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Use of Peruvian dye, Ayrampo (Opuntia Soehrensii) as a sensitizer in Grätzel cells of TiO_2, using graphite as a counter-electrode

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Abstract. In the search of new dyes that make large-scale manufacturing of dye sensitized solar cells, cheaper materials are sought rather than conventional ones that are produced only in laboratories. As is known, an application of nanotechnology is the conversion of solar energy into electrical energy through photovoltaic technology, since nanomaterials and/or films with nanometric thicknesses are used for the manufacture of sensitized solar cells with dye; on the other hand, the use of natural dyes as a sensitizer within the Grätzel cell of TiO_2 is proposed. These cells are made up of overlapping layers, each one has a determining and specific function, the dye being in charge of absorbing the photons and turning them into electrons, having great importance in the open circuit voltage and in the efficiency of the cell. The TiO_2 electrodes prepared by the Doctor Blade method were later sintering, and then sensitized with the Ayrampo. These pigmented films were characterized by FTIR, to find the types of bonds present. The cells were characterized by their current versus voltage curve to determine: FF, ISC, VOC, VPMM, IPMM and the efficiency of the solar cell. The impedance characterization of the cell was also performed to observe its internal behavior. The principle of operation of the cell is given by the photovoltaic effect, when solar radiation falls on the cell, the photon collides with the dye molecule, this gives enough energy to excite it and make the electron escape from the molecule of the molecule of the dye and move to the semiconductor TiO_2, when this occurs, a flow of electrons is created (e^-). Then the liquid electrolyte (I^-/I^-_3) regenerates the dye with one of its own electrons, electrons travel and create an electrical circuit. The I-V curve shows that the solar cell has a maximum efficiency at 0.75%.

Keywords-- solar cell, sensitizer, blocking layer, Peruvian dye, Opuntia Soehrensii.

I. Introduction

Pollution in these times has altered the natural balance of CO_2 levels in the atmosphere. The infrared absorption of solar radiation and the longevity of atmospheric CO_2 are causing the greenhouse effect. So, the biggest challenges facing current times are the global increase in energy demand and control over the level of CO_2 emissions. Therefore, one of the objectives of humanity is the development of alternative energy sources such as renewable energies, seeking the protection of the environment. Renewable energy is sourced by nature, being virtually inexhaustible, not only because it contains an immense amount of energy but also because it is capable of regenerating itself by natural means. One type of renewable energy is solar energy and one way to take advantage of this type of energy is the generation of photovoltaic sources such as solar cells. Photovoltaic technology has evolved in different stages. The first stage began in 1954 with silicon-based solar cells with an efficiency of 6% [1]. Silicon solar cells are currently among the most widespread, constituting about 82% of the photovoltaic market [2]. However, its manufacturing process is still high. The second generation is based on multiple layers of p-n junction semiconductors [3]. For example, those based on the CdTe/CdS junction have reached efficiencies greater than 16% [4],[5]. The materials used in these cells are very expensive and are not widely used on a commercial scale for terrestrial applications, having reported efficiencies of up to 10.4% based on these materials [1]. The third generation are the Dye Sensitized Solar Cells (DSC) or also called Grätzel cells. In 1991, at the Laboratories of the University of Lausanne in Switzerland, Michael Grätzel and Brian O'Regan sparked a revolution in the use of photoelectrochemical cells, using a porous nanocrystalline TiO2 electrode that they coated with a monolayer of an organic compound with ruthenium acting as a sensitizer [6]. This type of cells compared to previous generations are cheaper and have non-polluting components, but their disadvantage is lower efficiency compared to the old generations [3]. For this reason, research is being done to optimize its efficiency by testing different elements or techniques that help with this purpose. The purpose of this research work is the application of a natural dye in Grätzel cells, having Ayrampo (Opuntia Soehrensii) as a sensitizer. The Ayrampo is an integral plant because the fruit and the leaves are used, as shown in figure 2.

Peru is a country that has a great diversity of native flora and fauna, as well as a unique geography in the world. A fruit native to a species of flora in our country is the Ayrampo (Opuntia Soehrensii), a plant from the cacti family, native to the Andean region of Peru. Its fruit is used as a food coloring and traditional medicine, since in some places they prepare ice cream or porridge, attributing medicinal properties against: fevers, heart disease, stomach ulcers [7]. So, taking advantage of our natural resources and new technologies, such as nanotechnology, it is proposed to use dyes in the application of solar cells to have. another alternative in the transformation of solar energy into electricity. For this reason, given this situation, the world is moving towards the use of renewable energies and research into nanomaterials to take advantage of their specific properties. A type of renewable energy is solar energy and one way to take advantage of this type of energy is through photovoltaic technology. Now one type of photovoltaic cells are dye-sensitized solar cells. So, the way to make Ayrampo useful in this regard is as a sensitizer in a Grätzel cell.

A. *Dyes In Solar Cells*

The dye adheres to the surface of the working (semiconductor) electrode, coating it and coloring it. It is called a sensitizer because it is responsible for capturing the photons from solar radiation in the DSC, due to absorption in the visible range, while the semiconductor or electrode only captures the UV range. Dyes have natural or artificially created types of molecules as shown in the classification of dye in the use of Grätzel cells. Laboratory-processed dyes can be divided into two categories: metal-based organic complexes and metal-free organic dyes. Up to now, dyes with a metal-organic structure, based on ruthenium complexes, have achieved the best performance (greater than 10%) to date [8]. The classification of dyes in sensitized cells, as shown in figure 1.

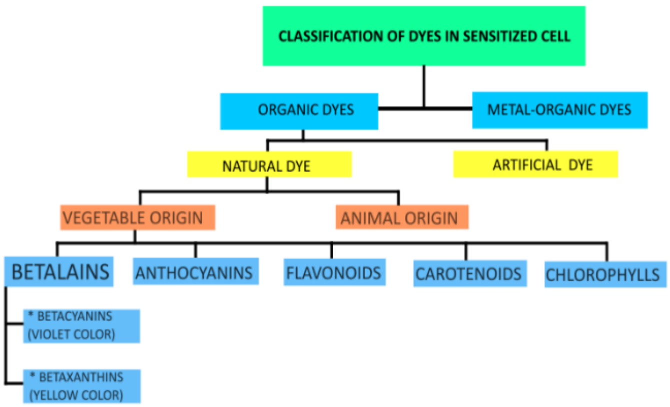

Fig. 1 Classification of dyes in sensitized cells.

B. *Organic Dyes*

As is known, there are two large groups of dyes that are used in the Grätzel cells, the metal-organic coloring and organic dyes, of articles and publications it can be seen that the coloring of the metal-organic group are of better performance, generally, the metal present in these types of dyes is Ruthenium (Ru), but this is a scarce and expensive metal. The most important Ruthenium dyes to date are: N719, N3, black, K19 and K77. The N3 being the pioneer dye reported in 1993 by Nazeeruddin [9].

When mass production of DSCs becomes feasible, Ru complex dyes will not be preferred. Therefore, great efforts were made to synthesize organic dyes for DSC. Since the year 2000, interest in organic dyes has increased steadily producing record efficiencies of 4% to 9% with fully organic dyes [3].

The recent advance in the molecular design of organic dyes has been thoroughly reviewed, where the main advantages of organic dyes are short synthetic routes, established so that structural modifications of the dyes are relatively easy [10].

Organic dyes have very narrow absorption bands compared to metal-organic dyes; they tend to have shorter electron lifetimes compared to conventional Ruthenium dyes [3],[10]. Dye molecules generally have carboxyl acid groups (-COOH) as fixing units, in the process of sensitization by binding with the semiconductor metal, a proton (H^+) is released on the oxide surface, leaving the negatively charged dye molecule [11].

Fig. 2 Photograph of the Ayrampo in Arequipa-Peru, left side the plant and the lower right side the fruit [12].

C. *Dye: Betalains*

As already mentioned, the Ayrampo fruit contains seeds covered by a parenchymal tissue that contains abundant dyes from the betalain group. The plants that contain these pigments are limited to 10 families of the order Centrospermae, whose shades are purplish and yellowish. The betalains are a group of plant pigments that contain nitrogen and are soluble in water. One of those families that contain betalains are the cacti, the presence of betalains in plants is mutually exclusive of the presence of anthocyanins. To date, about seventy betalains are known and all of them have the same basic structure (betalamic acid), as shown in figure 3. Betalains are divided into two groups: betacyanins, colored purple, and betaxanthins, colored yellow [7].

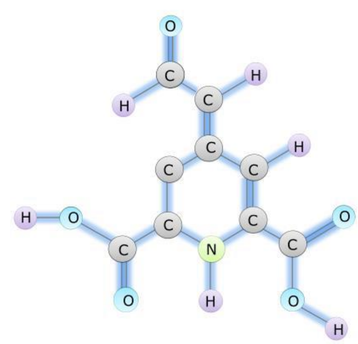

Fig. 3. Betalamic acid

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Betalamic acid, the basic structural unit of these pigments, is found condensed with an amino acid or amine in betaxanthins and conjugated with cyclo-dihydroxyphenylalanine (cyclo-DOPA) in betacyanins. Then we are going to use the Ayrampo, as a sensitizer in a Grätzel cell, as shown in figure 4.

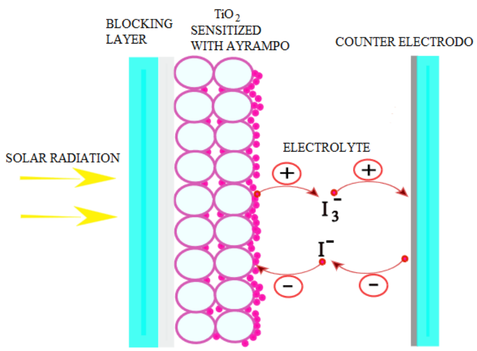

Fig. 4 Work of the electrolyte in the Grätzel cell sensitized with Ayrampo, the task of dye regeneration and its self-regeneration with contact with the counter electrode.

This molecule can incorporate sugars and acids through one of the two hydroxyl groups present in the aromatic ring, giving rise to two families of compounds: those derived from betanin (betanidin-5-O-β-glucoside) or from betanin, gomphrenin I (betanidin-6-O-β-glucoside) [13]. According to this information, we can conclude that, for betanin, the dye present in Ayrampo has the serious chemical form $C_{24}H_{27}N_2O_{13}$, in addition that its molar mass is 551.48 g/mol, the dye must present adequate energy levels with the other elements of the cell, as shown in figure 5.

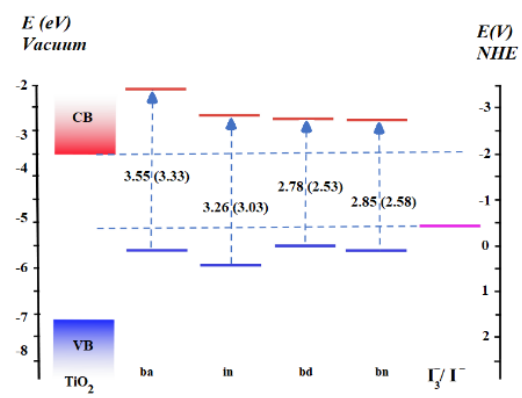

Fig. 5 Energy level of the betalain dye between the energy of the working electrode (semiconductor) and the electrolyte [14].

D. Blocking Layers

One of the ways to improve the performance of solar cells is the application of blocking layers at the interface between the electrode (semiconductor TiO_2) and the FTO of the substrate, since TiO_2 is a nanoporous layer, being in contact with the FTO There are places where there is not good contact between said cell components and the electron that propagates through the semiconductor, which ends up recombining before reaching the FTO of the substrate.

In this research work, the blocking layer has been used with the purpose of suppressing the recombination between the semiconductor/FTO interface of the TiO_2-based DSC. This involves the insertion of an ultra-thin TiO_2 film between the semiconductor (TiO_2)/FTO interfaces as shown in Figure 9. The insulating layer acts as a physical barrier to prevent direct contact between TiO_2 electrode (paste) and substrate. conductor F: SnO_2. This layer must have the appropriate thickness in order to maintain the tunneling efficiency of the electrons that are transported by the TiO_2 that pass to the F:SnO_2. This idea seems reasonable for the suppression of interfacial recombination. The blocking layer was obtained using the Pyrolytic Spray technique [18].

The thickness of the TiO_2 blocking layer was controlled by the number of cycles or passes with the sprayer.

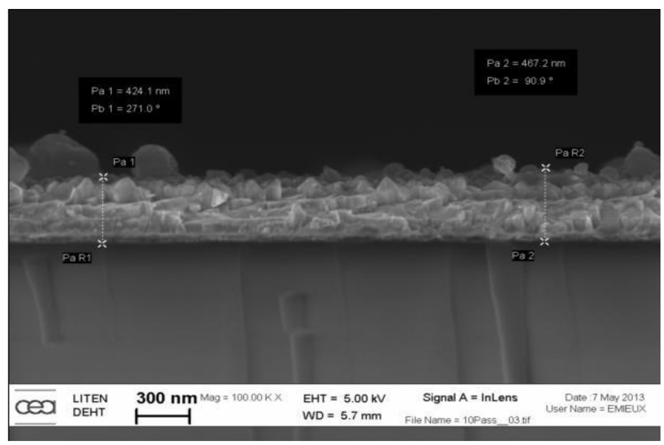

Fig. 6 SEM cross section of the compact TiO_2 layer between the FTO conductive glass and the nanoporous TiO_2 electrode [18].

Fig. 7 SEM front section of the 104.2 nm thick TiO2 blocking layer surface. Scale $2\mu m$ [18].

II. EXPERIMENTAL PART

To obtain the TiO_2 solution, the Sol-Gel method was used [15]. In 80 mL of distilled water, 0.61 mL of 70% nitric acid (HNO_3) is mixed, then the solution is stirred using a magnetic stirrer for about 15 minutes. Subsequently, 4 mL of titanium isopropoxide was placed at a temperature of 50 ºC for 15 minutes, then the temperature was raised to 100 °C, and stirring was continued for 2 hours 45 minutes.

Using the Pyrolytic Spray Technique [17]. As can be seen in Figures 6 and 7, the blocking layers are obtained. For this step, the Pyrolytic Spray equipment was used. For this, the TiO_2 solution prepared in advance was prepared. To achieve these blocking films or layers, the established parameters are: a temperature of 250°C and a pressure of 25 Bar [18], (the thickness of the blocking layer is controlled by the number of passes).

The electrode was obtained from a mixture of 20% TiO_2 nanoparticles with 80% pure ethanol, homogenized by stirring for 12 hours. With this mixture a coating was made on the blocking layer covering an area of 0.5 x 0.5 cm delimited by adhesive tape (magic tape) stuck on the conductive surface of the substrate; a loaf was used to spread this paste, this procedure is called the doctor Blade method, thus obtaining a coating of the semiconductor material [11].

Weigh Ayrampo in a 25 mL beaker, after add petroleum ether, then shake and separate the petroleum ether. Subsequently Add solvent 20% water, 80% ethanol. After Place in the ultrasound equipment, and make it vibrate. then we must dye extraction. Then put in centrifuge equipment and make it rotate for 20 minutes. After separate the phases in the tubes or bottles of the centrifuge equipment, then add Ethanol. After the solution is passed through filter paper, slowly, then take it to the rotary evaporator and extract the solvent with a vacuum pump machine, finally a solution of this dye, water and ethanol is placed in different proportions.

A. Cell Characterization

- *Electrochemical Impedance Spectroscopy (EIS)*

The operation of a DSC can be effectively described by means of an equivalent circuit that takes into account the different components and interfaces of the cell [19]. Said equivalent circuit is formed by resistive and capacitive elements, R and C, in series and parallel, and by elements of Warbug, W, that describe diffusion processes of ionic species in the electrolyte [20]. An equivalent circuit element used to accommodate impedance measurement is shown in figure 8 and 9 [21], [22].

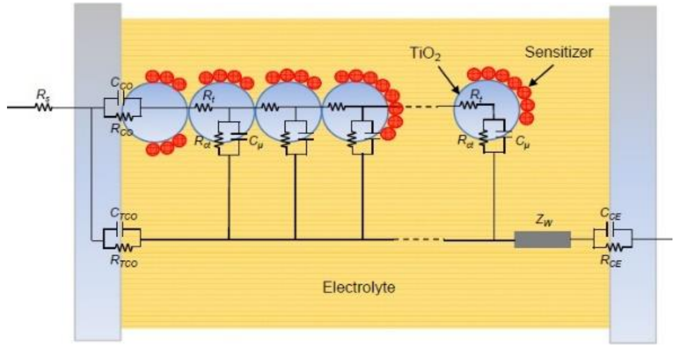

Fig. 8 Energy level of the betalain dye between the energy of the working electrode (semiconductor) and the electrolyte [15].

The equivalent circuit that was used for characterization, according to the literature, is recommended for the medium voltage type (~600mV)

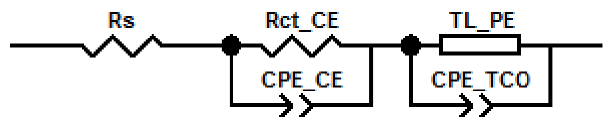

Fig. 9 Equivalent circuit to use in modeling for medium voltages [7]

In the equivalent circuit, RS corresponds to the series resistance, Rct_CE to the charge transfer resistance in the counter electrode, CPE_CE (constant phase element), is a capacitive element that models the behavior of double layer capacitances (in semiconductor/semiconductor interfaces). liquid, metal/liquid), is an imperfect capacitor, CPE_CE corresponds to the double layer capacitance at the electrolyte/graphite$-FTO$ interface at the counter electrode, CPE_TCO corresponds to the double layer capacitance at the TiO2/electrolyte interface.

- *Solar cell measurements.*

The DSC is connected to an external circuit as shown in figure 4. If the resistance of the external circuit is zero, the cell is short-circuited (SC) and the current reaches a maximum value ISC, while the voltage is zero. Conversely, if the resistance of the external circuit is infinite, the cell is open circuited (OC) and the maximum voltage V_{OC} occurs when the current is zero [24]. The scheme of measuring the voltage and current of the solar cell with Ayrampo, as shown in the figure 10.

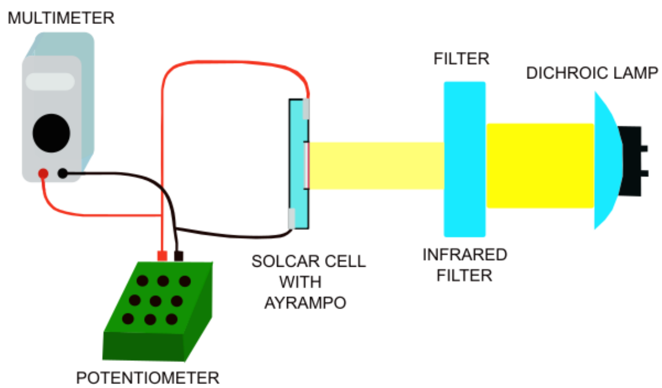

Fig. 10 Diagram of the process for obtaining the IV curve: Voltage versus current of the solar cell.

III. RESULTS

A. *Profilometry*

The average thickness of the films was measured with a Veeco Instrument Dektak 3 profilometer. These tests were carried out by the Commossariat à l'énergie atomique et aux énergie alternatives laboratory. (France), obtaining the results of table 1.

TABLE I

MEASUREMENTS TAKEN WITH A PROFILOMETER OF THE THICKNESSES OF THE PASTES DEPOSITED ON GLASS

Sample:	thickness
M1	19 µm
M2	20 µm
M3	20 µm

B. *FTIR infrared characterization*

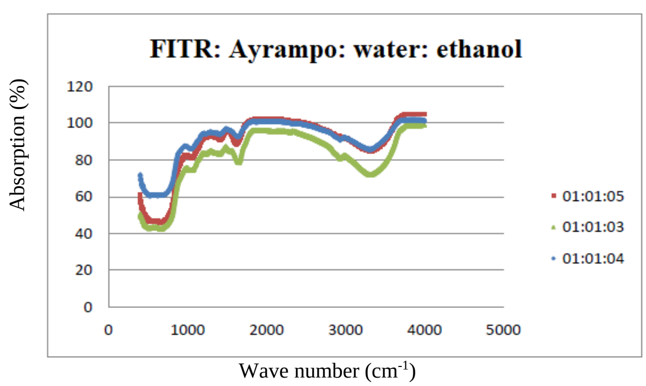

Fig. 11 Spectrum for the TiO2 film sensitized in the Ayrampo dye

TABLE II

TABLE OF WAVE NUMBER VALUES (cm^{-1}) FOR ORGANIC GROUP RECOGNITION.

Sample: 01:01:03 Wave number (cm^{-1})	Sample: 01:01:04 Wave number (cm^{-1})	Sample: 01:01:05 Wave number (cm^{-1})	Organic group identified (cm^{-1}) type of bond present
985.6	985.6	974.1	Assigned to vibrations Ti-O
1034.0	1030.0	1030.0	Corresponding to C-N 1000-1350
1379.1	1367.5	1369.5	The Methyls (CH3) C-H 1375-1380
1408.0	1408.0	1404.2	Due to C-O tensions of the carboxylic group
1631.8	1639.1	1641.1	N-H 1560-1640
1857.5	1869.0	1857.4	Vibrations of C=O carboxylic group are assigned
2941.4	2933.7	2933.7	Own to O-H vibrations of a carboxylic acid
3306.0	3306.0	3315.6	Assigned to O-H vibrations of water

C. *Electrochemical Impedance Spectroscopy (EIS)*

The representation of the absolute value of the imaginary impedance as a function of the real impedance is called the Nyquist diagram, a graph like the one observed in figures 10,11, 12 and 13 are obtained.

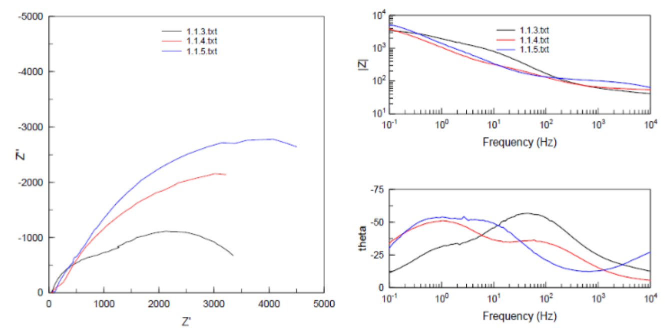

Fig. 12 Nyquist diagram, under solar radiation for a Grätzel cell with Ayrampo as sensitizer, with a variation in the solvent concentration. Ayrampo/water/ethanol a) 1:1:3, b)1:1:4 and c) 1:1:5 where it shows the relationship of the impedance of Z'(Ω) and Z"(Ω).

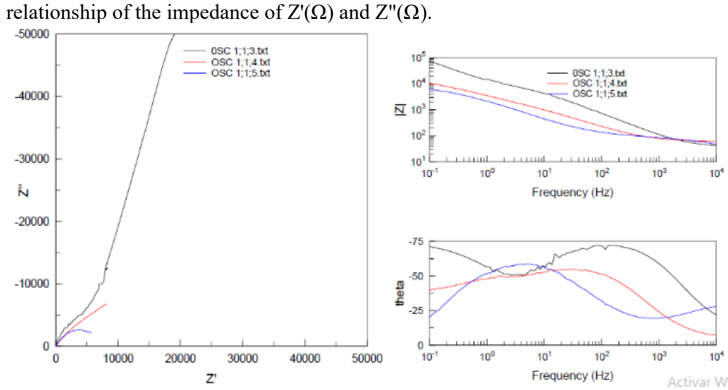

Fig. 13 Nyquist diagram, in the dark for a Grätzel cell with Ayrampo as sensitizer, with a variation in the concentration of the solvent. Ayrampo/water/ethanol a) 1:1:3, b)1:1:4 and c) 1:1:5 where it shows the relationship of the impedance of Z´(Ω) and Z´´(Ω).

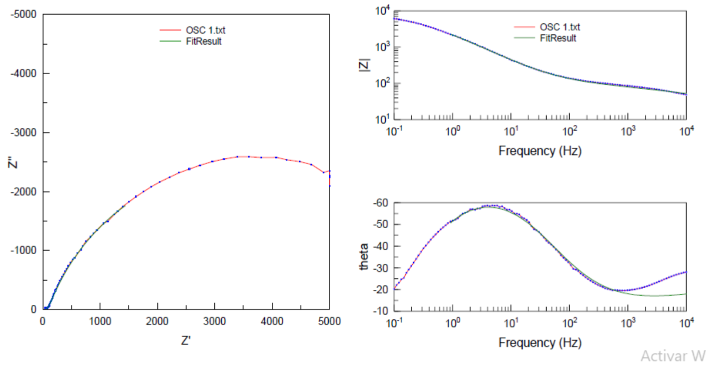

Fig. 14 Nyquist and Bode diagrams in the dark of the Ayrampo/water/ethanol ratio, in the proportion of 1:1:5. Where the data obtained is shown, blue points and the modeling carried out by the ZVIEW2 program, green lines.

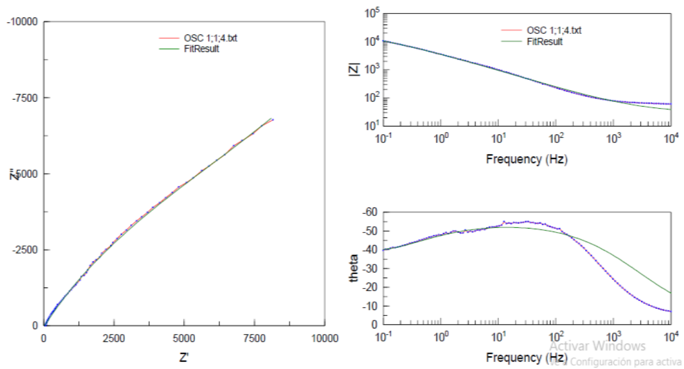

Fig. 15 Nyquist and Bode diagrams in darkness of the Ayrampo/water/ethanol ratio, in the proportion of 1:1:5. Where the data obtained is shown, blue points and the modeling carried out by the ZVIEW2 program, green lines.

TABLE III

RESULT OF THE MODULATION OF THE CELLS SENSITIZED WITH AYRAMPO, RESULTS OF THE TIMES AND NUMBER OF CYCLES.

Ayrampo/Water/Ethanol	1:1:3	1:1:4	1:1:5
$R_{TR}(\Omega)$	147.2	464.1	620.3
$R_T(\Omega)$	98.2	297.3	358.5
$C_\mu(10^{-6}$ F)	29.8	32.6	35.4
r_e(ms)	4.39	15.13	21.96
r_{trans}(ms)	2.93	9.69	12.69
Diffusion coefficient (D_e) (10^{-4} cm^2s^{-1})	13.67	4.13	3.15
Diffusion length (µm)	24.48	24.99	26.31
Number of cycles (r_e/ r_{trans})	1.50	1.56	1.73

D. Current versus Voltage I-V Curve

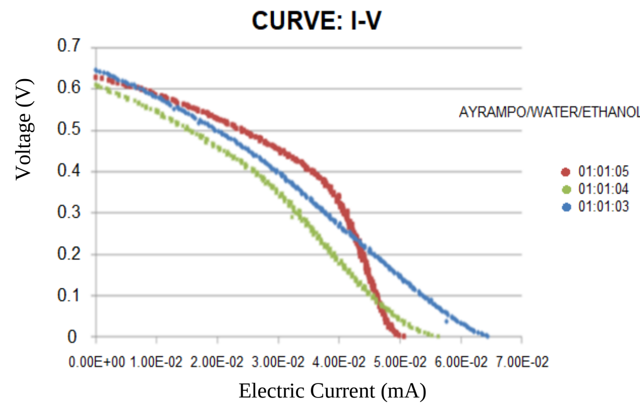

Fig. 16 I-V curve of Ayrampo/water/ethanol ratios of: a) 1:1:3, b)1:1:4 and c) 1:1:5

TABLE IV

PARAMETERS OF THE SOLAR CELL

Relation Ayrampo/ water/ Ethanol	Short circuit current (ISC) mA	Open circuit current (V_{OC}) V	Current maximum (I_{PMM}) mA	Voltage maximum (V_{PMM}) V	Current density (J_{SC}) mA/cm^2	Fill factor (FF)	Efficiency η (%)
1:1:3	0.064	0.644	0.035	0.335	0.33	0.28	0.62
1:1:4	0.053	0.650	0.031	0.345	0.27	0.34	0.56
1:1:5	0.063	0.627	0.038	0.381	0.29	0.37	0.75

IV. DISCUSSION

In order to have a better efficiency of the cell, it is sought to have a shorter transport time and a longer half-life of the electrons since this relationship in these times gives us the number of cycles or turns that the electron gives inside the cell before to recombine. For this reason, a greater difference between the two times is sought, that is, that the half-life time is much greater than the transport time.

Table II, shows the FTIR spectrum of the working electrode pigmented or colored with Ayrampo. As can be seen, among its characteristic bands in (cm^{-1}) are: 981.76 (cm^{-1}) assigned to vibrations O-H, 1031.27 (cm^{-1}) assigned $C-N$, 1372.03(cm^{-1}) assigned to vibrations of methyls ($CH3$) $C-H$, 1406.75 (cm^{-1}) corresponds to vibration of $C-O$ of the carboxylic group, 1637.33 (cm^{-1}) corresponds to vibrations of $N-H$, 1861.30 (cm^{-1})se assigns vibrations of C=O carboxylic groups, 2936.30 (cm^{-1}) assigned to COO- H stresses of a carboxylic acid, 3309.20 assigned to $O-H$ vibrations of water.

As can be seen, the curves are similar for each cell. The semicircles in the middle are shown, which are the ones that have the interaction of the interface between the working electrode/dye/electrolyte, that is, the recombination resistance and the chemical impedance at that interface, and in none of them is a third semicircle observed at low frequencies. , as shown in the Nysquit diagrams, said semicircle corresponds to the Warburg element (Zd), of diffusion of ions in the electrolyte, so it was not possible to obtain information on the diffusion of ions in the cell.

In all the figures there is a good correlation between the experimental data (circles) and the corresponding adjustments (green lines), which implies that the model used for data analysis is acceptable. From the Nyquist diagrams it is important to highlight the differences found between the curves recorded in the dark and under irradiation, which constitutes further proof of the sensitivity of these materials in the presence of radiation.

With the behavior shown with the EIS analysis, and with the I-V data, it can be said that the increase in the amount of ethanol to be more specific in the ratio of ayrampo/water/ethanol of (1:1:5) had a higher efficiency since the relationship between the half-life of the electrons and the transport time increases, this relationship gives us an idea that the electron increases the number of turns or cycles in the cell before it recombines, it can also be seen that the form factor increases, that is, it is another evidence that recombinations are decreasing, it is also observed that by increasing the amount of ethanol it was also observed that there is a better conversion efficiency from solar energy to electrical energy.

V. CONCLUSIONS

It is clearly observed that Ayrampo is a useful dye in the study and manufacture of Grätzel cells. With these results it can be said that we obtain new materials in the manufacture of dye-sensitized solar cells having a dye of Peruvian origin as a sensitizer, studies Our findings that not only this Peruvian dye can be applied in solar cells, research carried out in the laboratory shows that there is also an answer with dyes from: purple corn, uña de gato, mullaca.

As seen in table IV and from the I-V curves it can be seen that with these materials we obtain a good voltage ~640mV but a low current ~0.060mA, as Grätzel cells are known, they have more elements than a conventional cell, and each element has an important role, the role of the dye is to absorb the photons and inject the electrons to the working electrode, the performance of this dye is of low efficiency compared to dyes synthesized in the laboratory. The solvent of the dye solution has a direct influence on the efficiency of the cell, due to the affinity of the water with the dye, since it does not allow the dye to adhere very well to the working electrode.

The DSC with the highest ethanol concentration in the Ayrampo dye solution showed the highest energy conversion efficiency, thanks to a lower charge transfer resistance, higher ratio between electron lifetime and transit time, higher coefficient diffusion of electrons in comparison with the other cells since the pigmentation of the working electrode was more uniform, making the cell have a greater capture of photons, as well as a better injection of electrons to the working electrode due to the better coating of the electrode. work by avoiding recombination of the TiO_2/electrolyte interface. Research work has also been carried out with other Peruvian natural dyes where it shows potential to continue carrying out research and studies of these natural dyes in the Grätzel cells. A maximum efficiency of 0.75% was obtained.

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