometric and the side view of the electrolytic cell can be seen [13].

The guide brackets had the function of holding the electrodes and allowing their easy movement into the precise position. The gauges established the distance between electrodes, and they were placed between the upper part of the cell walls and the guide brackets. The mobile locks were used with the purpose of ensuring that the distance remained stable during all the experiment. Two of the four screws placed in the guide brackets acted as electrical connectors. All these pieces were placed in the cubic container that had a slot in the middle to ensure the position of the separator (see Fig. 2).

The alkaline electrolytic solution was prepared with distilled water and sodium hydroxide (Anedra®). The electrolyte was a solution of NaOH 20 w/w. When this solution was added to the electrolytic cell, a drop of sodium dodecyl sulphate was incorporated in order to reduce the superficial tension of the

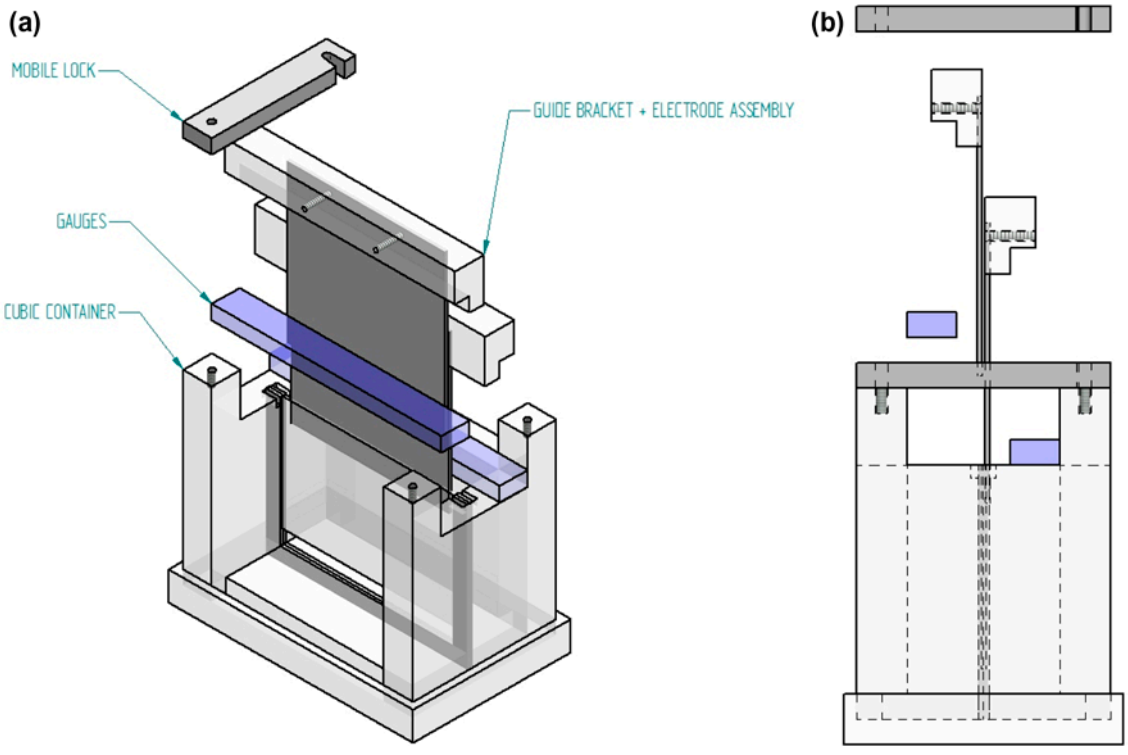

Fig. 1. (a) Isometric exploded view and (b) side view of the electrolytic cell.

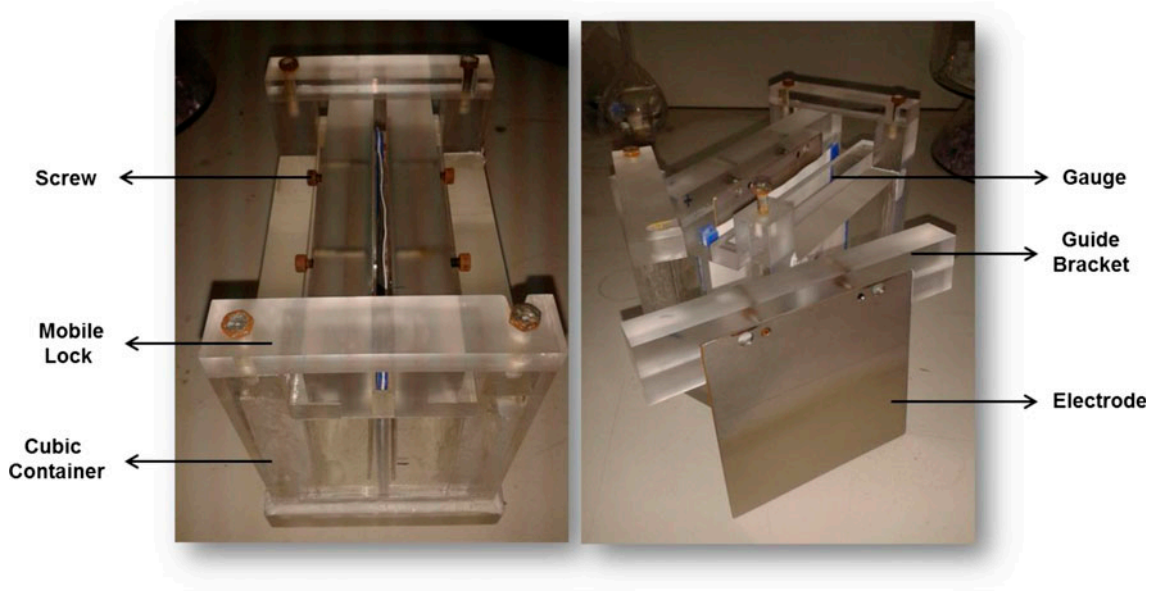

Fig. 2. Electrolytic cell.

solution, thus allowing the formation of smaller bubbles, which became detached from the electrodes at a faster rate.

When all the pieces of the system were in place, the cell was connected to a power source Fullenergy®HY3020 DC Power Supply (30 V/20 A). The voltage differences applied were between 0 and 3 V, scaling the measurements every 0.1 V. Between every determination, a period of time (30 s) was established to guarantee that the temperature of the electrolytic solution at the end of all the experiences did not increase more than 1 ℃.

Working conditions were atmospheric pressure and room temperature. Control parameters were voltage, current and temperature of the electrolytic solution. Results obtained were used in a graphic representation of current as a function of voltage, and that graphic was used to determine parameters such as decomposition voltage, resistance and conductance of the electrolytic solution through the obtained equation.

3. Discussion and results

Six different distances between electrodes were studied: 7.5, 6.5, 5.6, 4.45, 4.25 and 3.10 mm. We are going to call them as "systems". All the experiences were carried out four times for each distance between electrodes proposed, and the standard deviation is 0.10. The behaviour of current density as a function of applied voltage differences was analyzed, see Fig. 3. The values represented in the graphic were the result of averaging the values obtained in the four experiences for each distance.

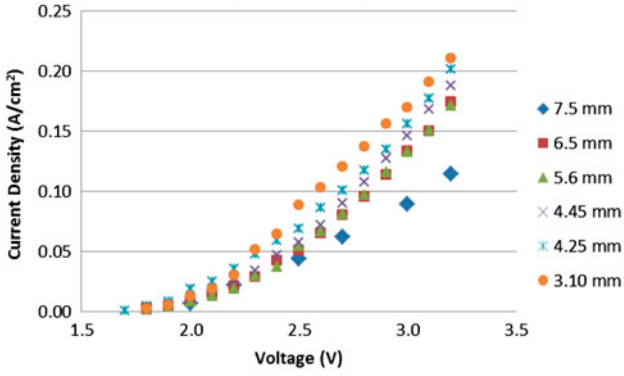

Fig. 3. Current density as a function of applied voltage differences.

Out of all the systems studied, the shortest distances between electrodes presented the highest current densities. However it was observed that in some of the systems (4.45, 5.6 and 6.5), the values obtained were very similar.

From the representation of the current density as a function of applied voltage differences for each system, the linear equations were obtained. Those equations allowed the determination of parameters such as

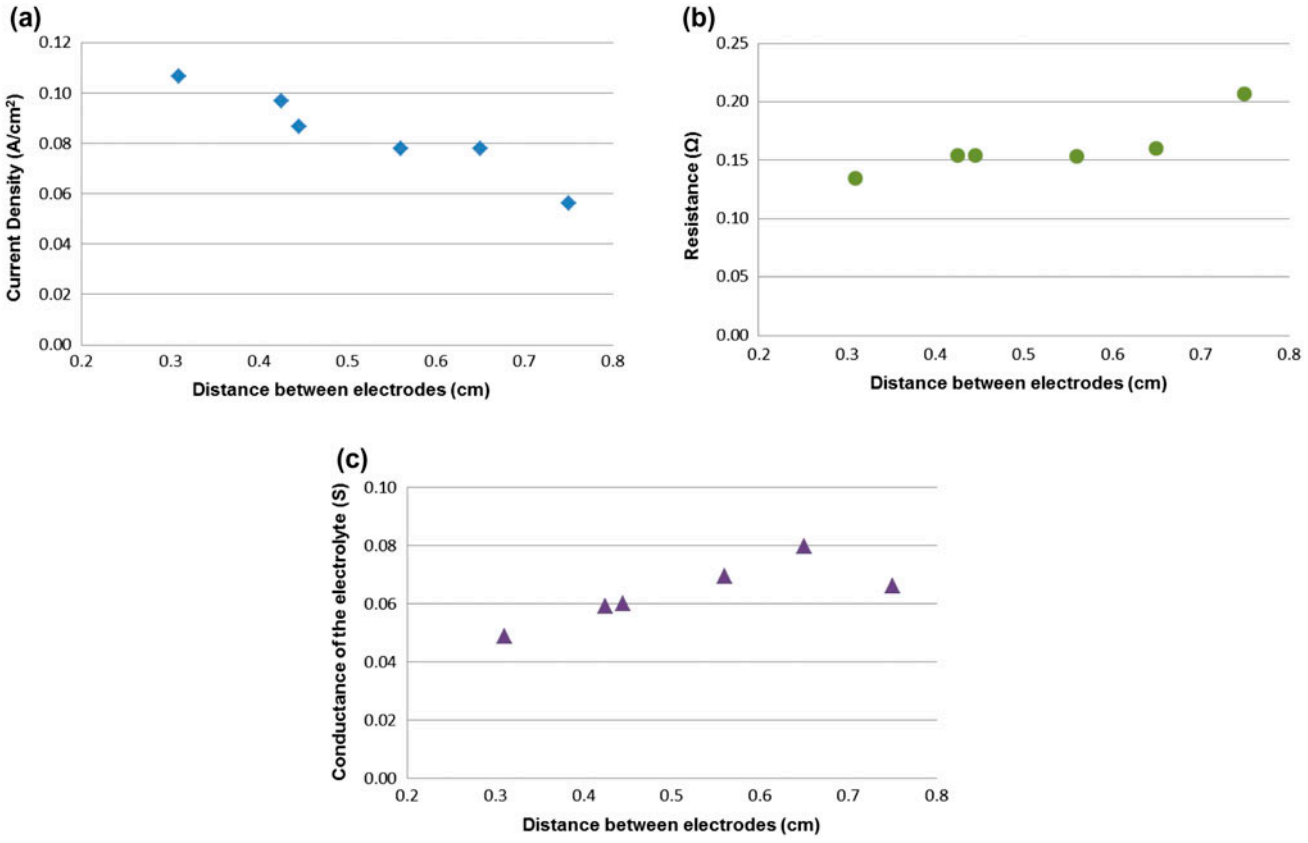

Fig. 4. Graphic representation of: (a) current density, (b) resistance, and (c) conductance of the electrolyte as a function of distance between electrodes.

decomposition voltage, resistance and conductance of the electrolytic solution. In Fig. 4, the results obtained for such parameters were represented as follows: (a) current density, (b) resistance, and (c) conductance of the electrolyte as a function of distances between electrodes for each system.

Analyzing the current density (Fig. 4(a)), it is clear that the smallest distances between electrodes presented the highest current densities. The behaviour of current density is almost linear with respect to distance between electrodes. Resistance (Fig. 4(b)) increases with distance between electrodes, but it was observed that for distances that were very close to each other (less than 0.2 mm), the value obtained for resistance was the same. The conductance of the electrolytic solution (Fig. 4(c)) reached its maximum at 6.5 mm (growing linearly), and then, it started to reduce its value. This could be as a consequence of the polarization of the electrodes and the greatest ions concentration in a smaller compartment.

Fig. 5 shows the same graphic representation of Fig. 3 with the only difference that the graphic was divided in two. The results obtained up to an applied voltage difference of 2.3 V were represented in Fig. 5(a) and the rest of the values in Fig. 5(b). The reason for doing that is that the six curves have a parabola appearance. So, the points that divert from the linearity were dismissed. These points were the ones that appeared in Fig. 5(a) which are the minimum values of applied voltage differences to allow water electrolysis to begin.

The linear equations for each of the systems were recalculated, and the parameters such as current density, resistance and conductance of the electrolytic solution were presented in Fig. 6.

The graphic representation for the current density and the conductance had the same form that the ones obtained for all the experimental points (Fig. 4(a) and (c)). In the cause of resistance, the value seemed to be the same and it increased in a considerable way in the longest distances proposed.

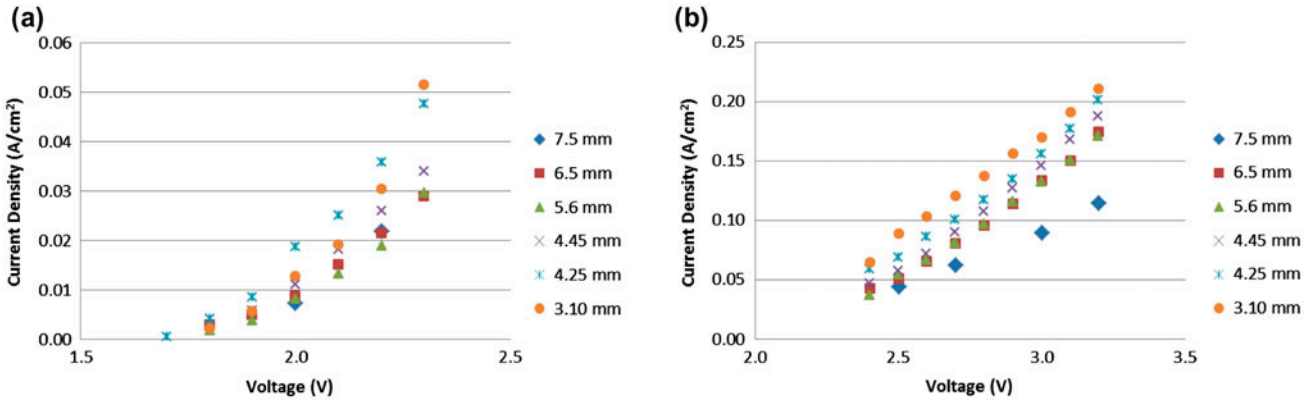

Fig. 5. Graphic representation of the current intensity as a function of voltage for (a) all the systems until 2.3 V and (b) since 2.4 V.

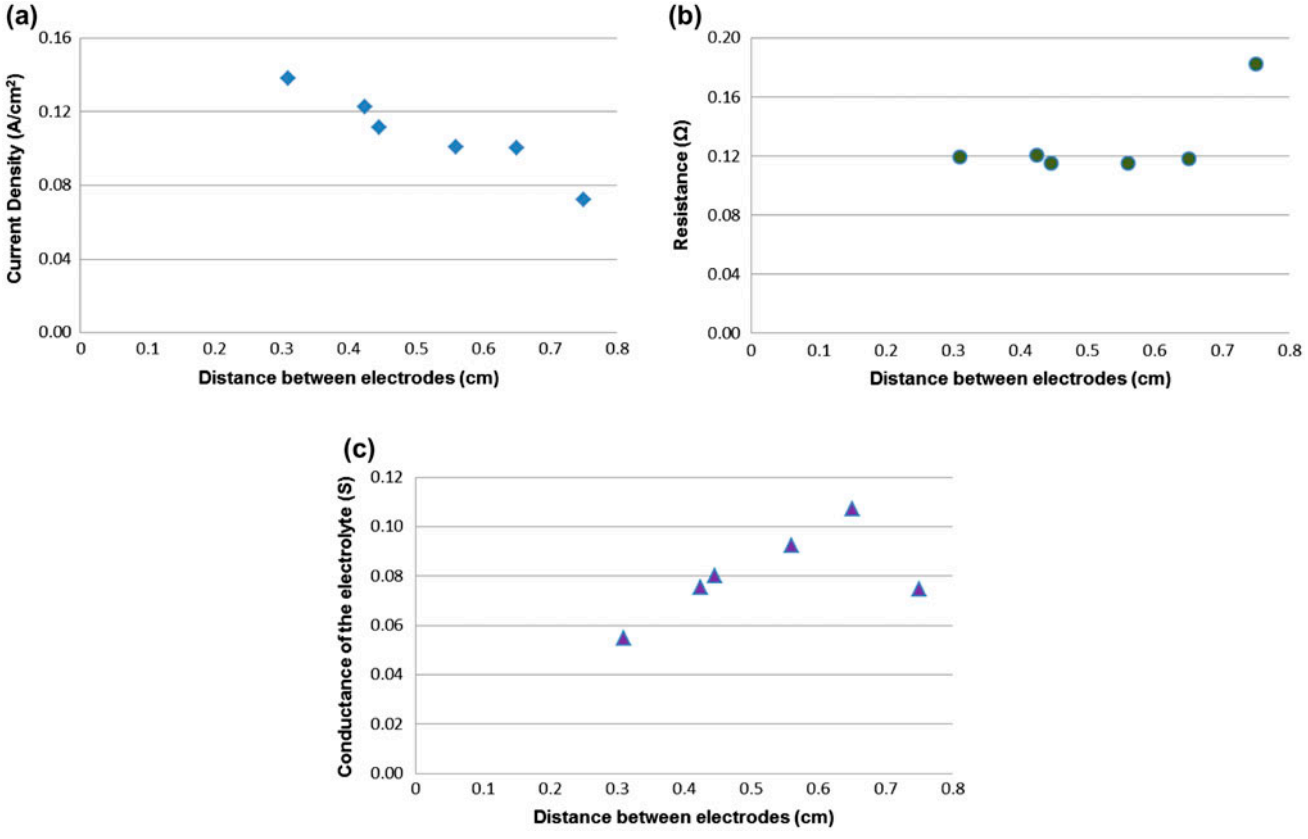

Fig. 6. Graphic representation of: (a) current density, (b) resistance and, (c) conductance of the electrolyte as a function of distance between electrodes.

4. Conclusions

The shortest distances between electrodes presented the best performance of the system, related to current density. Resistance increased with longer distances, as it was expected. In the distances where there was a difference of 0.2 mm, resistance was very similar as a consequence of the approach between determinations. Bubble resistance was not observed with these distances, but we continue working along that line.

Conductance of the electrolytic solution increased with the growth of distances although the last determination (7.5 mm) obtained an unexpected value.

The 3.10 mm distance presented the best performance of all the systems studied in this experimental work.

Zirfon® presents a good performance to be used in alkaline water electrolysis, and its cost allows reducing the global cost of an electrolyser in its construction and the cost of maintenance (as it was said four times less than Nafion®). Further analyses have to be performed with respect to the properties of this material to be compared with the common materials used in water electrolysis.

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